Sunday Afternoon, June 26, 2022

Tutorials
Room Auditorium - Session TS-SuA

Tutorial I

Moderators: Christophe Detavernier, Ghent University, Belgium, Erwin Kessels, Eindhoven University of Technology, the Netherlands

1:00pm **TS-SuA-1 How I Learned to Stop Worrying and Love the Surface***, **Seán Barry**,* Carleton University, Canada **INVITED**

Surface chemistry is a main driving force in atomic layer deposition (ALD). Although this chemistry is mostly driven by Brönsted acid-base chemistry (using H^+), there are several examples – particularly on metal surfaces – where Lewis acid-base chemistry dominates. These surface reactions naturally depend on the precursor, and often on the ligands, which are often the first interaction that the precursor will have with the surface. This is most obvious in molecular layer deposition (MLD) and in the burgeoning field of small molecule inhibition (SMI), where non-metal "small" molecules nucleate at the surface as a component of a film growth process, or to alter the surface ch3emistry of film growth.

This tutorial will look at both classic and newer precursors and show the typical surface chemistry these undergo. Pulling examples from ALD and MLD, surface chemistry at either protonated nucleation points (e.g., -OH, -NH_2) or Lewis acid or base sites (e.g., metal surfaces) will be discussed. How ligands are lost, and how ligands interact with the surface will be highlighted. This will lead into a discussion of the nucleation of MLD precursors, and the specific surface chemistries of SMIs.

Effective surface chemistry will be featured, and design aspects of effective precursors, ligands, and SMIs will be examined.

1:45pm **TS-SuA-4 Combined Atomic/Molecular Layer Deposition for Designer's Metal-Organic Materials and Inorganic-Organic Multilayers***, **Maarit Karppinen**,* Aalto University, Finland **INVITED**

Atomic layer deposition (ALD) of high-quality inorganic thin films has been one of the cornerstones of microelectronics already for decades, while its counterpart for organic thin films, i.e. molecular layer deposition (MLD), remained nearly un-exploited for long. In recent years, the hybrid of these two techniques, i.e. ALD/MLD, has been strongly emerging as a state-of-the-art route for novel designer's metal-organic thin films.

Currently, the ALD/MLD literature comprises ca. 300 original papers covering processes for most of the alkali and alkaline earth metals, 3d transition metals, and lanthanides as the metal component and a variety of aliphatic, aromatic and natural organic components. Excitingly, some of these processes yield in-situ crystalline coordination polymer or metal organic framework (MOF) like structures. Another attractive aspect is that many of the metal-organics realized through ALD/MLD are fundamentally new materials, difficult if not impossible to access through conventional synthesis. Moreover, since both ALD and MLD cycles are modular, they can be combined into any arbitrary precursor cycling pattern to grow elaborated superstructures, to introduce multiple and even mutually contradicting properties into a single material.

In this tutorial lecture, my intension is to: (i) introduce the breath of the ALD/MLD processes developed, (ii) address the constraints/possibilities for growing in-situ crystalline metal-organic thin films, and (iii) highlight some promising ALD/MLD materials for their application potential in Li-ion batteries, flexible thermoelectrics and magnetics, as well as light-conversion and light-switchable materials.

2:30pm **TS-SuA-7 Plasma Assisted Atomic Layer Processing and Diagnostics***, **Sumit Agarwal**,* Colorado School of Mines **INVITED**

Plasmas play an important role in enabling atomic layer deposition (ALD) and atomic layer etching (ALE) processes for a wide variety of materials including dielectrics, semiconductors, and metals. In ALD of oxides, nitrides, and metals, plasmas of gases such as O_2, N_2, NH_3, and H_2 are typically employed in one half-cycle while the reaction in the other half-cycle is thermally activated. In ALE, a plasma may be used in both steps including surface modification and activation. The use of a plasma enables low temperature growth and anisotropic etching, but also adds complexity to these processes as the radicals, energetic ions, electrons, and ultraviolet photons influence the surface reactions, chemical composition, and microstructure. Additionally, in plasma-assisted ALD, achieving conformal growth in high-aspect-ratio structures can be challenging due to radical recombination on the sidewalls of the structures. In plasma-assisted ALE, an added challenge is to obtain material selectivity during anisotropic etching of nanoscale features across different aspect ratios over large areas. In this tutorial, I will first describe the key features of these plasma-assisted processes, and then discuss the associated technological challenges. Next, I will describe plasma diagnostic tools that can be used to measure key plasma parameters including the radical composition, the ion energy distribution function, and electron density. Finally, I will discuss *in situ* surface optical diagnostics tools used in ALD and ALE tools to better understand the chemical and physical processes occurring on the surface.

3:15pm **TS-SuA-10 Synthesis and Integration of 2D Materials Using ALD***, **Ageeth Bol**,* University of Michigan, Ann Arbor **INVITED**

2D materials have been the focus of intense research in the last two decades. For example, their ultrathin body, optical band gap and unusual spin and valley polarization physics make them very promising candidates for a vast new range of (opto-)electronics and catalysis applications. So far, most experimental work on 2D materials has been performed on exfoliated flakes made by the 'Scotch tape' technique. The major next challenge is the large-area synthesis of 2D materials with control over their properties by a technique that ultimately can be used in industry. This tutorial will focus on ALD for large-area synthesis of 2D transition metal dichalcogenides for application in nano-electronics and catalysis and will highlight the precise control over the thickness, morphology, composition and phase of the 2D-TMDs that can be obtained by ALD**.**

Another challenge in the 2D materials field is how to connect these materials efficiently to the outside world. For example, properly functioning contacts and dielectrics need to be fabricated on top of the 2D material to make functioning nanodevices. ALD is the method of choice for depositing ultrathin dielectrics, because of its ability to deposit high quality, ultrathin films at low temperatures. Furthermore, ALD could offer benefits for metal deposition, such as the formation of more intimate contact, as ALD is a chemical process. The second half of this tutorial will therefore focus on ALD approaches to deposit dielectrics and contacts on 2D materials without deterioration their properties.

4:00pm **TS-SuA-13 How Did (and Will) Atomic Scale Processing Change the Logic and Memory Industries?***, **Giuseppe Alessio Verni**, A. Illiberi,* ASM, Belgium*; P. Deminskyi,* ASM Microchemistry Ltd., Finland*; M. Givens,* ASM, Belgium **INVITED**

As the scaling of device density continues to follow Moore's law, industry has resorted to adopt increasingly more complex architectures and 3D geometries while simultaneously driving down most of the critical dimensions to the nanoscale. This tutorial aims at briefly reviewing the evolution of device scaling in Logic and Memory and outlining how future architectures such as Complementary FET (CFET) and 3D-DRAM are going to impact material and processing requirements. We will first present an overview of atomic scale processing technologies which have been in use in industry for the past 10 years, including atomic layer deposition (ALD) and atomic layer etching (ALE). Atomic Layer Processing (ALP) will then be discussed as the main technology capable of providing disruptive new materials to market while being compatible with advanced 3D geometries with tight space requirements such as Gate-all-around (GAA). The discussion will present examples of how ALP can overcome the integrations challenges arising with these architectures, enabling, for example, multi-Vt devices on the same substrate. To conclude, we will look at the future integration schemes and discuss what emerging opportunities and challenges will exist for ALD and ALE.

4:45pm **TS-SuA-16 Artificial Interphases for Interface Control in Li-ion Batteries***, **Philippe Vereecken**,* IMEC, Belgium **INVITED**

Energy density, charging time (C-rate) and Life time are the key figures of merit for Li-ion batteries. In this invited talk we will focus on the application of continuous closed thin films as artificial interfaces in large capacity batteries. We will deal mostly with the perspective of device performance where the ALD and MLD processes merely provide the films and enable their ultrathin, continuous and conformal nature. Nanoscale film thickness allows for a low interface and cell resistance even when the materials themselves are poor conductors. For example. LiPON (N-doped Li_3PO_4) is a solid electrolyte interesting because it is stable against metallic lithium but, because of its poor ionic conductivity ($<10^{-6}$ S/cm) only practically useful for thicknesses under few hundred nanometers. Materials which are not solid electrolytes by their own merit (e.g., TiO_2) still have ion-transparent properties up to several tens of nanometer and can be used as ion transparent artificial interfaces in contrast to, for example, alumina which is an insulator for Li-ions. However, solid-state reactions with the active material can form $LiAl_2O_4$ at the interface which is again a solid electrolyte. These thin solid electrolytes can provide protection against electrolyte decomposition when deposited in the porous powder composite electrode layer. However, for coating of the individual active material particles, ideally materials which have both electronic and ionic conducting (or transparent) properties. These dual conductors allow both good electronic contact with the conductive additive (carbon black) and with the electrolyte (liquid or solid).

Artificial interphase coatings are often seen only as a chemical buffer layer or electronic barrier. However, most active electrode materials are semiconductors and thus heterojunctions are formed for which the electron transfer can be engineered to one's advantage. In this paper, we will show how planar thin-film stacks can be used as a model system to study, understand and engineer these interfaces, which can then be translated into a solution for the actual powder composite electrode architectures.

Finally, volume changes during charge and discharge are limiting the cycle life-time of batteries, especially for rigid solid-state batteries. Also ALD thin-films suffer from the mechanical strain and the benefits of the "closed" protective film are lost. Therefore, MLD of hybrid organic/inorganic coatings is explored to enable more elastic coatings for improved cycle life time.

Atomic Layer Etching
Room Arteveldeforum & Pedro de Gante - Session ALE-SuP

Atomic Layer Etching Poster Session

ALE-SuP-1 Anisotropic Atomic Layer Etching of Sn by Formation of Hydride/Chloride*, Doo San Kim*, *Y. Jang, H. Gil, G. Yeom,* Sungkyunkwan University, Korea (Republic of)

Anisotropic ALE studies were conducted on Sn, which is one of the materials with a high extinction coefficient applicable to extreme ultraviolet (EUV) photo-lithography mask, by modifying the Sn surface with H/Cl radicals and followed by the removal of the modified layer by Ar^+ ions using an ion beam. During the adsorption of H/Cl radicals, it was possible to form highly volatile SnH_xCl_y and $SnCl_x$ without spontaneous etching on the Sn surface while the adsorption of H radicals etched the Sn surface by forming volatile SnH_x. The chemically modified $SnH_xCl_y/SnCl_x$ was etched by Ar^+ ions at ~2.6 Å/cycle through optimized ALE processes. In addition, high etch selectivity could be obtained with Ru which is generally used as a capping layer of the EUV photo mask. The degree of physical and chemical damages on the Ru surface was investigated during the adsorption and desorption of the Sn ALE process, and no physical and chemical damages could be found on the Ru surface during the Sn ALE process.

ALE-SuP-2 Atomic-Scale Control of a Native Oxide Thickness on Si for Direct Wafer Bonding*, Youngseok Lee*, *Y. You, C. Cho, I. Seong, W. Jeong, J. Lee, S. Kim, S. You,* Chungnam National University, Korea (Republic of)

Since direct wafer bonding technology has recently been attracting an enormous interest for three-dimensional integration of semiconductor devices, it has been reported that plasma treatment on wafer surfaces has advantages in, for instance, achieving high bonding strengths with low annealing temperature. We empirically found that in Si-SiO_2 bonding, a native oxide layer on Si plays an important role and thus a control of the native oxide thickness significantly affects the resulting bonding strength. In our experiments, physical sputtering of Ar plasma ions finely controlled a native oxide thickness of a Si wafer, and the change in the native oxide thickness and the resulting bonding strength with a SiO_2 wafer were assessed via ex situ ellipsometry and a double cantilever beam method, respectively. In this presentation, we will discuss the correlation between a native oxide thickness and bonding strengths and the underlying mechanism.

ALE-SuP-3 Atomic Layer Etching of Al_2O_3 with NF_3 Plasma Fluorination and Trimethylaluminum Ligand Exchange*, Hyeongwu Lee*, *J. Kim, D. Shim, Y. Kim, H. Chae,* Sungkyunkwan University (SKKU), Korea (Republic of)

In this study, a cyclic isotropic plasma atomic layer etching (ALE) process for aluminum oxide was developed with two steps of plasma fluorination and ligand volatilization with trimethylaluminum (TMA). In the plasma fluorination step, the Al_2O_3 surface was fluorinated to $AlOF_x$ with NF_3 plasma at 100 °C. As the plasma fluorination time increased, the atomic fraction of fluorine on the surface was increased and then saturated to a value of 25% after 50s of plasma fluorination. The formation of the $AlOF_x$ layer was confirmed by X-ray photoelectron spectroscopy analysis. The depths of the fluorinated layers were in the range 0.79–1.14 nm at different plasma powers. In the removal step, the fluorinated layer was removed by a ligand exchange reaction with TMA at an elevated temperature range of 250–480 °C. The etch per cycle (EPC) was 0.20–0.30 nm/cycle and saturated after 30 s in the temperature range of 290–330 °C. EPC increased in the temperature range of 250–300 °C during the removal step with the ligand exchange reaction and reached the maximum at 300 °C. The fluorine atomic fraction on the surface was reduced to 14% after the removal. The average surface roughness of Al_2O_3 was reduced from 8.6 Å to 5.3 Å after 20 cycles of etching. In conclusion, Al_2O_3 was successfully etched at the atomic scale by the cyclic plasma ALE process.

ALE-SuP-4 Low-Temperature Plasma Atomic Layer Etching of Titanium Nitride*, Heeju Ha*, *D. Shim, J. Kim, Y. Kim, H. Chae,* Sungkyunkwan University (SKKU), Korea (Republic of)

Titanium nitride (TiN) has been used as a metal gate electrode from 2D FinFETs to 3D FinFETs due to its proper mid-gap work function, high thermal stability, and excellent adhesion. Metal gates require a low-temperature process to prevent device degradation. Therefore, atomic-scale etching techniques at low temperatures are required for TiN films in 3D structures. In this work, plasma atomic layer etching (ALE) was developed for TiN using 3 steps of plasma oxidation, plasma fluorination, and thermal removal. In the plasma oxidation step, TiN was oxidized to form TiO_2 with O_2 plasma at 100℃. The TiO_2 thickness was saturated with O_2 plasma after an exposure time of 300s and saturated thickness increased from 0.29 to 1.23nm with increasing temperature and RF power. In the plasma fluorination step, TiO_2 layer was converted to TiO_xF_y with CF_4 plasma at 100℃. The F atomic percentage on the surface was saturated at 12% with RF power below 15W. In the thermal removal step, TiO_xF_y layer was completely removed above 150℃. The removal rate of TiN ranged from 0.24 to 1.71 nm/cycle by controlling the TiO_2 thickness determined earlier. The roughness of TiN surface decreased from 1.27nm to 0.26nm after 50 cycles of ALE process. The suggested TiN ALE process is expected to provide an effective process for atomic-scale three-dimensional structures.

ALE-SuP-5 Prediction of Chemical Evolution and Its Impact on PEALE of Silicon Nitride with Hydrofluorocarbons*, Erik Cheng*, *G. Hwang,* University of Texas at Austin*; P. Ventzek, Z. Chen, S. Sridhar, A. Ranjan,* Tokyo Electron America

Viable plasma enhanced atomic layer etching (PEALE) of silicon nitride (SiN) by inert ion bombardment of a hydrofluorocarbon (HFC) treated surface has been demonstrated, but the nature of the surface through HFC adsorption and SiN removal is poorly understood. A comprehensive first-principles based simulation investigation of this process suggests Ar^+ ion bombardment of an adsorbed HFC is accompanied by damage of the SiN and implantation of small H, F, and C containing fragments into the substrate. The quasi-equilibrium (QE) film structure is predicted to be associated with a significant density of coordination defects, an approximately half Gaussian distribution of H, F, C in the bombardment direction, and a stoichiometry determined by the HFC used. Model QE structures of appropriate structure and composition were then constructed based on the observed evolution of SiN films under simulated PEALD conditions. These structures were bombarded by argon ions to describe volatilization of the film. We find that F is critical for etch enhancement. A transition from etch initiation, through etch with emanation of nonequilibrium products, and then equilibrium products as a function of F load and ion energy is observed. The inhibiting or enhancing role of H and C load relative to F load is also demonstrated. Loading H instead of F is associated with minimal to no etch enhancement, whereas loading C results in the suppression of etch reactions from the formation of highly stable SiC.

ALE-SuP-6 Achieving High Uniformity in Atomic-Scale Etching via a Purgeless Atomic Layer Etching Approach*, Yebin You,* *Y. Lee, C. Cho, I. Seong, W. Jeong, J. Lee, S. Kim, Y. You, M. Choi, T. Yuk, S. You,* Chungnam National University, Korea (Republic of)

Since plasma had been employed to the etch process of semiconductor manufacturing, etch uniformity has been one of the most important issues, and in this atomic scale era, high etch uniformity is of increasing importance. In achieving atomic-scale uniformity, atomic layer etching (ALE) has arisen as a next-generation etch technique due to its self-limiting characteristic. The long processing time of ALE however hinders the wider employment of ALE in the semiconductor industry. In this presentation, we will propose a novel ALE method where no purging step is required and discuss its applicability with the evaluation of its ability to obtain high etch uniformity over a wafer-scale area.

ALE-SuP-7 Thermal Atomic Layer Etching of Tantalum Nitride With Plasma Surface Oxidation and Fluorination*, Hojin Kang*, *H. Chae, Y. Kim,* SKKU, Korea (Republic of)

Conventional copper (Cu) interconnect technology requires a diffusion barrier between Cu and dielectric structures because Cu diffuses rapidly in the dielectric.[1] Tantalum nitride (TaN) is one of the promising materials for Cu diffusion barrier due to low electrical resistance and thermodynamic stability.[2] Nanoscale thick TaN is challenging to grow because the nucleation on surface leads to islands in large scale, and the surface is not smooth enough for device fabrication.[3] Etch back process with ALE cycle is one way to reducing the surface roughness.[4] In this work, ALE process for TaN was developed with the following sequential reaction: surface oxidation and removal with fluorocarbon plasmas. In the surface modification step, the TaN surface was oxidized to tantalum oxide (TaO_x) using O_2 plasma. The oxygen atomic concentration was saturated to 31% after 300 second and the thickness change of the converted TaO_x layer was about 1.4 nm. In the removal step, the TaO_x layer was converted to tantalum fluoride (TaF_x) by fluorocarbon plasmas in a temperature range of 25 to 300°C. The etch rate of TaN increased in the temperature range of 25 to 300 °C during the removal step. The etch rate of TaN was self-limited at 1.3 nm/cycle in the time of 120 seconds with a fluorocarbon plasma.

References

[1] W. F. Wu, K. L. Ou, C. P. Chou, and C. C. Wu: J. Electrochem. Soc. 150 (2003) G83.
[2] Ramberg, C. E., Blanquet, E., Pons, M., Bernard, C., & Madar, R . Microelectron Eng 50(1-4), (2000) 357.
[3] Volpi, F., Cadix, L., Berthomé, G., Coindeau, S., Encinas, T., Jourdan, N., & Blanquet, E. Thin Solid Films 669 (2019) 392.
[4] George, S. M., & Lee, Y. ACS Nano,10, (2016) 4889.

Keywords: Atomic layer etching, Tantalum nitride etching

ALE-SuP-8 New Oxidants for Cu ALE via In Situ XAS Mechanistic Study*,*
Adam Hock*, P. Panariti,* Illinois Institute of Technology

Sub-10 nm scaling comes with unprecedented challenges for semiconductor fabrication. Atomic Layer Etching (ALE) is a technique that is becoming increasingly important in semiconductor fabrication, however, it has yet to be widely adopted. Many examples of ALE use harsh chemistry such as halogenated compounds or plasma, which result in damaged and non-conformal structures. Copper is an important interconnect material, so scalable copper ALE is of high importance and further research of both metallic Cu activation and etch are required. Oxidation of metallic Cu surfaces with unselective oxidants (H_2O_2, O_3, oxygen plasma etc.) tend to produce multiple oxidation states of Cu (+1 and +2) as well as Cu mobility at elevated temperatures. This study reports a comparison between conventional oxidants as well as milder, more selective oxidizing agents that produce a more controlled oxidation of Cu surfaces.

X-ray absorption spectroscopy (XAS) was used to directly observe Cu oxidation under oxidation conditions.Temperatures from ambient to 145°C were screened with oxidants and oxidation was found to be to Cu_2O to detection limits.The depth was controllable from less than 2nm to complete oxidation under the conditions studied.The oxidation could be controlled by process conditions and, more importantly, by the nature of the oxidation reagent.These data are compared to *in situ* TEM measurements of Cu particles and measured oxidation thickness as a function of oxidant exposure and found to be comparable.The XAS technique was further benchmarked using conventional XPS measurements.These measurements illustrate that XAS is able to probe surface activation for ALE.In addition, XAS provides metal coordination number, oxidation state, and other mechanistic information about the surface metal state.These measurements combine to provide a better understanding of the relationship between oxidant strength versus depth as a function of various oxidants. These results give insight into the etch-per-cycle as well, Cu surface roughening, and other metrics for the final films.

Plenary Session
Room Auditorium - Session PS-MoM1

Plenary Session I

Moderators: Christophe Detavernier, Ghent University, Belgium, Erwin Kessels, Eindhoven University of Technology, Netherlands

9:00am **PS-MoM1-2 Plenary Lecture: New Process Requirements Driven by More Than Moore and More Moore Device Integration Innovations***, **Steven Steen**,* ASML*; P. Leray,* IMEC, Belgium **INVITED**

Over fifty years of semiconductor innovation has targeted transistor device scaling in order to sell ever increasing functional performance at equivalent cost per function. This relentless drive for miniaturization and functional integration on Silicon has been described by Gordon Moore [1] and has colloquially become *Moore's law*. Continued scaling will bring new challenges in process and integration that will enable “more Moore”. An orthogonal trend in the industry captured under the designation of “More than Moore” focuses on the continued cost and density scaling through other means than just geometric scaling. The non-volatile memory segment has been the first to

transition from 2D to 3D devices to enable continued NAND bit cost scaling. The additional performance scaling levers are being considered for DRAM and Logic and will introduce new dimensions to process requirements. The approach to the wider innovation will be expected to deliver the promise of continued performance, cost and functionality improvements for the next decades. In this presentation we will discuss “more Moore” and “more than Moore” device technologies and show how these bring new process integration challenges.

9:45am **PS-MoM1-5 ALD 2020 Innovator Awardee Talk: Innovations in ALD Chemistry Open the Door to Applications***, **Mikko Ritala**,* University of Helsinki, Department of Chemistry, Finland **INVITED**

The success of ALD is built on chemistry. Whenever one wants to exploit the unique benefits of ALD with a new thin film material, proper precursors fulfilling the ALD criteria must be found for that material. Often new chemistry is needed for also those materials that have already earlier been deposited by ALD because the existing processes are not compatible with the new application. The connection works also the other way: once a new material and process is added to the ALD portfolio, it may be adopted into applications other than that originally possibly developed for. This talk will make an overview of development of ALD chemistry from the past to the future. Through selected examples it will be shown how innovations in precursor chemistry have made it possible to exploit ALD in new applications. Challenges, opportunities and directions for the ALD chemistry development and research will be discussed.

ALD processes consist of two or more precursors. Accordingly, breakthrough innovations can be made through metal precursors, non-metal precursors, and the ways how these are combined. Examples will show all three approaches being used. Area selective ALD adds further needs and possibilities for innovations, like area selective etching of polymers.

Knowledge on ALD processes progresses through different levels. The first and also the most important one is finding the chemistry that deposits the desired film, while higher levels add progressively our understanding on that how the chemistry actually works. While the former is straightforward to test, the latter is much more challenging and rarely fully complete. Examples of successful reaction mechanism studies from the past and an outlook to the future will be given.

ALD Applications
Room Van Rysselberghe - Session AA-MoM2

ALD for Solar Energy

Moderators: Wei-Min Li, Jiangsu Leadmicro Nano-Equipment Technology Ltd., Paul Poodt, Holst Centre / TNO

10:45am **AA-MoM2-1 Atomic Layer Deposition for Silicon-Perovskite Tandem Cells*, Bart Macco*,** *N. Phung, E. Kessels, M. Creatore,* Eindhoven University of Technology, Netherlands **INVITED**

Solar cells are one of the pillars of the energy transition, where cells based on silicon wafers dominate this market of currently over 200 gigawatts per year. Though not widely known, ALD is now omnipresent in these silicon cells, where on the order of 10 billion wafers are coated with Al_2O_3 passivation layers per year, often using batch or spatial ALD.[1]

While silicon solar cells will dominate the market for the foreseeable future, the anticipated “next big thing” are so-called monolithic tandem solar cells which combine a silicon bottom cell and a perovskite top cell. These tandem cells have skyrocketed in efficiency to almost 30% (compared to 26.7% for silicon only), and have an incredible momentum both in R&D and pilot production.

These tandems cells are highly relying on functional thin films and as such this offers many more opportunities for ALD. Materials “beyond simple ALD Al_2O_3” are needed, including passivation, charge transport and buffer layers as well as tunnel recombination junctions with transparent conductive oxides. At the same time, the application has stringent demands such as extremely low cost, pinhole-free conformal films to avoid electrical shunts and often the need for processing on sensitive perovskite (e.g. max. temperature of ~100 ^{o}C). As will become clear, the distinct merits of ALD such as soft deposition, relatively low-temperature processing, conformality and excellent control over doping and stoichiometry are highly relevant in this field. This will be highlighted through selected case studies. These include ALD SnO_2, a well-established buffer layer which is present in most *(if not all)* recent record tandem cells, as well as recent innovations from our group being ALD NiO hole-selective contacts on the perovskite side [2] and ZnO:Al-based electron contacts on the silicon side.[3]

Finally, I would like to thank the whole PERCSpective consortium for their contributions.

[1] B. Macco, “What can Atomic Layer Deposition do for solar cells?,” *AtomicLimits.com*, 2019. https://www.atomiclimits.com/2019/10/15/what-can-atomic-layer-deposition-do-for-solar-cells-a-few-afterthoughts-from-my-ald-conference-tutorial/.

[2] N. Phung *et al.*, “Enhanced Self-Assembled Monolayer Surface Coverage by ALD NiO in p-i-n Perovskite Solar Cells,” *ACS Appl. Mater. Interfaces*, 2021, doi: 10.1021/acsami.1c15860.

[3] B. Macco *et al.*, “Atomic-layer-deposited Al-doped zinc oxide as a passivating conductive contacting layer for n+-doped surfaces in silicon solar cells,” *Sol. Energy Mater. Sol. Cells*, vol. 233, no. September, p. 111386, Dec. 2021, doi: 10.1016/j.solmat.2021.111386.

11:15am **AA-MoM2-3 ALD Al_2O_3/SiO_x Multilayers for c-Si Surface Passivation: Modification of Interface Properties by Voltage Stress and Plasma Treatments*, Armin Richter*,** *H. Patel, C. Reichel, P. Masuch, J. Benick, S. Glunz,* Fraunhofer ISE, Germany

Al_2O_3 is one of the most effective dielectric surface passivation layers for silicon solar cells. Due to the high amount of negative fixed charges, it is particularly suited for the passivation of p-type Si surfaces. However, other surface passivation schemes indicated recently that there is still room for improvement which becomes more and more important with increasing solar cell performance.

In contrast to single layers, multilayers with thicknesses of only a few nanometers of the individual layers open the opportunity to modify material properties on a nanometer scale. Multilayers of Al_2O_3 and SiO_2, for instance, have been studied recently for the application in MOSFETs because they allow to tune the flat-band voltage shift simply by varying the number of single layers in the multilayer. The origin of this voltage shift are dipoles, which are formed only at the SiO_2/Al_2O_3 interface with one polarity but not at the Al_2O_3/SiO_2 interface with the opposite polarity.

In this work we investigate systematically if such Al_2O_3/SiO_2multilayers are also beneficial for Si surface passivation. We used ALD to prepare the multilayer because of its ultimate deposition control and being at the same time industrially relevant. With CV measurements we studied the interface characteristics (interface defect density D_{it} and total effective fixed charge density Q_{tot}) to gain insights into the electronic properties of the multilayers.

Our results reveal that by varying, for instance, the number of layers in the stack or the deposition and post deposition anneal temperature, the surface passivation of the multilayers is very similar to that of Al_2O_3 single layers but not significantly improved. In fact, we found that Q_{tot} of the multilayers is actually even lower than that of the Al_2O_3 single layers. We studied further the influence of voltage stress. We found that it strongly effects Q_{tot} for both the multilayers and Al_2O_3 single layers and that voltage stress of the right polarity results in a significantly increase of Q_{tot}. However, too high voltage stress deteriorates D_{it}, i.e. the chemical passivation.

In addition, we studied also whether in-situ plasma treatments during the deposition of the multilayer effects its electronic properties. We found that especially H plasmas after the SiO_2 deposition results in a quite substantially improved surface passivation, significantly better than that of the Al_2O_3 single layer. A detailed analysis of the interface properties will be provided in the final paper. As such, our results indicate a promising way of improving the Si surface passivation. However, our results can be also interesting for other semiconductor devices.

11:30am **AA-MoM2-4 Atomic Layer Deposition of Aluminium Doped $Zn_{1-x}Mg_xO$ as Transparent Conducting Films for Photovoltaics*, Poorani Gnanasambandan*,** *N. Adjeroud, R. Leturcq,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

We investigate atomic layer deposited aluminium doped zinc magnesium oxide films with varying Al content as transparent conducting films with tunable bandgap. While Aluminium doping of zinc oxide increases the electrical conductivity, it decreases the transmission due to absorption close to the band edge [1].On the other hand, with addition of Mg, the optical properties and bandgap of ZnO can be tuned making them well-suited for photovoltaic applications [2].

Most previous studies on aluminium doped zinc magnesium oxide (Al:ZMO) involved sputtering. While ALD has been used to investigate both aluminium doped zinc oxide (AZO) and magnesium doped zinc oxide (ZMO) [2][3], studies on Al:ZMO were limited to few ratios [4]. Also, the ALD studies fixed the Al-Zn doping concentration around 3% and varied the Mg doping. We aim to increase the electrical conductivity and tune the bandgap by varying both Al and Mg doping concentration.

Optimizing a quaternary process by mixing three binary ALD process involves immense challenges [5]. We achieve high degree of control on composition by optimizing the growth conditions with supercycle parameters such as pulse ratios and bilayer period. With the advantage of precise composition control, we study ALD grown Al doped $Zn_{1-x}Mg_xO$ with x varying from 0.2 to 0.3 and varying aluminium doping concentrations from underdoped to over doped cases. We elucidate the effect of doping on the band alignment, electrical and optical properties.

[1].Zhang, Wu, et al. "Tailoring of optical and electrical properties of transparent and conductive Al-doped ZnO films by adjustment of Al concentration." Materials Science in Semiconductor Processing 74 (2018): 147-153.

[2]. Törndahl, T., et al. ‘Atomic Layer Deposition of Zn1−xMgxO Buffer Layers for Cu (In,Ga)Se2 Solar Cells’. Progress in Photovoltaics: Research and applications 15.3 (2007): 225-235.

[3]. Peng, Qing, Anil U. Mane, and Jeffrey W. Elam. "Nanometer-Thick Mg x Zn (1–x) O Ternary Films for Photovoltaics." ACS Applied Nano Materials 3.8 (2020): 7732-7742.

[4]. Fleischer, Karsten, et al. Aluminium Doped Zn 1 − x Mg x O – a Transparent Conducting Oxide with Tunable Optical and Electrical Properties. Applied Physics Letters 101.12 (2012): 121918.

[5]. Mackus, Adriaan JM, et al. "Synthesis of doped, ternary, and quaternary materials by atomic layer deposition: a review." *Chemistry of Materials* 31.4 (2018): 1142-1183.

11:45am **AA-MoM2-5 An in-Situ Infrared Spectroscopy Study on the Influence of ALD SnO_2 on Formamidinium-Based Metal Halide Perovskite*, A.E.A. (Andrea) Bracesco*,** *J. Jansen, W. Kessels,* Eindhoven University of Technology, Netherlands*; V. Zardetto,* Solliance Solar Research, Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

The conversion efficiency of metal halide perovskite solar cells (PSCs) has reached 25.7%.[1] This record was achieved through engineering of the optoelectronic properties of the absorber and charge-selective and efficient interfaces between charge transport layer (CTLs) and the absorber. Recently, the focus has shifted towards the replacement of organic CTLs, often leading to parasitic absorption and long-term device instability. Metal oxides prepared by gas phase deposition methods, such as ALD, are prime candidates. The ALD merit of control over film stoichiometry, conformality and uniformity has led to several applications in PSCs. In this respect, ALD SnO_2, in combination with fullerene-based electron transport layers (ETLs), is the state-of-the art in p-i-n PSCs, imparting thermal and environmental stability to the device.[2] However, when attempting to replace the fullerene ETLs by ALD SnO_2 processed directly on the perovskite absorber, a poor device performance is observed, due to severe chemical changes imparted to the inorganic fraction of the perovskite, as previous XPS studies showed.[3,4]

In this contribution, we shift the focus of the investigation on the organic fraction of the perovskite absorber, specifically on the formamidinium cation (FA) in a $CsFAPb(I,Br)_3$ perovskite. By adopting in situ IR spectroscopy, we evaluate the effect that ALD processing conditions, such as substrate temperature, vacuum, and exposure to half and full ALD SnO_2 cycles (tetrakis(dimethylamido)-Sn(IV) (TDMA-Sn) and H_2O), have on FA IR spectral features. We observe that the cation is not affected by vacuum (10^{-5} mbar) and exposure to water half-cycles. Instead, prolonged exposure to a temperature range of 50-100°C (standard SnO_2 processing temperature on perovskite with/out the fullerene-based ETL) leads to the loss of N-H stretching modes. We speculate that FA deprotonates into formamidine, which is then released from the surface. Lastly, we report that the loss of FA, is also detected when the perovskite surface is exposed to a 500 ms pulse of TDMA-Sn. Moreover, the precursor-perovskite surface interaction leads to the formation of sym-triazine, i.e. a decomposition product of formamidine, which becomes trapped at the perovskite/SnO_2 interface. These studies enable to decouple the several effects of direct ALD processing on perovskite and highlight the major role played by the Sn-precursor in affecting the perovskite surface chemistry.

[1]H. Min et al., Nature,598, 444–450, 2021

[2]V. Zardetto et al., Sustainable Energy Fuels, 1, 30-55, 2017

[3]A. F. Palmstrom et al., Adv. Energy Mater., 8-23, 1800591, 2018

[4]A.E.A. Bracesco et al., JVSTA, 38, 063206, 2020

ALD Fundamentals
Room Auditorium - Session AF1-MoM2

New Precursors and Processes I

Moderators: Sean Barry, Carleton University, Canada, Elisabeth Blanquet, SIMaP, CNRS, University Grenoble Alpes

10:45am **AF1-MoM2-1 Atomic Layer Deposition of Ruthenium Dioxide Thin Films Based on Redox Reactions between RuO_4 and Alcohols***,* ***Matthias Minjauw****, N. Poonkottil, A. Werbrouck, C. Detavernier, J. Dendooven,* Ghent University, Belgium

Ruthenium dioxide (RuO_2), the only stable oxide of Ru metal, is a workhorse in several applications including supercapacitors, catalysis, and electrochemical devices owing to its high conductivity, good chemical stability, and a work function value higher than metallic Ru.[1] However, atomic layer deposition (ALD) literature reports on this material are scarce. Existing ALD processes based on metalorganic Ru precursors demand careful tuning of the O_2 partial pressure in order to deposit RuO_2 films, because a too low O_2 partial pressure leads to Ru metal deposition. These processes often require a relatively high deposition temperature (>180°C) and suffer from significant nucleation delays.[2]

An ALD method for the deposition of RuO_2 films without any significant nucleation delay, employing alcohols and RuO_4 as reactants is presented. Using methanol and RuO_4, a growth per cycle (GPC) of 1Å is obtained, at a deposition temperature as low as 60°C (**Figure 1**). The reaction of higher chain alcohols such as ethanol, 1-propanol and 2-propanol with RuO_4 also results in RuO_2 thin films, with a GPC that increases with the number of carbon atoms in the alcohol chain. The investigated reactant combinations display typical self-saturating ALD properties. The as-deposited films are amorphous irrespective of the alcohol used but can be transformed into crystalline rutile RuO_2 by annealing in helium or in air at around 400 °C (**Figure 2**). The deposited films are conductive as evident from a value of 230 μΩ.cm measured for a 20 nm film deposited by the methanol-based process, and the conductivity improved after the anneal. Based on a combination of in situ mass spectrometry, in situ Fourier transform infrared spectroscopy, and in vacuo X-ray photoelectron spectroscopy results, we propose a reaction mechanism for the developed process (**Figure 3)**. During the alcohol pulse, the top RuO_2 surface is partially reduced RuO_x ($x<2$), and the alcohol molecules are oxidized into CO_2 and H_2O on the RuO_2 surface. This reaction also leaves some carbon monoxide (CO) residues on the surface. During the next RuO_4 pulse, the CO surface species are oxidized to CO_2 and the RuO_x surface is oxidized back to RuO_2, while additional RuO_2 is deposited onto the surface.

References:

1. Ryden et al., *Physical Review B* **1970,** *1* (4), 1494.
2. Austin et al., *Chemistry of Materials* **2017,** *29* (3), 1107-1115.

This work is funded by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No.765378.

11:00am **AF1-MoM2-2 Low Temperature ALD of Ni from Novel Precursors***,* ***Anton Vihervaara****, T. Hatanpää, K. Mizohata, G. Popov, M. Chundak, M. Ritala,* University of Helsinki, Finland

High quality metal thin films are an essential material class in the development of new technologies. Ni thin films may be used in a variety of applications, including protective coatings, catalysis and microelectronics. For example, nickel is a valid candidate for replacing copper as an interconnect material. Nickel also has ferromagnetic properties, and nickel films could be the key in the development of magnetic memories.

Out of all thin film deposition methods, ALD is the best suited for the manufacturing of complex 3D structures that are essential in future technologies. Several ALD processes for Ni metal already exist, but new ones are constantly sought out to overcome limitations of the existing ones. In order to have very thin but also completely continuous films, it is important to keep the deposition temperature low. Typically, a lower deposition temperature leads to smaller grains and thus to smoother films. Our approach focuses on novel ALD precursors, both the metal precursors and reducing agents, as the key factors limiting the deposition temperature are the reactivity and vapor pressure of the precursors.

1,4-bis(trimethylsilyl)-1,4-dihydropyrazine ($(Me_3Si)_2DHP$) is a promising reducing agent that has been used to deposit Ti and Sn films from their respective chlorides.[1,2] Reducing Ti^{4+} to metallic state is especially challenging due to its low redox potential. These studies indicated general reactivity of $(Me_3Si)_2DHP$ towards metal halides. However, in our experiments, $(Me_3Si)_2DHP$ did not work well with our nickel halide precursor at low temperatures. Instead, its germanium analogue 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine ($(Me_3Ge)_2DHP$) showed great potential as a novel powerful reducing agent.

In this study, we developed a new ALD process for Ni metal from the novel precursors $NiCl_2(PEt_3)_2$ and $(Me_3Ge)_2DHP$. Smooth nickel films were deposited on different substrate materials at 110 °C which is the lowest deposition temperature for Ni metal found in the literature. ALD characteristics were confirmed and saturation achieved with both precursors. Growth rate is 0.2 Å/cycle when the film is not continuous and decreases to 0.1 Å/cycle after the film becomes pinhole-free. Besides a small amount (7 at.%) of carbidic carbon, the films have only small amounts of impurities. Most notably the chlorine content is below 0.2 at.%. Furthermore, $(Me_3Ge)_2DHP$ shows promising results with other metal halide precursors too, and can therefore open new avenues for ALD of metals at low temperatures.

[1] E. C. Stevens et al., *J. Vac. Sci. Technol. a*, 2018, **36**, 06A106.

[2] J. P. Klesko et al., *Chem. Mater.*, 2015, **27**, 4918–4921.

11:15am **AF1-MoM2-3 Enhanced Cation Control in ALD of Alkali Metal Containing Films by Avoiding Water-Reservoir Effects***,* ***Henrik H. Sønsteby****,* University of Oslo, Norway

Alkali metal containing the films get increasing attention in a world moving towards green- and sustainable energy and chemistry. Lithium containing thin films are important as e.g. solid electrolyte interface layers in batteries. Sodium containing materials may provide low-cost options for the next generation of batteries, and some potassium compounds are important ferroelectrics that may abolish the lead-hegemony within sensors and actuators. The heavier alkali metals, rubidium and cesium, are crucial components in perovskite solar cells and may also provide routes to novel functional perovskite materials.

As important as they may sound, alkali metal containing compounds (with the exemption of lithium) has seen very little activity within the ALD community. ALD processes for Na and K were introduced in 2014, and was followed by Rb and Cs in 2018 and 2020, respectively. Processes for important functional materials like NaCoO2, (K,Na)NbO3 and K(Ta,Nb)O3 have been developed, but all of them struggle with loss of control due to significant water reservoir effects. This is due to strong hygroscopicity of intermediary species, storing water in the films that react with the alkali metal precursors during deposition. In some cases this may be controlled by careful process optimization, but this severely compromises the reproducibility of published processes.

In an attempt to remove the water reservoir effects, we have developed new processes for alkali metal containing thin films. These make use of the same alkali metal precursors as before (t-butoxides), but removes water outright, relying on O3 as the oxygen source. We observe that this completely eliminates the water reservoir effect, giving a much more stringent process control. This means that there are no changes in the process chemistry during deposition, leading to homogeneous films with easier access to controlled tuning of the cation composition.

In this talk, I will use in situ metrology and ex situ diffraction studies to show how these new ozone based processes provide far superior alkali metal containing thin films. I will use the complex oxide K(Ta,Nb)O3 as an example, providing significant impact as an important component in electrooptical applicaitons. I will show that crystallinity and epitaxy is achieveable at lower temperatures than with the water based process, with much higher compositional control.

These findings are important in a wide range of fields, from sustainable energy to next generation electronic devices, where ALD will play a crucial role in the development of new devices.

11:30am **AF1-MoM2-4 Atomic Layer Deposition of Lead Halides: $PbBr_2$ and $PbCl_2$*, Georgi Popov,*** *C. Van Dijck, L. Junkers,* University of Helsinki, Finland*; G. Bačić,* Carleton University, Canada*; A. Weiss, M. Mattinen, A. Vihervaara, P. Jalkanen, K. Mizohata, J. Räisänen, M. Kemell, M. Leskelä,* University of Helsinki, Finland*; S. Barry,* Carleton University, Canada*; M. Ritala,* University of Helsinki, Finland

In our previous work we used lead(II) bis[bis(trimethylsilyl)amide], $Pb(btsa)_2$, and tin(IV) iodide for ALD of PbI_2.[1] We hypothesized that similar chemistry is straightforwardly extendable to ALD of other metal halides. Here we put this hypothesis to the test by using analogous chemistry for ALD of $PbBr_2$ and $PbCl_2$. The chemistry can indeed be extended to these lead halides, but we also encountered a number of technical challenges and unexpected outcomes.

The vapor pressure of $SnBr_4$ made ALD of $PbBr_2$ from $SnBr_4$ and $Pb(btsa)_2$ challenging in our ALD reactors. The vapor pressure of $SnBr_4$ is too high for internal hot source and too low for external cold source. Therefore, for ALD of $PbBr_2$ we employed $TiBr_4$, a compound very similar to $SnBr_4$ but with a lower vapor pressure. $TiBr_4$ could be delivered from a hot source. The $PbBr_2$ films deposited with $Pb(btsa)_2$ and $TiBr_4$ are uniform, pure and crystalline. The $PbBr_2$ process displays characteristics typical for an ALD process such as saturation of the growth per cycle values with respect to precursor doses.

Development of an ALD process for $PbCl_2$ required the largest research effort. $Pb(btsa)_2$ and $SnCl_4$ did deposit $PbCl_2$, but the process did not show saturative behavior and had other non-ideal features. With a new lead precursor bis[lead(II) *N,N'*-di-*tert*-butyl-1,1-dimethylsilanediamide], $(Pb(gem))_2$[2], the deposition was saturative but the films contained tin. Similarly, a process using $Pb(btsa)_2$ and $TiCl_4$ suffered from titanium incorporation.

As a last-ditch effort we tried $GaCl_3$ as the chlorine source. The quality of the first films grown with $GaCl_3$ was disastrous, however relatively minor gallium incorporation encouraged us to continue our pursuit for a $PbCl_2$ ALD process. Through a series of optimizations in the $GaCl_3$ delivery system we were able to develop a process that produces crystalline, pure and uniform $PbCl_2$ films and has the characteristics typical for ALD. Additionally, the optimized delivery system solved the challenges associated with the use of $SnBr_4$.

Our interest in ALD of lead halides is application driven. Various post treatments can convert lead halides into halide perovskites, materials with outstanding opto-electronic properties, that can be improved even further in mixed halide perovskites.[3] We are currently studying whether combining ALD processes of different lead halides and post processing of the resulting films will afford perovskites with mixed composition such as $CH_3NH_3PbI_{3-x}Br_x$.

[1] Popov et al. Chem. Mater. **2019.** 10.1021/acs.chemmater.8b04969

[2] Bačić, PhD Thesis, Carleton University **2021**. 10.22215/etd/2021-14420

[3] Zarick et al. *J. Mater. Chem. A.* **2018**. 10.1039/c7ta09122b

11:45am **AF1-MoM2-5 Carbene Based Precursors for the ALD of Coinage Metals*, Nils Boysen,*** Ruhr University Bochum, Germany*; A. Philip,* Aalto University, Finland*; D. Rogalla,* Ruhr University Bochum, Germany*; M. Karppinen,* Aalto University, Finland*; A. Devi,* Ruhr University Bochum, Germany

Thin layers of coinage metals like copper and silver are of immense importance for a variety of technological applications. While the atomic layer deposition (ALD) of copper thin films is fairly well developed and several suitable copper precursors are known, the same is not true for silver. The very limited number of silver precursors which combine a high thermal stability, volatility, and reactivity has been a hindrance for the convenient fabrication of silver thin films by ALD. Seen from a chemical perspective, organometallic Cu(I) and Ag(I) compounds feature remarkable similarities in their structure, ligand-to-metal interaction, and reactivity.

In this study, we opted for a systematic transfer of structural motifs from N-Heterocyclic carbene (NHC) stabilized copper(I) complexes bearing anionic diketonate ligands to the resulting isostructural Ag(I) complexes, while the structure, thermal properties and reactivity was comparatively analyzed. As a result, five new monomeric Cu complexes and four new isostructural Ag complexes with the general formula [M(NHC)(diketonate)] (M = Cu, Ag) were successfully synthesized (Scheme 1). Through a rational and incremental change of the substitution pattern of the anionic backbone based on diketonates, clear trends in their structural and thermal parameters could be observed. Nuclear magnetic resonance (NMR) spectroscopy, single-crystal X-ray diffraction (SC-XRD) and electron-impact mass spectrometry (EI-MS) revealed a first interesting trend in the bonding and structure of the complexes: Despite featuring a monomeric nature in the solid, liquid, and gaseous phase, differences in structure, bond lengths and bond angles were observed depending on the employed metal for complexation. An extensive search in the Cambridge Structural Database (CSD) enabled to ascertain the differences seen in bonding between the isostructural Cu and Ag complexes while revealing additional similarities and differences. The evaporation profile and thermal characteristics as analyzed by thermogravimetric (TG) measurements highlight that the Cu complexes feature a higher thermal stability compared to the isostructural Ag analogs (Figure 1). Proof-of-principle ALD with [Cu(NHC)(acac)] was carried out at low temperatures (145 °C) for depositing metallic Cu using hydroquinone as the reducing agent which were subsequently analyzed by XRD, SEM (Figure 2) and RBS/NRA.

The findings from this study set a new milestone in the understanding of the influence of systematic anionic ligand choice on the applicability of Cu(I) and Ag(I) precursors in vapor-phase deposition processes.

12:00pm **AF1-MoM2-6 Low Temperature ALD of Metals and Nitrides Using Thermally Generated Radical Precursors*, Goran Bacic,*** Carleton University, Canada*; C. Dezelah,* ASM Microchemistry Ltd., Finland*; S. Barry,* Carleton University, Canada

Radicals are the main reactive species in remote plasma-enhanced atomic layer deposition (PEALD). The highly reactive nature of radicals can enable deposition at substantially reduced temperatures compared to thermal ALD. However, plasma-generated radicals are unstable transient species that can have limited diffusion, causing non-uniform deposition inside small features like trenches and vias. To overcome the limitations of plasma-generated radicals, we propose to harness the reactivity of these species more effectively by designing precursors that thermally generate radicals directly inside the deposition chamber.

In this presentation, we will report our efforts to design thermal H• and $\bullet NH_2$ radical-generating precursors for ALD of metals and nitrides, respectively. A good thermal radical precursor should generate a stable radical species that itself does not react further with the growing film or substrate, analogous to spectator ions in solution. While stable radical chemistry in solution has a rich and diverse history, there is little precedent for the use of radicals or their precursors in the synthesis of metal and nitride materials, and there was virtually no description of their use in the gas phase. Moreover, the factors that reportedly influence radical stability (e.g., extended π-systems, huge steric bulk) are at odds with traditional precursor design.

We took a concerted theoretical and experimental design approach and propose several precursor candidates displaying many or all of the desired properties: small E—H or E—NH_2 homolytic bond dissociation enthalpies (BDE < 70 kcal/mol), high volatility (T_{1Torr} < 100 °C), high thermal stability (T_{dec} > 300 °C), high reactivity (T_{ALD} < 300 °C), low cost (<4 steps to synthesize), and low health and environmental risk. Volatility and thermal stability were determined by thermogravimetric analysis (TGA), with most precursors achieving a vapor pressure of 1 Torr below 100 °C and showing thermal stability up to at least 300 °C. We explored solution-phase reactivity toward industrially relevant ALD precursors by NMR spectroscopy and further studied precipitates from these solution test reactions by SEM and TEM. ALD process development using a commercial reactor for each precursor was accelerated by in-situ quartz crystal microbalance (QCM) analysis. Finally, due to their highly reactive nature, special attention was given to synthesis scale-up and potential health and environmental risks of our best precursors.

ALD Fundamentals
Room Van Eyck - Session AF2-MoM2
High Aspect Ratio/High Surface Area/Powder ALD

Moderators: Jolien Dendooven, Ghent University, Belgium, Juhani Taskinen, Picosun Oy

10:45am **AF2-MoM2-1 Influence of the High Aspect Ratio Geometry to ALD Thin Film Growth***, **Oili Ylivaara,*** VTT Technical Research Centre of Finland*; M. Utriainen, P. Hyttinen,* Chipmetrics Oy, Finland*; R. Puurunen,* Aalto University Aalto School of Chemical Engineering, Finland

ALD is a thin film growth method enabling device down-scaling beyond Moore's law[1]. Device down-scaling gives boundary conditions to thin film quality in a sense of film uniformity, conformality and homogeneity, which need to be characterized even a few nanometers thin. Shrinking device dimensions and film thicknesses set new challenges to process development and quality control as thin film analysis and characterization becomes challenging. PillarHall™ LHAR test structure has proven its value in ALD conformality characterization[2-4]. High aspect ratio (HAR) geometry in PillarHall has characteristically infinitely wide trench with height of 500 nm and width of 10 mm. However, in real applications the geometry and pitch size vary. The question is how variable HAR geometries correlate with PillarHall in conformality and ALD growth analyses? In this study, we used nanolaminate ALD process and set of variable high aspect ratio test structure geometries as substrates. Thermal ALD Al_2O_3-TiO_2 nanolaminate growth was studied at three different temperatures, at 110, 200 and 300 °C. Targeted film thickness was 25 nm. For nanolaminate, sublayer thicknesses were targeted to 1 nm both for Al_2O_3 and TiO_2. For comparison results were compared with LHAR chips coated with reference ALD Al_2O_3 grown at 300 °C. Five different conformality test chip designs were coated in a one run and analyzed: PillarHall LHAR4 with three different channel heights namely 100, 500 and 2000 nm. A prototype PillarHall LHAR3 test chip with narrow lateral channels widths from 2 to 78 µm (so called FIN-design) and vertical HAR (VHAR) test structure of an array of vertical pores, 1 µm in diameter and 219 µm in depth. During the coating chips were place in center of the wafer holder to minimize the conformality variation at the wafer surface level. After the coating LHAR samples were analyzed by optical microscopy, spectroscopic reflectometry, and for VHAR samples electron microscopy cross-section was used. We show that with PillarHall, we can study in more detail the film growth in the channel, geometry dependence and study the process saturation in the channel. We also study of applicability of narrow channels of FIN-design, width from 2 to 78 µm, and compare the results with the Gordon model[5].

REFERENCES

[1] International Roadmap for Devices and Systems (IRDS™) 2021 Edition IRDS™ 2021: More Moore

[2] Gao, F. et al., J VAC SCI TECHNOL A, 33 (2015)

[3] Ylilammi, M. et al., J APPL PHYS, 123 (2018)

[4] Yim and Ylivaara, et al., Phys. Chem. Chem. Phys. 22 (2020)

[5] Gordon, R. G., Chem. Vapor Depos., 9 (2003)

11:00am **AF2-MoM2-2 Ultra-Low Temperature ALD of Pure Antimony for Grain Boundary Engineering of Thermoelectric Materials***, **Amin Bahrami,** S. He, R. He, S. Lehmann, K. Nielsch,* Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden e. V., Germany

Antimony (Sb) in thin film form is considered as a nano-optical material which is of interest for potential applications, such as photonic computing or high-speed holographic displays. It has been used as lens material in super-resolution near-field structures and broadband saturable absorber among others. In addition to optoelectronic properties, Sb is widely used as a dopant in tuning the transport properties of many thermoelectric materials such as PbTe, Half-Heusler compounds and so on. In this study we propose new ALD formulation for low temperature deposition of pure Sb down to 70 °C making this process applicable on the surface modification of low and medium temperature thermoelectric materials such as Mg_2Sb_3, Bi_2Te_3. Pure and conformal thin films of elemental Sb were prepared by ALD using $Sb(OEt)_3$ and $(Et_3Si)_3Sb$ as precursors with a growth per cycle (GPC) of 0.18 Å at deposition temperature of 70 °C. The electrical conductivity of the films grown on mica at 70 °C (1.13´10^{4} S/cm) is slightly higher than that of reported by Pore *et al.* (1.07´10^{4} S/cm). NbFeSb half-Heusler particles were successfully coated with ultra-thin layer of Sb and consolidated using high pressure sintering techniques. The results show addition of few atomic layer of Sb on NbFeSb particles can significantly enhance the electrical conductivity of the studied half-Heusler compound which was reduced during the high-pressure sintering.

11:15am **AF2-MoM2-3 Infilling Macroscopic Nanoparticle Networks via ALD***, **Benjamin Greenberg**, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Nanocomposites formed by infilling nanoparticle networks have unique thermal, mechanical, optical, and electronic properties. Typically, the networks are substrate-supported nanoparticle thin films with thickness on the order of 1 µm or less, and infilling is accomplished via ALD precursor dose times on the order of 1 s. In this work, we investigate the infilling of nanoparticle networks that are at least 1,000 times thicker. We press metal oxide nanopowder with particle size on the order of 100 nm to form nanoporous compacts with >1 mm thickness and ~50% solid volume fraction, and we coat the pores with ZnO by static-dose ALD, holding precursor vapor in the ALD chamber for several minutes per half-cycle. For comparison, we also produce an alternative nanocomposite by first coating the metal oxide nanopowder with ZnO in a particle ALD rotary reactor and then pressing the resultant core/shell nanopowder into a porous compact. In both cases, we use scanning electron microscopy, energy-dispersive X-ray spectroscopy, and electrical conductivity measurements to evaluate the uniformity and connectivity of the ZnO networks that form within the nanocomposites. Additionally, we examine ALD precursor diffusion and reaction kinetics and estimate saturation times through analysis of the deposition chamber pressure traces, and we compare our empirical findings to predictions based on a Knudsen diffusion model.

11:30am **AF2-MoM2-4 Zinc Acetylacetonate on Mesoporous Supports by Atomic Layer Deposition***, **Jihong Yim**, E. Haimi,* Aalto University, Finland*; M. Mäntymäki,* University of Helsinki, Finland*; V. Kärkäs,* Aalto University, Finland*; R. Bes,* University of Helsinki, Finland*; A. Arandia, J. Velasco, T. Viinikainen,* Aalto University, Finland*; S. Huotari,* University of Helsinki, Finland*; R. Karinen,* Aalto University, Finland*; M. Putkonen,* University of Helsinki, Finland*; R. Puurunen,* Aalto University, Finland

The self-terminating nature of atomic layer deposition (ALD) enables the preparation of uniform coatings on high-surface-area materials.[1] Our general aim is to use ALD to prepare zinc promoted heterogeneous catalysts for carbon dioxide hydrogenation into methanol.[2] In this work, we aimed to obtain uniform coating of zinc on mesoporous monoclinic zirconia and gamma alumina particles in a fixed-bed flow-type ALD reactor.

Zinc acetylacetonate [$Zn(acac)_2$], a non-toxic reactant with a good stability in air, was used as an ALD reactant. Thermogravimetric analysis confirmed $Zn(acac)_2$ to be a potential reactant. $Zn(acac)_2$ was vaporized at 120 °C and carried by N_2 to the calcined support for 3 h. For zirconia, the effect of the calcination temperature (400 to 1000 °C, typically 600 °C), process temperature (160 to 240 °C, typically 200 °C), and number of cycles (1-3, 2nd reactant: oxygen) on zinc loading were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). For zirconia and alumina, the amount of $Zn(acac)_2$ evaporated was varied. Zinc distribution within a solid support particle was analyzed by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (Fig. 1 and Fig. 2 of the supplementary information). A diffusion-reaction model[3,4] was used to simulate the saturation profile of zinc within theoretical pores (Fig. 3).

Electronic structure of zinc was analyzed by X-ray absorption spectroscopy (XAS). The oxidation of acac ligands on the samples was observed by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) combined with mass spectrometry (MS). The zinc content on zirconia saturated to ca. 1.3 wt-% (2.2 Zn nm^{-2}) with increasing amount of Zn(acac)$_2$. The zinc content decreased from ca. 2.2 to 0.3 wt-% with increasing calcination temperature, most likely resulting from the decreasing zirconia surface area. The zinc areal number density (ca. 2.2 Zn nm^{-2}) remained almost constant.

This work was supported by the Academy of Finland (COOLCAT project, grant no. 329978, ALDI project, grant no. 331082, and Matter and Materials, grant No. 318913) and by R. L. Puurunen's starting grant at Aalto university. Hannu Revitzer and Ilkka Välimaa are thanked for the ICP-OES analysis.

References

3. R. van Ommen, A. Goulas, and R. L. Puurunen, *Atomic layer deposition, in Kirk-Othmer Encyclopedia of Chemical Technology,* John Wiley & Sons, Inc. (2021).
4. A. Arandia et al*., manuscript in preparation* (2022).
5. M. Ylilammi et al*., J. Appl. Phys.,* **123**, 205301(2018).
6. J. Yim and E. Verkama et al., submitted. Preprint DOI: 10.33774/chemrxiv-2021-2j4n1.

11:45am **AF2-MoM2-5 Synthesis of High Surface Area Metal Oxide Catalyst Supports***, **Robert Baumgarten**, P. Ingale, K. Knemeyer, R. Naumann d'Alnoncourt, M. Driess,* BasCat – UniCat BASF JointLab, Technische Universität Berlin, Germany*; F. Rosowski ,* BASF SE, Process Research and Chemical Engineering, Germany

Group 13 metal oxides (e.g. Al_2O_3, Ga_2O_3 and In_2O_3) are utilized for a broad range of electronic applications such as semiconductors, optoelectronics and sensors. Besides, they represent essential components of heterogenous catalysts. Al_2O_3 is employed industrially as support material or catalyst itself for various reactions like epoxidation of alkenes and dehydration of alcohols [1]. Moreover, Ga_2O_3 has been intensively studied for the dehydrogenation of light alkanes and In_2O_3 catalysts gained a lot of attention due to the ability of converting CO_2 into methanol [2, 3].

In heterogeneous catalysis, reactions mostly occur at active sites on the material's surface. Therefore, high surface area and homogeneous dispersion of deposited interfaces (e.g. metal oxides) are decisive for enhanced activity [4]. Yet, standard synthesis techniques like impregnation and precipitation often lead to unwanted agglomeration. One well-established technique which overcomes uncontrolled coating is atomic layer deposition (ALD). ALD leads to uniform, nanoscale films on a materials surface and is therefore progressively attracting attention as potential synthesis-tool for catalysts [5]. However, most ALD investigations target flat substrates whereas for catalyst synthesis, powders with high surface area and porosity are demanded.

In order to enable the full potential of ALD-synthesized catalysts, the deposition behavior on porous powders has to be further elucidated. Previously, we demonstrated the growth behavior of AlO_x on mesoporous silica using the ALD process of trimethylaluminum and water [6]. In the current study, we approach other catalytically active oxides of group 13 metals like gallium (GaO_x) and indium (InO_x). Both oxides were deposited on high surface area silica powder *via* ALD and their growth behavior was studied intensively using *in-situ* thermogravimetry, XRD, STEM, FTIR and NMR. Furthermore, both processes were compared to the powder ALD process of AlO_x and reference samples prepared *via* incipient wetness impregnation.

References

[1]Schlögl, R.; Hess, C.; Nanostructured catalysts: Selective oxidations; *Royal Society of Chemistry: Cambridge*, **2010**, ISBN 9781847559876.

[2]Martin, O.; Pérez-Ramírez, J. *et al*.; *Angew. Chem. Int. Ed Engl.***2016**, 55, 6261–6265.

[3]Castro-Fernández, P.; Müller, C.R. *et al*.; *ACS Catal.***2021**, 11, 907–924.

[4]Somorjai, G.A.; Li, Y.; Introduction to surface chemistry and catalysis, 2nd ed.; *Wiley: Oxford*, **2010**, ISBN 978-0-470-50823-7.

[5]O'Neill, B.J.; Huber, G.W. *et al*.; *ACS Catal.***2015**, 5, 1804–1825.

[6]Strempel, V.E.; Rosowski, F. *et al*.; *Nanomaterials***2018**, 8.

12:00pm **AF2-MoM2-6 ALD on Porous Substrates: From General Formulation to Fibrous Substrates and Scaling Laws***, **Wojciech Szmyt**, C. Guerra-Nuñez,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; L. Huber,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; C. Dransfeld,* TU Delft, Netherlands*; I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

In order to achieve the uniform coating in the ALD process, a sufficient gas exposure (exposure time and gas concentration) needs to be provided. This requirement becomes particularly relevant for highly porous and high aspect-ratio substrates, where the gas transport into the substrate structure is limited by diffusion (diffusion-limited regime), or for ALD precursor systems exhibiting low surface reaction rate (reaction-limited regime). This work (Szmyt *et al*., Chem. Mat. 2022, 34, 1, 203-216) reports how the distinction between diffusion- and reaction-limited ALD regimes is directly quantitatively related to the width of the reaction front and the profile of chemisorption coverage in a single cycle ALD, all of them being determined by the natural length unit of the system. We introduce a new parametrization of the system based on its natural system of units, dictated by the scales of the physical phenomena governing the process. We present a range of scaling laws valid for a general porous substrate, which scale intuitively with the natural units of the system. The scaling laws describe (i) the coating depth in a diffusion-limited regime with respect to the gas exposure, (ii) the chemisorption coverage in a reaction-limited regime with respect to the gas exposure, and (iii) the width of the reaction front in the diffusion-limited regime. For the first time, the distinction between diffusion- and reaction-limited ALD regimes is directly quantitatively related to the width of the reaction front and the profile of chemisorption coverage in a single cycle ALD. The model system for the multicycle diffusion-limited coating of random fibrous mats was validated with an experiment of ALD on a forest of tortuous carbon nanotubes (CNTs).

Atomic Layer Etching
Room Baekeland - Session ALE-MoM2

Thermal and/or Isotropic ALE I

Moderators: Steven M. George, University of Colorado at Boulder, Anil Mane, Argonne National Laboratory

10:45am **ALE-MoM2-1 Photon-Activated Metal Ale***, X. Yang, B. Coffey, **John Ekerdt**,* University of Texas at Austin **INVITED**

Long nucleation delays during area selective ALD of metals can lead to unwanted growth outside the patterned regions.Unwanted nucleation also results when a passivating film begins to breakdown.In the event non-selective nucleation occurs on passivated regions, we describe a low temperature ALE route to etch clusters/islands on the passivated regions faster than the desired film.This low temperature route exploits the general finding by others that metal oxides can be etched by a variety of vapor phase etchants – the issue is controlled oxidation while minimizing damage to adjacent surfaces.We present a low temperature route that involves vacuum ultraviolet (VUV) activation of O_2 to produce atomic oxygen and ozone, with atomic oxygen being the dominant species that oxidizes the near surface region of Pd and Ru.Oxidation extents differ between continuous films and discontinuous films enabling the removal of metal islands without significantly etching the film.Pd and Ru can be etched at temperatures ranging from 50 °C – 200 °C by co-exposing the zero-valent metal to 1 Torr of O_2 and VUV photons ($6.5 < h\nu < 11.3$ eV) from a D_2 lamp.Density functional theory and nudged elastic bandcalculations are used to understand the diffusion of oxygen into the metal and the kinetic barriers that limit oxidation to the first and second layers.Metal oxidation proceeds because the flux of atomic oxygen is sufficient to compensate for competing recombinative desorption of molecular oxygen.The oxides of Pd and Ru are etched in an ALE half cycle with 0.50 Torr HCOOH vapor exposure for 30 sec.Metal islands/nuclei are completely oxidized in an exposure cycle while oxidation of a film is limited to approximately one atomic layer.

Photon activation of O_2 in the gas phase above the surface to atomic oxygen leads to an inherently isotropic process since the atomic oxygen can diffuse to any exposed surface before the atomic oxygen is lost through gas-phase loss reactions.This talk will also discuss the use of halogenated hydrocarbons that can possibly adsorb at the process temperature and be activated in the adsorbed state to restrict metal oxidation to those surfaces exposed to the photons.

11:15am **ALE-MoM2-3 Plasma-Assisted Thermal-Cyclic Etching of Silicon Germanium Selective to Germanium***, **Kazunori Shinoda,*** Hitachi , Japan*; H. Hamamura,* Hitachi, Japan*; K. Maeda, M. Izawa,* Hitachi High-Tech, Japan*; T. Nguyen, K. Ishikawa, M. Hori,* Nagoya University, Japan

Silicon germanium (SiGe) and germanium (Ge) may play an important role in future generations of semiconductor devices. For example, one candidate of future logic devices will be a Ge-channel gate-all-around field-effect transistor (GAA FET), which may require lateral selective etching of the SiGe sacrifice layer with respect to the Ge-channel layer. Isotropic, self-limiting cyclic etching of SiGe selective to Ge will thus be attractive in developing future generations of logic devices. This paper addresses plasma-assisted, thermal-cyclic etching of SiGe, which is selective to Ge. Experiments were conducted with several SiGe and Ge samples with different Ge content. Radical-exposed surfaces of the samples were produced in plasmas excided with hydrofluorocarbon-based gas mixtures that contain nitrogen. Nitrogen was added to the gas mixture because it is essential for forming ammonium-salt-based modified surfaces. Photoelectron-emission measurements were conducted after transferring the samples in vacuum into an x-ray photoelectron spectroscopy (XPS) system under ultra-high vacuum. The XPS spectra obtained after radical exposure consisted of a nitrogen 1s peak at 402 eV, which was likely ascribed to the N-H bond. One explanation of this observation is that a modified surface that consists of ammonium salt formed on the surface of the samples after radical exposure. The intensity of the N-H peak decreased as the Ge composition in the samples increased. The nitrogen 1s peak at 402 eV disappeared when the samples were heated at 100°C. This suggests that the ammonium-salt-based modified surface decomposes and desorbs from the film during heating. We conducted cyclic etching of SiGe and Ge samples with an etching tool developed for 300-mm wafers. Radical exposure and infrared heating were repeated multiple times with this tool. The etching depths of the samples were evaluated using in-situ ellipsometry. The thickness of the SiGe decreased as the number of cycles increased. The etched amount of SiGe in one cycle ranged from 3 to 7 nm. The etched amount of the Ge in one cycle was smaller than that of the SiGe. A maximum SiGe selectivity of 5 was obtained with respect to Ge at optimum stage temperature during radical-exposure steps. The selectivity was due to the selective formation of the ammonium-salt-based modified surface on SiGe compared with that on Ge. The etched amount for one cycle of SiGe and Ge exhibited saturation behavior as the radical-exposure time increased. Self-limiting thermal-cyclic etching of SiGe selective to Ge was thus successfully demonstrated.

11:30am **ALE-MoM2-4 Thermal Atomic Layer Etching of Cobalt with Chlorine Plasma and Hexafluoroacetylacetone (Hhfac)***, **Yongjae Kim,** H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Korea (Republic of)

Copper is widely adopted for interconnect lines in semiconductor devices, but the resistance increases of copper is rapidly increasing due to surface scattering of electrons. [1] Cobalt is considered as an alternative metal because cobalt does not require a barrier/liner and has less resistance than copper below 10nm in dimension. [2] Chemical-mechanical polishing (CMP) processes are used for planarization in interconnect, but they leave interlayer dielectric (ILD) defects due to slurry particles and mechanical forces. Atomic layer etching (ALE) process can be an alternative to reducing the defects in cobalt removal. In this work, ALE process was performed for cobalt in an inductively coupled plasma (ICP) reactor. The ALE process consists of two steps: surface modification with chlorine plasma and ligand volatilization with hexafluoroacetylacetone (Hhfac). In the first step, the surface of cobalt is chlorinated to $CoCl_2$ using chlorine plasma. In the second step, the $CoCl_2$ layer was removed by ligand volatilization with Hhfac. Cobalt ALE process was conducted with changing process temperature at 100~250 degree, and the ALE window was confirmed. Etch rate of cobalt was self-limited at the Hhfac injection time of 90 second. The thickness of the cobalt film before and after the ALE process was confirmed by cross-sectional SEM imaging. The etch rate of cobalt could be controlled below 1 nm/cycle. Surface roughness was compared according to process temperature and chlorine plasma power.

References

[1] D. Bobb-Semple, K. L. Nardi, N. Draeger, D. M. Hausmann, and S. F. Bent, Chem. Mater 31, 1635 (2019)

[2] N. Bekiaris, Z. Wu, H. Ren, M. Naik, J. H. Park, M. Lee, T. H. Ha, W. Hou, J. R. Bakke, M. Gage, Y. Wang, and J. Tang, In 2017 IEEE International Interconnect Technology Conference (IITC), IEEE, 1 (2017)

Keywords: Atomic layer etching, Cobalt etching

11:45am **ALE-MoM2-5 Thermal-Cyclic Atomic Layer Etching of Cobalt by Plasma Oxidation and Organometallization***, **Sumiko Fujisaki,*** Hitachi Ltd,. R&D group, Japan*; Y. Yamaguchi,* Hitachi, Ltd., R&D group, Japan*; H. Kobayashi,* Hitachi High-Tech, Japan*; K. Shinoda, M. Yamada, H. Hamamura,* Hitachi, Ltd., R&D group, Japan*; K. Kawamura, M. Izawa,* Hitachi High-Tech, Japan **INVITED**

The technology node has been scaled down to below 10 nm, and gate-all-around (GAA) FET and C-FET are expected to be utilized in logic devices in the near future.

Isotropic atomic-layer etching (ALE), which can perform atomically precise removal, plays an important role in semiconductor manufacturing under these circumstances. Highly selective ALE is required to process new materials for miniatulized 3D devices. Over the past several years, isotropic ALE of various materials has been reported, including thermal ALE for metal oxides and thermal-cyclic ALE for nitride films [1]. To meet the requirements concerning the variety of materials to be etched, isotropic ALE of cobalt must be developed—for example, for advanced interconnect metallization. Thermal ALE of cobalt by using formic acid and ligands has been reported [2]. Also, the authors have successfully demonstrated isotropic ALE of cobalt film with smoothly etched surfaces by introducing a two-temperature process [3].

The experimental apparatus used in this study is a 300-mm ALE tool equipped with an inductively coupled plasma source and infrared (IR) lamps. One cycle of the thermal-cyclic ALE process is divided into two major steps: oxidation and organometallization. In the first step, the surface of cobalt film is oxidized by oxygen plasma at low temperature, and in the second step, it is converted into an organo-cobalt complex by diketone at high temperature. The organo-cobalt complex then desorbs from the film surface due to its higher volatility. This two-temperature process is crutial because it enables well-controlled etching that leads to a smoothly etched surface. Our ALE tool exhibits a short processing time thanks to its IR lamps for rapid heating. It is desirable that the cobalt oxide formed in the first step be completely removed in the second step (i.e., within one cycle), so the etched amount is controlled by the oxidation thickness of cobalt and the number of cyclic repetitions.

The mechanism of the cobalt ALE reaction was examined by x-ray photoelectron spectroscopy (XPS). Several oxygen 1s peaks were detected in the range of 525 to 535 eV after plasma oxidation at various temperatures. A peak at 530 eV, which preferentially decreased after being exposed to diketone, is the dominant oxidation state for organometallization, and is presumably ascribed to divalent cobalt oxide. It also implies that some other oxidation states of cobalt are removed after converting to the oxide with a 530-eV oxygen 1s XPS peak.

[1] K. Shinoda et al., J. Phys. D: Appl. Phys. **50**, 194001 (2017).

[2] C. Winter, AVS 65th, PS+EM+TF-ThM5 (2018).

[3] S. Fujisaki et al., ALE Workshop, ALE1-MoA6 (2020).

ALD Applications
Room Van Rysselberghe - Session AA1-MoA

ALD for Catalysis

Moderator: Ashley R. Bielinski, Argonne National Laboratory

1:30pm **AA1-MoA-1 ALD Preparation of TiO_2-MnO_x/SiO_2 Catalyst for Selective Catalytic Reduction of Nitrogen Oxides***, **Saeed Saedy,*** Delft University of Technology, Netherlands*; D. Kazimierz ,* Paul Scherrer Institut, Switzerland*; D. Urbanas,* Vilnius Gediminas Technical University, Lithuania*; D. Ferri,* Paul Scherrer Institut, Switzerland*; J. van Ommen,* Delft University of Technology, Netherlands

The most efficient NO_x abatement process is the selective catalytic reduction using NH_3 (NO_x NH_3-SCR). The commercial V-based NH_3-SCR catalysts have a narrow high-temperature operational window of 350-450°C; this requires installing the catalyst bed before desulfurization and dust removal units, which initiates catalyst deactivation. To avoid this, the SCR unit is currently being placed in the so-called tail-end configuration, which results in exhaust gases temperature below the operational window of the commercial catalysts. Manganese oxide (MnO_x) catalysts show superior NH_3-SCR activity at low temperatures (LT). The various oxidation states (Mn^{2+},Mn^{3+},and Mn^{4+}) of MnO_x, are known to play an essential role in the LT activity of MnO_x catalysts; hence, the existence of multiple oxidation states of Mn is pivotal for its SCR activity. On the other hand, the crystalline MnO_x does not contribute effectively to NH_3-SCR; thus, the dispersion of MnO_x strongly affects SCR activity. The routine catalyst synthesis methods like precipitation impregnation, and sol-gel, are less suitable for preparing MnO_x SCR catalysts since they often require high-temperature post-treatments, which increase the crystallinity of particles and decrease dispersion.

Atomic layer deposition (ALD) offers a reliable LT coating method, with subnanometer control over the process. ALD makes it possible to obtain metal oxide nano-coatings at temperatures significantly lower than conventional methods. In this work, we have employed fluidized bed ALD to deposit highly dispersed MnO_x on SiO_2 for LT NH_3-SCR catalysis. The ultra-fine MnO_x NPs were grown on SiO_2 at 150°C and 1 bar. Additionally, we deposited TiO_2 on ALD prepared MnO_x/SiO_2 to increase the acidity of the catalyst, which is crucial for NH_3 activation during the SCR process. The XPS analysis revealed three oxidation states of Mn^{2+}, Mn^{3+},and Mn^{4+} in these samples, which are essential for NO_x-SCR. Also, powder XRD could not detect any crystalline phases of MnO_x, suggesting that ALD synthesis avoided the crystalline MnO_x; consistently, the MnO_x NPs were scarcely observable using TEM, demonstrating extreme dispersion of MnO_x over SiO_2. NH_3 temperature-programed desorption analysis demonstrated that the acidity of the MnO_x/SiO_2 sample is significantly increased after TiO_2 ALD, increasing the NH_3 activation on TiO_2-MnO_x/SiO_2. The obtained TiO_2-MnO_x/SiO_2 with such characteristics provide a promising catalyst for low-temperature selective catalytic reduction of nitrogen oxides. Accordingly, the catalytic activity evaluation showed~85% NO conversion for the TiO_2-MnO_x/SiO_2 sample, while the MnO_x/SiO_2 sample showed a NO conversion of~30%.

1:45pm **AA1-MoA-2 Unravelling the Mechanism of Electrochemical Activation of ALD Cobalt Phosphate by Digital Control Over Its Chemical Composition***, G. van Straaten, R. Zhang, E. Kessels,* Eindhoven University of Technology, The Netherlands*; R. van de Sanden, M. Tsampas,* Dutch Institute for Fundamental Energy Research, Netherlands*; **Mariadriana Creatore,*** Eindhoven University of Technology, The Netherlands

Storage of electricity into molecules is the most viable answer to the intermittency of renewable sources. In this respect, H_2O splitting to H_2 and O_2 is key to enable the usage of H_2 as fuel for transport, as well as building block together with CO for the electrosynthesis of hydrocarbons. For the O_2 evolution half reaction (OER), cobalt phosphate (CoPi) is interesting because it behaves as bulk electro-catalyst, with electrochemically active Co^{3+} centers. In parallel with others [1], we have demonstrated the synthesis of amorphous CoPi films by ALD [2]. CoPi was prepared by combining ALD of CoO_x from cobaltocene and O_2 plasma, with cycles of trimethyl phosphate and O_2 plasma, according to an ABCD scheme [2,3]. We have also shown that ALD CoPi films are characterized by OER performances beyond those achieved by traditional electro-deposited films [3].

In the present contribution we focus on the mechanism behind the enhancement of the catalytic activity of ALD CoPi when tuning the Co-to-P ratio in the film. We show that CoPi films progressively undergo activation under alkaline conditions (ph=8-14) with increasing number of cyclic voltammetry (CV) cycles. During this activation process induced by the infiltration of the electrolyte in the bulk of the film, the current density increases in parallel with the leaching of phosphorus out of the electro-catalyst and the shift of the oxidation state of cobalt from Co^{2+} to Co^{3+} [4]. In parallel, the film undergoes a change in morphology upon activation. CV analysis and Rutherford backscattering measurements indicate that after activation, as much as 22% of all cobalt content in the film becomes accessible to the electrolyte and is activated. The electrochemical surface area (ECSA), i.e. the surface area accessible to promote H_2O splitting, increases up to a factor of 30, accompanied by a current density of 5 mA/cm^2. The increase in ECSA is strongly dependent on the composition of the pristine CoPi films: while the above-mentioned increase holds for CoPi films with a Co-to-P ratio of 1.6, for films with a Co-to-P ratio of 1.9 the ECSA only increases by a factor 4. We find that for all investigated Co-to-P ratios, the electrochemical activity scales linearly with ECSA upon activation. It can be concluded that the digital control over the chemical composition of CoPi offers a novel merit to ALD: unravelling the mechanism behind CoPi electrochemical activation.

[1] J. Ronge et al., Nanoscale Adv. 1, 4166 (2019)

[2]V. Di Palma et al., Electrochem. Commun. 98, 73 (2019)

[3] V. Di Palma et al., J. Vac. Sci. Technol. 38, 022416 (2020)

[4] R. Zhang et al., ACS Catal.11, 2774 (2021)

2:00pm **AA1-MoA-3 Increasing ALD Complexity: How to Transform Ternary Oxide Films Into Tunable Bimetallic Thin Films and Nanoparticles***, J. Feng, **Matthias Filez**, M. Minjauw, E. Solano, C. Detavernier, J. Dendooven,* Ghent University, Belgium

ALD of ternary compounds ($A_mB_nC_o$) typically combines two binary ALD processes, each consisting of a metal precursor source and a co-reactant. Recently, however, we have demonstrated that ternary compounds, in casu $MRuO_x$ (M = Al, Pt), can be deposited using a single binary ALD process, thus reducing deposition complexity.[1] During such process, metal-organic precursors ($MeCpPtMe_3$ and TMA) are combined with RuO_4, the latter functioning both as metal source and co-reactant which combusts organic ligands. Yet, such multi-constituent co-reactant limits deposition to ternary compounds, such as $MRuO_x$, while often metallic MRu films or nanoparticles (NPs) are desired. Herein, we show that by increasing the complexity of the original $MRuO_x$ process by adding extra ‘functionalities’, such as reduction or even etching steps, bimetallic films and NPs can be deposited with full thickness and compositional control. This approach therefore significantly extends the applicability of the original process toward bimetallic compounds.

We first show that ALD of bimetallic PdRu films can be achieved by inserting a RuO_4 step in the $Pd(hfac)_2$ / H_2-plasma (H_2*) process, leading to a three-step $Pd(hfac)_2$ / RuO_4 / H_2* process with a high growth per cycle of 0.19 nm/cycle.[1, 2] Herein, RuO_4 acts both as an oxidizing agent and a Ru source, while H_2* reduces the surface. Thin films resulting from this process are Ru-rich, and we show that the Pd content can be increased by not including the RuO_4 step in every cycle, thus decreasing the incidence rate of the RuO_4 step in the ALD process (Fig. 1).

Next, by replacing part of the RuO_4 units in the three-step process by O_2*, the morphology of the PdRu is transformed from thin films to bimetallic nanoparticles (BMNPs, Fig. 2). This change of morphology is attributed to the etching of the deposited Ru as volatile RuO_4 during the O_2* steps. In situ grazing-incidence small-angle X-ray scattering and X-ray fluorescence revealed that the composition and size of the BMNPs can be adjusted independently by changing the proportion of RuO_4 versus O_2* pulses in the sequence, and the total number of ALD cycles, respectively. Finally, grazing-incidence wide-angle X-ray scattering and electron energy loss spectroscopy revealed that the RuPd BMNPs are crystalline, and Ru and Pd intimately mixed, suggesting the formation of solid-solution RuPd nanoalloys.

[1]Minjauw, M. M. et al. (2022).*Dalt. Trans.* Advance Article (DOI: 10.1039/D1DT03543F)

[2]Feng, J. Y. et al. (2020).*Phys. Chem. Chem. Phys.*, **22**, 9124–9136.

2:15pm **AA1-MoA-4 Tunable TiO_2-BN-Pd Nanofibers by Combining Electrospinning and Atomic Layer Deposition to Enhance Photodegradation of Acetaminophen***, **Syreina Alsayegh,*** Institut Européen des Memabranes, France*; M. Bechelany,* Institut Européen des Membranes, France*; F. TANOS,* Institut Européen des membranes, France*; A. NADA, G. LESAGE, F. Zaviska,* Institut Européen des Membranes, France*; M. Weber,* Laboratoire des Matériaux et du Génie Physique LMGP , France

The demand for fresh and clean water sources increases globally, and there is a need to develop novel routes to eliminate micropollutants and other harmful species from water. Photocatalysis is a promising alternative green technology that has shown great performance in the degradation of persistent pollutants. Titanium dioxide is the most used catalyst owing to his attractive physico-chemical properties, but this semiconductor presents limitations in the photocatalysis process due to the high band gap and the fast recombination of the photogenerated carriers. Herein, a novel photocatalyst has been developed, based on titanium dioxide nanofibers (TiO_2 NFs) synthesized by electrospinning. The TiO_2 NFs were coated by atomic layer deposition (ALD) to grow boron nitride (BN) and palladium (Pd) on their surface. The UV-Vis spectroscopy measurements confirmed the increase of the band gap and the extension of the spectral response to the visible range. The obtained TiO_2/BN/Pd nanofibers were then tested for photocatalysis, and showed a drastic increase of acetaminophen (ACT) degradation (>90%), compared to only 20% degradation obtained with pure TiO_2 after 4h of visible light irradiation. The high photocatalytic activity was attributed to the good dispersion of Pd NPs on TiO_2-BN nanofibers, leading to a higher transfer of photoexcited charges carriers and a decrease of photogenerated electron-holes recombination. To confirm their reusability, recycling tests on the hybrid photocatalyst TiO_2/BN/Pd have been performed, showing a good stability over 5 cycles under UV and Visible light. Moreover, toxicity testsas well as quenching tests were carried out to check the toxicity in the formation of byproductsand to determine active species responsible for the degradation. The results presented in this work demonstrate the potential of TiO_2/BN/Pd nanomaterials, and open new prospects for the preparation of tunable photocatalysts.

Keywords: TiO_2-BN-Pd nanocomposites; nanofibers, electrospinning; atomic layer deposition; photocatalysis; acetaminophen

2:30pm **AA1-MoA-5 Ultra-Low Dimensional Ir-Ru Thin-Film by Atomic Layer Deposition on Porous Titanium Felt Substrate for Electrochemical Water Splitting Application***, **Rahul Ramesh**, N. Park, T. Cheon,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)*; M. Byeon, T. Hong,* Busan Center, Korea Basic Science Institute, Korea (Republic of)*; S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Iridium (Ir) and ruthenium (Ru) are crucial ingredient in various applications, and their proper utilization is essential due to the extreme rarity of those elements. For example, in the case of electrocatalysis, only the surface participate in the reaction, and whatever lies beneath (within the nanoparticle or thin film) are un-utilized. Therefore, fabrication of Ir/Ru thin-film with high uniformity and conformality onto high surface area porous substrate is beneficial to reduce the metal content and increase its utilization. Atomic layer deposition (ALD) can be used to deposit uniform and conformal films with precise thickness control. In this study, we report the fabrication of ultra-low dimension (~5 nm) Ir-Ru thin film on to porous Ti felt substrate using a sequential approach with two precious metal ALD processes. The nano-secondary ion mass spectrometer depth-profiling (Nano-SIMS) results confirm the homogeneous, conformal and uniform growth of Ir-Ru thin film as predicted from the ideal ALD growth characteristic and XTEM on Si substrate. The electrochemical performance of Ir-Ru nanolayer electrode towards hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are evaluated in an acid electrolyte (0.5 M H_2SO_4). The Ru film shows the highest onset for HER (-112 mV), the Ir (5 nm) and Ir-Ru (5 nm) has an HER onset potential of ~-50 mV. In the case of the OER voltammogram, all the electrodes with precious metal films show the current due to OER. Contrary to the HER, here Ru shows the highest activity both in terms of OER onset potential and the overpotential at a specific current density; noteworthy the slightly better activity of 5 nm Ir film is attributed to the Ru nucleation layer (~2 nm) deposited on to the Ti substrate for uniform deposition of Ir, since, there is a huge nucleation delay for Ir ALD on Ti-based substrate. The stability of the film is characterized by chrono-potentiometric stability analysis for 24 hours at an OER current density of 10 mA cm^{-2}. As expected the Ru film is very unstable during OER and complete dissolution of 5 nm film happens at around ~4 hour of operation. However, the Ir-Ru (5 nm) display enhanced stability and is attributed to the inclusion of Ir. In conclusion, ALD can be used as an efficient technique to coat ultra-low dimension Ir-Ru thin film/nano-materials on to porous substrate with precise thickness control and high conformality, which is beneficial in terms of utilization and cost-effectiveness of electrocatalyst.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (2021R1A2C1007601 and 2021M3H4A3A02099209.

2:45pm **AA1-MoA-6 Influence of Co/Ni Ratio on OER-catalytic Performance of Atomic Layer Deposited Nickel Cobalt Oxide***, **Renee van Limpt**,* Eindhoven University of Technology, Netherlands*; M. Lavorenti, M. Tsampas,* Dutch Institute for Fundamental Energy Research, Netherlands*; A. Creatore,* Eindhoven University of Technology, Netherlands

A promising approach to answer the challenge of intermittency of renewable sources such as wind and solar energy, is to store green electricity into H_2 via H_2O electrolysis. Sustainable electrolysis can be achieved, for example, under alkaline conditions, with the sluggish oxygen evolution reaction (OER) representing the main limitation. Mixed oxides of the earth-abundant cobalt and nickel are considered promising OER electrocatalysts. Cobalt nickel oxide ($Co_xNi_{1-x}O_y$) can adopt both the Co_3O_4 spinel and the NiO rock-salt structure depending on the cobalt concentration. The present study aims at exploring the effect of cobalt concentration in $Co_xNi_{1-x}O_y$ on the OER catalytic activity to expand on previous literature studies which are either limited to single phase structures[1, 2] or disregard the effect of bulk (film thickness >5 nm) effects[3].

Atomic layer deposition (ALD) offers the opportunity to tune the stoichiometry and therefore the structure of $Co_xNi_{1-x}O_y$. This work therefore employs plasma-enhanced ALD by combining a cobalt cyclopentadienyl ($Co(Cp)_2$)[4] based process for CoO_x with a nickel methylcyclopentadienyl ($Ni(MeCp)_2$) process[5] for NiO_x. Energy Dispersive X-ray mapping shows no variation in elemental composition, indicating that nickel intermixes with cobalt to form an alloy. X-ray spectroscopy (XPS) furthermore reveals the presence of mixed Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+} valence states, with an increase in the Ni^{3+}-to-Ni^{2+} ratio for increasing cobalt concentrations. Preliminary x-ray diffraction measurements furthermore suggest a transition from rock-salt to spinel phase with increasing cobalt concentration, indicating that nickel occupies the octahedral sites in the spinel structure at high cobalt concentrations. The OER activity of $Co_xNi_{1-x}O_y$ films (~30 nm) is determined by cyclic voltammetry (CV) in 1M KOH. The current density at 1.8 V vs RHE increases whilst the onset potential decreases, with a decrease in cobalt concentration in the film. An increased number of CV cycles leads to an increase in the current density, suggesting the activation of the bulk of the electrocatalyst. After CV, XPS reveals a dominant Ni^{3+} oxidation state in the film and an increase in oxygen concentration and hydroxide phase. These results indicate that the rock-salt phase is favourable for OER, implying that further research should focus on low cobalt- content $Co_xNi_{1-x}O_y$.

[1]R. N. Singh et al., *Electrochim. Acta*, 2000.

[2]A. Asho etl al., *Int. J. Hydrogen Energy*, 2019.

[3]L. Trotochaud et al., *J. Am. Chem. Soc.*, 2012.

[4]M. E. Donders et al. *J. Electrochem. Soc.*, 2011.

[5]D. Koushik *et al.*, *J. Mater. Chem. C*, 2019.

3:00pm **AA1-MoA-7 Fundamental Studies of s-ALD Grown Iridium Thin Films on Planar Substrates for Acidic Water Splitting***, J. Shen ,* TNO-Holst Centre, Netherlands*; P. Shirvanian,* TNO-STIP, Netherlands*; E. Balder,* TNO-Holst Centre, Netherlands*; B. van Dijk,* TNO-STIP, Netherlands*; N. Huijssen, A. Bronneberg, P. Poodt, **Mahmoud Ameen**,* TNO-Holst Centre, Netherlands

One of our greatest challenges for the upcoming decades is the transition to a sustainable way of generating, storing, and converting energy. Green hydrogen produced by PEM Water Electrolyzers (PEMWE's) is part of the solution, but still faces several challenges. Among the major challenges towards widespread adoption and commercialization of PEMWE's are the cost, performance, and durability of iridium (Ir) material as used to catalyze the oxygen evolution reaction (OER) [1]. Sluggish OER kinetics and ensuing large overpotential above the thermodynamic equilibrium level required to drive the reaction will inevitably result in PEMWE inefficiency along with high catalyst loadings. It has previously been demonstrated that atomic layer deposition (ALD) can be used to deposit high quality and stable electrocatalyst layers with a low Ir loading [2], but the low deposition rate of ALD limits up-scaling for mass production. Spatial atomic layer deposition (sALD) has emerged as a viable tool for the atomically precise design and synthesis of materials with high deposition rates on both large substrates (square meters) and roll-to-roll [3].

Herein, we present an atmospheric-pressure spatial ALD process of Ir/IrO_x ultra-thin films on flat substrates. We investigate the temperature window of the ALD process down to 80 degrees. We study the growth characteristics as well as the thin film properties using ellipsometry, inductively coupled plasma mass spectrometry (ICP-MS), X-ray photoelectron spectroscopy (XPS) and grazing incidence X-ray diffraction (GIXRD). Furthermore, we evaluate the OER catalytic behaviour and durability using rotating disc electrode (RDE). Our study sheds light on structure, thickness, and morphology of Ir deposits and corresponding OER catalytic properties. The findings will pave the way towards identifying optimal catalytic system with the promise of ultra-low Ir loading at high OER performances.

[1] Shirvanian, P. and van Berkel, F., 2020. Novel components in Proton Exchange Membrane (PEM) Water Electrolyzers (PEMWE): Status, challenges and future needs. A mini review. Electrochemistry Communications, 114, p.106704.

[2] Laube, A., Hofer, A., Ressel, S., Chica, A., Bachmann, J. and Struckmann, T., 2021. PEM water electrolysis cells with catalyst coating by atomic layer deposition. *international journal of hydrogen energy*, *46*(79), pp.38972-38982.

[3] Poodt, P., van Lieshout, J., Illiberi, A., Knaapen, R., Roozeboom, F. and van Asten, A., 2010. On the kinetics of spatial atomic layer deposition. *Journal of Vacuum Science & Technology A*, *31*, pp. (01A108-1)-(01A108-7).

3:15pm **AA1-MoA-8 Functionalization of MoS_2 With Noble Metal by Atomic Layer Deposition for Hydrogen Evolution Reaction***, **JungYub Lee**, J. Kim, I. Sohn, S. Chung, H. Kim,* School of Electrical and Electronic Engineering, Yonsei University, Korea (Republic of)

Hydrogen is a good, sustainable alternative energy that can replace fossil fuels that cause air pollution and global warming. To produce hydrogen, electrochemical water splitting is the promising sustainable method without producing carbon containing pollutant.[1]

Platinum has been widely used for hydrogen evolution reaction(HER) for its high performance compared to other materials. However, platinum faces the problem in commercial use because of its low cost efficiency. In order to replace platinum, Transition Metal DichalCogenides(TMDCs) have been actively researched, which have a high surface-to-volume ratio and provide a sufficient number of active sites.[2] To further enhance the HER performance of TMDCs, many research has focused on the structure of TMDCs, defect engineering and heterojunction with graphene. However, this research will highlight the signficance of Pt and its better performance than those methods. To prove, this study will funtionalize TMDCs with the very small amount of noble metals, including Pt and Ru. Atomic Layer Deposition(ALD) will be a key technique to control the amount of noble metals and synthesize the uniform, conformal TMDCs on graphite foil.

Here we prepared catalyst using the noble metal functionalized MoS_2 synthesized on graphite foil by ALD. Various experimental methods were performed to analyze film growth characteristics including X-ray photoelectron spectroscopy (XPS) , Raman spectroscopy, Scanning Electron Microscope (SEM), X-ray diffraction and etc. The electrochemical properties of HER catalyst show high exchange current density and low Tafel slope compared with ALD MoS_2 film.

References

[1] D.H Kim, J.G. Song, H.M. Yang, H.K. Lee, J.S. Park. H.J. Kim, Nanoscale, 2019, 11, 844

[2] Xiaxin Zou, Yu Zhang, Chem. Soc. Rev., 2015, 44, 5148

ALD Applications
Room Van Rysselberghe - Session AA2-MoA

ALD for Energy Storage

Moderators: Ageeth Bol, University of Michigan, Ann Arbor, Philippe Vereecken, IMEC, Belgium

4:00pm **AA2-MoA-11 Conversion Reactions and Redox Changes on the Surface of Lithium-Ion Battery Cathode Materials during Chemical Vapor Treatment for ALD***, P. Darapaneni, A. Mane, Z. Hood, **Jeffrey Elam**,* Argonne National Laboratory

Atomic layer deposition (ALD) has emerged as a promising technology for applying ultrathin protective coatings on lithium-ion battery (LIB) cathode surfaces to improve their cycling stability. While there have been numerous reports evaluating the electrochemical performance of these surface-modified cathode materials, the chemical changes induced on the surface of the cathode materials by the ALD coatings and the individual ALD precursors are not fully studied. We performed a systematic investigation to understand the interfacial changes of 12 different cathode materials upon coating with aluminum oxide (Al_2O_3) using trimethyl aluminum (TMA) and H_2O, and aluminum fluoride (AlF_3) using TMA and hydrogen fluoride pyridine (HFPy). We also explored the effects of the individual TMA and HFPy precursors on the cathode surfaces.The surface composition and microstructure of these cathode materials, which range from simple transition metal oxides (e.g., NiO and MnO) to complex multi-element cathode materials (e.g., $LiNi_xMn_{1-x-y}Co_yO_2$, NMC), were studied via X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM). The XPS measurements reveal that the transition metals in the cathode materials undergo selective oxidation/reduction depending upon the nature of the precursor, the coating, and the cathode material. Furthermore, XPS and STEM measurements show the conversion of surface carbonate species to the corresponding metal fluorides upon HF exposure.This conversion reaction is self-limiting but extends hundreds of nanometers below the surface in the case of Li_2CO_3.ALD and chemical vapor treatment provide new avenues to systematically control the interface of the cathode materials in LIBs that are not possible by conventional coating methods.

4:15pm **AA2-MoA-12 Titanium Carboxylate MLD Hybrid Films as Protective Coatings for Lithium-Ion Batteries***, **Sofie S. T. Vandenbroucke**, L. Henderick,* Ghent University, Belgium*; L. De Taeye,* IMEC, Belgium*; J. Li,* Ghent University, Belgium*; K. Jans, P. Vereecken,* IMEC, Belgium*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

Li-ion battery cathodes age due to phenomena as transition metal dissolution, electrolyte oxidation and volume expansion. [Vetter J., et al. (2005) *J. power sources*] A protective coating can be applied to the cathode's surface to avoid direct contact with the electrolyte. Many studies have shown the protective effect of conformal and pinhole-free ALD films. However, inorganic films are rigid and may crack upon volume expansion of the cathode. [Ban C., et al. (2016) *Adv. Mat. Int.]* MLD offers the same deposition controllability as ALD but can be used to deposit hybrid films that are more flexible to accommodate potential volume expansions. In this work, titanium carboxylate thin films are deposited using tetrakis(dimethylamido)titanium (TDMAT) and various dicarboxylic acid precursors: oxalic acid, malonic acid, succinic acid, glutaric acid and 3,6-dioxaoctanedioic acid (Fig 1). The latter containing two ethylene oxide units per molecule, potentially increasing the Li-ion conductivity. [Xue Z., et al. (2015) *J. Mat. Chem. A*]

The growth of the titanium carboxylate thin films is studied using in situ ellipsometry at a substrate temperature of 100 and 160 °C. Only the TDMAT/oxalic acid process displays good saturation behavior, while a parasitic CVD component is present during the TDMAT pulse for the other processes (Fig 1). FTIR and XPS confirm the successful deposition of titanium carboxylate films. The films are found to be stable in air up to 50 days in contrast to many metalcone MLD films. In addition, FTIR, XRR and XRF measurements show that the films remain intact upon immersion into the liquid electrolyte used for electrochemical characterization (1 M $LiClO_4$ in propylene carbonate).

The electrochemical properties of 5 nm films grown with TDMAT/oxalic acid, TDMAT/3,6-dioxaoctanedioic acid and TDMAT/glycerol (titanicone film [Van de Kerckhove K., et al. (2016)*Dalton Trans.*]), respectively, are compared on top of three ideal electrode systems: anatase TiO_2, TiN and $LiMnO_2$ (LMO). The titanium carboxylate films have little to no effect on the Li-ion kinetics of the TiO_2 electrode system. This is in contrast to the titanicone film displaying a detrimental effect on the kinetics. All films effectively suppress electrolyte oxidation when exposing the TiN electrode system to elevated potentials (Fig 2). On the LMO electrode an activation step is necessary for all films, after which a good Li-ion mobility through the titanium carboxylate films is observed without the severe irreversible reactions detected for the titanicone film. Overall, the titanium carboxylate films seem promising candidates as flexible coatings to protect Li-ion battery cathodes.

4:30pm **AA2-MoA-13 Surface Coating and Grain Boundary Engineering of NMC811 Materials for Next-Generation Li-Ion Batteries***, **Zahra Ahaliabadeh**, V. Miikkulainen,* Aalto University, Finland*; M. Mäntymäki,* University of Helsinki, Finland*; T. Kallio,* Aalto University, Finland

Nickel-rich layered metal oxide $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) is one of the most promising cathode materials owing to its high energy density. Therefore, these cathode materials have a prime interest for the electric vehicle battery manufacturers to build next-generation lithium-ion batteries. However, NMC811 suffers from several irreversible parasitic reactions and interfacial/structural instability that lead to severe capacity fading and impedance buildup during prolonged cycling. Thin surface protection films coated on the electrode material are feasible and effective solutions to solve these challenges. It can mitigate degradative chemomechanical reactions at the electrode–electrolyte interphase, which helps to increase cycling stability. However, most of the coatings including metal oxide may impede the diffusion of lithium ions, and therefore, limit the performance of the cathode material. Thus, the physical and chemical properties of the coating materials are effectual factors in providing optimized protection for the electrode materials. In our research, we worked on the deposition of Li-containing metal oxide layers with different thicknesses through atomic layer deposition method, on the surface of NMC811. Lithium titanate, was coated on the NMC811 electrode and found to be effective in the elimination of surface impurities and reducing the capacity loss. Characterization analysis such as Scanning electron microscopy (SEM-EDS) and Transmission Electron Microscopy (TEM) results confirmed the diffusion of the coating in to the NMC grain boundaries which helped to stabilize the structure, as evidenced by providing longer lifetime with an 87% capacity retention after 100 cycles. Besides the characterization and electrochemical analysis, *in-situ* dilatometry and *in-situ* XRD analysis showed irreversible volume change for NMC811 bare while it was mostly reversible for the coated ones during the cycling. The results revealed that the dilation behavior of the electrode, resulting in crack formation and particle degradation, has been significantly suppressed for the coated samples. The ability of the coatings to mitigate the electrode degradation mechanisms, provides insight into a method to enhance the performance of Ni-rich positive electrode materials. To enhance the electrochemical performance of NMC811 under high-voltage ranges, the addition of organic molecule to the coating is suggested. Such a hybrid coating layer can combine the functions of promoting Li^+ ion transport, as well as enhancing the electrical conductivity due to the coating structural properties. This new coating is under examination and its results will be demonstrated later.

4:45pm **AA2-MoA-14 Hybrid Inorganic/Organic Polycarbonate Track-Etched Membranes With Tunable Pore Size and Surface Functionality for Redox Flow Batteries***, **Rajesh Pathak**,* Applied Materials Division, Argonne National Laboratory*; X. Fang,* Indiana University−Purdue University Indianapolis*; R. Shevate, V. Rozyyev, A. Mane,* Applied Materials Division, Argonne National Laboratory*; X. Wei,* Indiana University−Purdue University Indianapolis*; Z. Xia,* Argonne Center for Molecular Engineering, Argonne National Laboratory*; L. Zhang,* Chemical Science and Engineering Division, Argonne National Laboratory*; S. Babinec,* Argonne Collaborative Center for Energy Storage Science (ACCESS), Argonne National Laboratory*; S. Darling,* Argonne Center for Molecular Engineering, Argonne National Laboratory*; J. Elam,* Applied Materials Division, Argonne National Laboratory

Abstract

Redox flow batteries (RFBs) hold great promise for the stationary storage of renewable energy from solar and wind power because they combine high safety with low cost, and because they decouple energy density and power density through the physical separation of redox-active species in liquid solutions. Despite these positive attributes, the high cost of existing RFBs limits their widescale deployment in the electric power grid.Significant cost reduction is possible if new technologies for the manufacture of low-cost, highly selective ion transport membranes can be developed.In this study, we explore isoporous polycarbonate track-etched membranes (PCTEs) modified by sequential infiltration synthesis (SIS) and atomic layer deposition (ALD) to tune the pore size and pore surface chemistry as a platform for developing low-cost, high-performance RFB membranes. We perform a systematic study of Al_2O_3 SIS and ALD in PCTE to establish the range of conditions that yield precise control over the membrane pore size.Next, we functionalize the pore wall surfaces with a variety of ALD metal oxide coatings to tune the surface charge and hydrophilicity.Finally, we evaluate the membrane properties and performance in aqueous organic redox flow batteries with (ferrocenylmethyl)trimethylammonium chloride (FcNCl)/methyl viologen (MV) in noncorrosive neutral sodium chloride supporting electrolyte to establish structure-function-property relationships.We anticipate that this work will provide a pathway to developing low-cost inorganic/organic ion transport membranes for RFB applications.

Keywords: atomic layer deposition; sequential infiltration synthesis; neutral aqueous organic redox flow battery; selective ion-transport; high-permeability; (ferrocenylmethyl)trimethylammonium chloride; methyl viologen

5:00pm **AA2-MoA-15 TiO_2 ALD Thin Films Characterization for SiC Capacitor***, R. César, **José Diniz**,* University of Campinas - UNICAMP, Brazil

Silicon carbide (SiC) has become a very promising material in the microelectronics industry due to its properties. In this way, being widely used in the development of MOSFET, diodes and MOS capacitors, mainly used in high temperature and high power applications. However, the SiC interface presents higher charge density that limits the use of SiO2 as gate dielectric. Dielectric options such as aluminum oxide and titanium oxide (TiO2) have been studied for passivation of interfacial defects. TiO2 stands out due to its qualities such as: high dielectric constant, chemically and thermally stable. Thus, this work presents the study carried out with thin films (15, 25 and 35 nm) of TiO2 deposited by ALD to be used as gate dielectric in SiC capacitors. The structural characterization consists of ellipsometry and spectroscopy Raman. The electrical characterization was performed using capacitance by voltage (CxV) and current by voltage (IxV) using silicon MOS capacitors. Through the ellipsometry technique it was possible to obtain the refractive index (η) values of the TiO2 films, which ranged from 2.06 ~ 2.32. The refractive index of the stoichiometric TiO2 is 2.41. This result indicates that these films have a higher concentration of oxygen than titanium. Raman spectroscopy showed that all films have a rutile crystalline structure, identified by the letter R in Figure 1 (Appendix), and the presence of the anatase crystal structure, identified by the letter A in Figure 1 (Appendix). From CxV and IxV curve, it was possible to it was possible to extract the data that compose the 1, 2 and 3 tables (Appendix). It can be seen from all tables that the VFB values are decreasing in all three cases, indicating the relationship of VFB with the device geometry. Another very important parameter presented by the three thicknesses is the absence of hysteresis. It is very common for TiO2 films deposited by ALD to present hysteresis values greater than 10 mV. Hysteresis is related to charge trapped at the dielectric/semiconductor interface, generated during the device manufacturing process. Therefore, it can be assumed that the capacitors developed in this work have low trapped load values. The 25 and 35 nm thick oxide capacitors presented dielectric constant values with a decreasing behavior, and 15 nm thick oxide capacitor showed an ascending behavior. However, the films showed dielectric constant values ranging from 11 ~ 56. Thus, it can be concluded that these TiO2 films deposited by ALD have rutile and anatase crystal structure, high dielectric constant and low charge density and leakage current density values, being ideal for use in SiC capacitors.

5:15pm **AA2-MoA-16 ALD Can Enable Competitive, U.S.-Sourced Graphite Production***, **Arrelaine Dameron**, D. Higgs, B. Hughes,* Forge Nano

U.S. demand for LIBs is projected to grow to >400GWh by 2030 but U.S. battery manufacturing is currently dependent on foreign (primarily China) supply of graphite materials. The coated spherical purified graphite (CSPG) production processes are energy intensive and derived from petroleum. The spherical graphite is purified by leaching, caustic and thermal treatments to remove metal impurities and is then coated by a liquid phase tar (derived from petroleum processing) that fills surface pores and reduces the surface area. The tar itself is also fractionated and purified through size separation and solvent extraction to produce the ideal precursor feedstock. The coated particles are then dried and baked at >1200 °C for days in an inert-gas oven.

FN has developed ALD coatings to disrupt the pitch coating process. FN has previously shown ALD coatings can improve CSPG graphite. Recently, FN has also demonstrated that ALD can improve uncoated graphite to a higher performance (capacity and rate tolerance) and longer lifetime than pitch coated graphite with all the added advantages of economically and environmentally improved process to generate a competitive domestic supply of battery grade graphite. This process is applied to the purified and spheronized graphite and then can be directly packaged or cast into anode materials. Drying, thermal treatment and further physical processing are not required. This low vacuum or atmospheric pressure process can we applied continuously at low temperature (<150 °C instead of 1200 °C) greatly increasing the throughput of the process while decreasing the carbon footprint significantly. This nano-coating process can replace traditional tar pitch coating processes for spherical graphite used in the anode of LIB. Combining up incoming US manufacture of high purity graphite and FN's nano-coatings will enable domestic production of low-cost anode-grade graphite materials for lithium-ion batteries and simplify supply chain logistics, while reducing national security risk. Establishing a completely U.S. battery supply chain, using disruptive U.S.-based technology, will deliver both material supply resilience and improved production rates. Use of ALD-coated spherical graphite will also deliver a lower cost and safer battery for U.S. consumption. ALD-coated spherical graphite is a drop-in replacement for foreign sourced materials and seamlessly integrated into standard Lithium-ion battery production methods. This talk will demonstrate the various benefits of ALD coatings on graphite for LIB, scaling these processes to production scale, and compare ALD graphite relative to the incumbent CSPG technology.

5:30pm **AA2-MoA-17 Plasma-Enhanced Atomic Layer Deposition of Nickel and Cobalt Phosphate for Lithium Ion Batteries**, ***Lowie Henderick**, R. Blomme, J. Keukelier, M. Minjauw,* Ghent University, Belgium*; J. Meersschaut,* IMEC, Belgium*; J. Dendooven,* Ghent University, Belgium*; P. Vereecken,* IMEC, Belgium*; C. Detavernier,* Ghent University, Belgium

Since the introduction of a lithium iron phosphate electrode in Li-ion batteries (LIB's), metal phosphates have become increasingly important. Apart from LIB's, metal phosphates have also been proven promising towards e.g. electrocatalytic water splitting, biocompatible coatings, etc., which is why research on their deposition also becomes increasingly important. Atomic Layer Deposition (ALD) has emerged as a deposition technique with unique nanotailoring capabilities, making the combination of both research fields gain a lot of interest. Although it has been challenging to find a suitable phosphate precursor, the use of trimethyl phosphate (TMP) has allowed for the deposition of a variety of metal phosphates (Henderick et al. (2022) *Appl. Phys. Rev.*). Unfortunately, its poor reactivity limits the deposition of metal phosphates with e.g. a high phosphorus-to-metal (P/M) ratio. Interestingly, the use of a TMP plasma (PE-ALD) allowed for the deposition of other, more connected (more P-O-P bonds, figure 1), metal phosphates.

In this work, a novel PE-ALD process was developed for the deposition of nickel phosphate ($NiPO_x$), which was not yet available through ALD. The process is based on an earlier report where a TMP plasma (TMP*) is combined with an oxygen plasma (O_2*) and a metal precursor. Using nickelocene as the metal precursor, saturated growth of an amorphous $NiPO_x$ was observed at a substrate temperature of 300°C, with a growth per cycle of 0.2 nm/cycle (figure 2). Using XPS, the nickel is thought to be in the 2+ oxidation state, while the position of the oxygen and phosphorus peak agree with the formation of a phosphate-like material.

As $NiPO_x$ is currently of interest as a LIB electrode, the material was also electrochemically characterised together with cobalt phosphate using a previously reported ALD process (Rongé et al. (2019) *Nanoscale Adv.*). Both materials showed electrochemical activity (figure 3), although at a lower voltage window than what is supposed to be achievable with these phosphates. This relatively low operating voltage is expected to originate from the 2+ oxidation state of nickel (and cobalt) in the as-deposited material, while a 3+ oxidation state would be needed for the high energy redox reactions to take place. Both materials did show a good rate performance with a reasonable cycle life.

We hope that the novel PE-ALD process developed in this work can help to extent the knowledge on ALD of metal phosphates. We also hope that it sparks interest towards further fine-tuning such processes to optimise the layers towards their respective application (e.g. LIB's and/or other potential applications).

ALD Fundamentals
Room Auditorium - Session AF1-MoA
New Precursors and Processes II

Moderators: Romain Gaillac, Air Liquide, Mikko Ritala, University of Helsinki

1:30pm **AF1-MoA-1 Atomic Layer Deposition of CsI and $CsPbI_3$**, ***Alexander Weiß**, G. Popov, E. Atosuo, P. Jalkanen, A. Vihervaara, M. Vehkamäki,* University of Helsinki, Finland*; H. Sipilä, A. Niemela,* Fenno-Aurum Oy Ltd, Finland*; M. Ritala, M. Kemell,* University of Helsinki, Finland

Cesium iodide (CsI) is one of the most studied and applied scintillator materials. It exhibits a band gap located in the UV region (5.42 eV) and an outstanding detective quantum efficiency (DQE). Owing to these properties CsI was established as material of choice for indirect x-ray imaging in radiology[1], amongst other applications. Moreover, CsI thin films are precursors to some halide perovskite absorbers that are used in Perovskite Solar Cells (PSCs). This young research field recently gained high interest because of the potential to deliver low-cost solar energy. However, there are still two challenges for PSCs to become widely commercially available: The difficulty in scaling-up and the instability of the perovskite in ambient conditions.

Our approach to tackle the scalability issue relies on Atomic Layer Deposition (ALD) because of its high controllability to deposit thin films on large areas and complex-shaped surfaces. We believe that developing an ALD process for CsI can also address the stability issue: Literature reports give evidence that perovskite solid solutions have better stability than pure perovskites. Key to these solid solutions is the controlled addition of several cations and/or anions into the perovskite structure. In our previous work, we already demonstrated an ALD process for PbI_2 thin films and its conversion into methyl ammonium lead iodide $CH_3NH_3PbI_3$ (MAPI)[2]. Developing an ALD process for CsI and combining it with the PbI_2 process to deposit $CsPbI_3$ would be the first step towards depositing solid solution perovskites with ALD from $CsPbI_3$ with MAPI.

In this work, we report a new ALD CsI process that uses cesium bis(trimethylsilyl) amide (Cs(btsa)) as the cesium precursor and tin(IV) iodide (SnI_4) as the iodine precursor. The high volatility of Cs(btsa) enables deposition of phase pure CsI at low temperatures (140 °C). In the range of 150 – 170 °C the process exhibits a temperature independent growth per cycle (GPC) value of 3.3 Å. The GPC saturates rapidly with respect to both precursor pulses and purge durations, and is independent of the number of deposition cycles. Furthermore, we demonstrate the deposition of ternary $CsPbI_3$ perovskite thin films with a two-step approach: First, we deposit CsI thin film via ALD. In the second step, the CsI film is exposed to our previous PbI_2 ALD process yielding directly $CsPbI_3$ perovskite. This combination of CsI and PbI_2 ALD allows to prepare phase pure γ-$CsPbI_3$ and δ-$CsPbI_3$ thin films, depending on the number of PbI_2 deposition cycles.

[1] Keiko et al. *U. S. Patent Appl. Publ.* **2011**. US20130068953A1

[2] Popov et al. *Chem. Mater.* **2019**, *31* (3), 1101-1109.

1:45pm **AF1-MoA-2 Co(II) Amide, Pyrrolate, and Aminopyridinate Complexes: Assessment of Structure and Thermal Properties as ALD Precursors**, ***Jorit Obenlüneschloß**, D. Zanders,* Ruhr University Bochum, Germany*; M. Land, S. Barry,* Carleton University, Canada*; A. Devi,* Ruhr University Bochum, Germany

Thin films of cobalt metal are subject of high research and economic interest owing to their potential to facilitate performance increases in integrated circuitry (IC) devices at continuously shrinking dimensions. Its good conductivity and stability are among the reasons cobalt is handled as a replacement to copper. To implement cobalt thin films, atomic layer deposition (ALD) is a favorable fabrication technique allowing precise device architectures to be coated uniformly with sub nanometer thickness control.[1]

In ALD, the choice of precursor is of crucial importance because its thermal behavior and reactivity are paramount for successful deposition of a desired thin film material. Revisiting the library of Co precursors, all nitrogen coordinated precursor complexes are underexplored; surprisingly as Co(II) diazadienyls have successfully ventured into the field.[2]

Motivated by this premise, we studied a variety of new nitrogen coordinated Co complexes and their potential for ALD. They have been synthesized and thoroughly characterized by EA, EI-MS, SC-XRD, TGA and vapor pressure estimations.[3]

An entry point to this study was found in the Co(II) bis(trimethysilyl)amide dimer **1**. This very compound was reacted with a selection of amides, imides, amide-adducts, pyrroles, and amido-amines (Fig. 1). With structural and chemical ligand variations in the form of aromatic moieties, varying ring size, substitution patterns, bonding character and strategic incorporation of silylamide functionalities, a variety of cobalt compounds was successfully obtained (Fig. 1). The modifications were performed to gain a broader understanding of influences on reactivity, stability, and volatility with the aim of tailoring the compounds suitable for ALD.

Whereas some of the forwarded complexes followed the expected structural trends, others adopted distinctive and unexpected coordination motives (Fig. 2). This was reflected by their thermal behavior and underlined that gradual ligand alteration can have a vast impact Additionally, the assessment of volatility also shows distinct differences between the employed ligands (Fig. 3). Especially volatile with high stability were the Co(II) iminopyrrolate **9** and the silylamido-amine **11**. Those two newly uncovered precursors were found to be especially promising candidates for application in ALD process development.

[1] A. E. Kaloyeros, et al., *ECS J. Solid State Sci. Technol.* **2019**, *8*, 119–152.

[2] J. P. Klesko, et al., *Chem. Mater.* **2016**, *28*, 700–703.

[3] D. Zanders, J. Obenlüneschloß, et al., *Eur. J. Inorg. Chem.* **2021**, 5119–5136.

2:00pm **AF1-MoA-3 SnO Thin Films *via* Water Based ALD using a Sn(II) Precursor: Precursor Evaluation and ALD Process Development**, ***Niklas Huster,*** Ruhr University Bochum, Germany; *R. Ghiyasi,* Aalto University, Finland; *D. Zanders,* Ruhr University Bochum, Germany; *D. Rogalla,* RUBION, Ruhr University Bochum, Germany; *M. Karppinen,* Aalto University, Finland; *A. Devi,* Ruhr University Bochum, Germany

Tin(II) oxide is one of the few p-type semiconducting materials that possesses excellent electrical and optical properties. Hence this interesting material system is very appealing for applications in chemical sensing, as anode material for Li-ion batteries or as a transparent conductive oxide (TCO) in thin film transistor (TFT's), particularly due to the high hole mobility. Nevertheless, the deposition of stoichiometric SnO thin films is a challenging task. Atomic layer deposition (ALD) is a preferred process for thin film deposition as it is capable of yielding high quality, dense and uniform layers with an excellent control over film thickness as well as the ability to control the stoichiometry. Sn(II) oxide readily oxidizes to Sn(IV) and there are not many ALD processes known for obtaining highly stoichiometric SnO films. Thus, care must be taken with respect to process parameter selection and precursor choice.

Herein, we report the successful deposition of stoichiometric SnO thin films in a simple water based ALD process, employing the homoleptic, liquid tin(II) formamidinate precursor $[Sn(^{i}Pr_2fAMD)_2]$ that was recently reported for ALD of SnS.[1]. Based on the promising thermal properties (Figure 1), good thermal stability and high reactivity towards water, we employed this precursor for ALD of SnO. The newly developed ALD process yielded SnO layers in the temperature range of 120 °C to 180 °C on Si substrates. The formation of tetragonal romachite-type SnO films was confirmed by Grazing Incidence X-ray Diffraction (GI-XRD) while surface and bulk composition were verified by means of X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectroscopy (RBS) / Nuclear Reaction Analysis (NRA) (Figure 2). The films were found to exhibit the desired stoichiometry alongside high purity. Optical bandgaps of as-deposited and annealed films were determined *via* Tauc-plotting from UV-Vis measurements. This is a very promising ALD process development where the role of precursor and co-reactant choice enabled the phase control of SnO films.

[1]Kim *et al.*, *ACS Appl. Mater. Interfaces*, **2019**, 11, 45892−45902

2:15pm **AF1-MoA-4 Tuning the Texture of ZnO Thin Films Through the Addition of a Volatile Shape-Directing Agent in the AP-SALD System**, *C. Crivello, M. Weber,* LMGP Grenoble-INP / CNRS, France; *T. Jalabert, G. Ardila Rodriguez,* IMEP-LaHC UGA/CNRS/Grenoble INP, France; *M. Dibenedetto,* ***David Muñoz-Rojas,*** LMGP Grenoble-INP / CNRS, France

Zinc oxide draws attention for its relatively low cost, the wide bandgap of 3.37 eV,[1] and for its electrical and optical properties for applications such as gas sensors, solar cells, thin-film transistors and light-emitting diodes.[2,3] ZnO thin films can be obtained by different deposition methods, from sol-gel approach to sputtering, and gas-phases based approaches such as molecular beam epitaxy (MBE), chemical vapour deposition (CVD), atomic layer deposition (ALD).

Within the materials deposition techniques, Atmospheric Pressure Spatial ALD (AP-SALD) is gaining momentum since it is a high throughput and low-cost alternative to conventional ALD. AP-SALD is based on a physical separation (rather than temporal separation, as is the case in conventional ALD) of gas-diluted reactants over the surface of the substrate by a region containing an inert gas.[4]

In this presentation, we will show that a volatile shape-directing agent can be used to tune the texture and growth rate of ZnO thin films deposited by AP-SALD. While the use of such agents is common in liquid-based synthesis approaches, their use in the AP-SALD system has never been used to the best of our knowledge. (002)-oriented hexagonal wurtzite-type ZnO films were obtained at 200 °C, without any post-deposition treatment.

[1]Velázquez-Nevárez GA, Vargas-García JR, Aguilar-Hernández J, Vega-Becerra OE, Chen F, Shen Q, et al. Optical and Electrical Properties of (002)-Oriented ZnO Films Prepared on Amorphous Substrates by Sol-Gel Spin-Coating. Mater Res 2016;19:113–7. doi:10.1590/1980-5373-mr-2016-0808.

[2]Zhao M-J, Sun Z-T, Hsu C-H, Huang P-H, Zhang X-Y, Wu W-Y, et al. Zinc Oxide Films with High Transparency and Crystallinity Prepared by a Low Temperature Spatial Atomic Layer Deposition Process. Nanomaterials 2020;10:459. doi:10.3390/nano10030459.

[3]Dong J, Han D, Li H, Yu W, Zhang S, Zhang X, et al. Effect of Al doping on performance of ZnO thin film transistors. Appl Surf Sci 2018;433:836–9. doi:10.1016/j.apsusc.2017.10.071.

[4] Muñoz-Rojas D, Huong Nguyen V, Masse de la Huerta C, Jiménez C, Bellet D. Spatial Atomic Layer Deposition. Chem. Vap. Depos. Nanotechnol., IntechOpen; 2019. doi:10.5772/intechopen.82439.

2:30pm **AF1-MoA-5 Recent Advances in Rare Earth Precursors for ALD**, ***Jean-Pierre Glauber,*** *M. Schmickler, P. Kaur, S. Beer, N. Boysen,* Ruhr University Bochum, Germany; *A. Devi,* Ruhr Universität Bochum, Germany

Rare earth (RE) containing thin films are indispensable for several different applications owning to their broad number of intrinsic functional properties. Especially, RE-oxides and -sulfides are of high interest for various applications such as high-κ dielectrics (Y_2O_3, CeO_2), optical fibers in lasers (Yb_2O_3), spintronics (EuS) or photovoltaics (Nd_2S_3). However, to gain fundamental insights and accelerate the development of these devices, reliable synthesis routes that yield high-quality material are required.[1] Vapor phase deposition methods such as atomic layer deposition (ALD) can meet these demands, but to develop promising processes for the formation of the RE-containing materials, precursors with certain pre-requisites are of utmost importance.[2] Besides sufficient volatility and thermal stability at the operating conditions, the precursors need to exhibit a high reactivity towards the employed co-reactant.

Commonly used ligands with oxygen-metal bonds suffer from a low reactivity towards the co–reactants due to strong RE–O bonds, which limits their applicability in ALD processes. On the other hand, precursors with guanidinate (dmg), amidinate (amd) and formamidinate (famd) ligand moieties have gained prominence since their all-nitrogen coordinated ligands ensure high reactivity toward mildly reactive co-reactants such as H_2O, while retaining volatility and thermal stability.[2,5]

Consequently, a series of RE containing precursors, with the formula $[M(L)_3]$ (M = Y, Ce, Eu, Yb; L = dpdmg, dpamd, dpfamd) were synthesized (Figure 1), structurally analyzed, and their thermal properties evaluated.[1-5] Furthermore, the tunability of the thermal properties via a variation of the ligand side chains was demonstrated for Y formamidinates [3] as well as for amidinates and guanidinates of Ce and Yb [2] with systematic thermogravimetric analysis studies (TGA).

Density functional theory (DFT) calculations of the reaction between selected Y, Yb and Ce precursors with H_2O revealed a pronounced reactivity towards mild oxidizing agents and underlined their suitability for ALD processes.[2,3] Actual ALD experiments of Y formamidinate- and Ce guanidinate-based precursors with H_2O as the co-reactant confirmed the results from DFT and yielded high-quality thin films of Y_2O_3 [3,4] (Figure 2) and CeO_2 [2], respectively. A high reactivity of the $[Eu(L)_3]$ (L = dpdmg, dpamd, dpfamd) towards O_2 and S_2 was obtained from DFT studies, further underlining the suitability of these ligand motifs in precursors for vapor phase deposition fabrication methods.[1]

2:45pm **AF1-MoA-6 Novel Growth Inhibitor in Atomic Layer Deposition for Conformal Coverage on High Aspect Ratio Trenches***, **Kok Chew Tan**, J. Jung, C. Yeon, S. Lee, J. Kim, J. Nam, T. Park, Y. Park,* Soulbrain, Korea (Republic of)

The continuous miniaturization of semiconductor devices has triggered growing interests in new strategy for depositing conformal coatings on complex geometry which are critical for device reliability. Despite ALD being a mainstream technique for conformal coatings, features with increasing aspect ratio have rendered this conventional ALD increasingly challenging to achieve the desired step coverage.

Various approaches have been conducted to improve film conformality and film quality on high aspect ratio (HAR) trenches such as screening of molecules with potential chemistry as inhibitor and tuning of ALD process parameters. In this work, we have narrowed down our approach by successfully identifying molecules with suitable chemistry (alkyl-halides) that could act as growth inhibitor in the first pulse step of ALD. This inhibitor enables the control of inherent kinetics of gas transport within the trenches by reducing the surface reactive sites for precursors on the top region while allowing more precursors to diffuse deeper into the trenches, thus improving film conformality in high aspect ratio trenches. Besides growth inhibition, the selected inhibitor could function as film quality enhancer and could also be easily removed during reactant pulse step without contaminating the films.

By leveraging the selected inhibitor chemistry and ALD deposition characteristics, our approach has demonstrated significant improvement in TiN film conformality to 90% in HAR trench features, as determined by the ratio of bottom side film thickness to top side film thickness **[1]**. In terms of film resistivity, an observable 50% improvement was obtained owing partially to large decrease in Cl impurity as determined by SIMS depth profiles **[1]**. The introduction of inhibitor has also exhibited promising benefits in the ALD of high-*k* dielectric film, HfO_2. Improvement in HfO_2 film conformality to 97% in HAR trench features as well as significant improvement of 95% in leakage current due to enhancement in film quality were simultaneously observed **[2]**.

Based on these experimental evidences, our approach has been proven its promising potential as an innovative solution to address the challenges of depositing highly conformal films of excellent quality on high aspect ratio features such as DRAM trench capacitor and 3D NAND.

References:

7. C. Yeon, J. Jung, H. Byun, K.C. Tan, T. Song, S. Kim, J.H. Kim, S.J. Lee and Y. Park, AIP Advances 11, 015218 (2021).
8. K.C. Tan, J. Jung, S. Kim, J. Kim, S.J. Lee and Y. Park, AIP Advances 11, 075008 (2021).

3:00pm **AF1-MoA-7 Solution ALD: A Versatility Process for the Growth of Sulfides and Selenides***, **Maissa Barr**, B. Zhao, P. Von Grundherr,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; V. Koch,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; J. Charvot ,* University of Pardubice: Pardubice, CZ, Czechia*; M. Halik,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; F. Bureš,* University of Pardubice, Czechia*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

We have proposed and demonstrated a novel thin film deposition technique by transferring the principles of atomic layer deposition (ALD), known with gaseous precursors, towards precursors dissolved in a liquid. The technique can also be considered as a generalization of already established methods such as the 'layer by layer' growth or the 'successive ion layer adsorption and reaction' (SILAR). 'Solution ALD' (sALD) shares the fundamental properties of standard 'gas ALD' (gALD), specially the self-limiting growth and the ability to coat conformally deep pores. It has been already shown that it is possible to transfer standard reactions from gALD to sALD such as TiO_2 deposition . However, sALD also offers novel opportunities such as overcoming the need for volatile and thermally robust precursors.

To illustrate this, we establish sALD procedures for depositing films of non oxides layers such as Pb-compound deposition, MOF, selenides and sulfides. Those examples highlight how ionic, polar, or high-molecular weight precursors that only exist in the condensed phase are now rendered amenable to being utilized in surface-controlled thin film formation by sALD for depositing materials that would otherwise be more difficult or more expensive to achieve by gALD or hazardous. The deposition was achieved on small (2 cm*1 cm) and large samples (up to 10 cm*10 cm). The ALD behavior has been shown. The influence of the deposition parameters on the morphology, the crystalline structure and the chemical composition has been investigated by scanning electron microscopy, atomic force microscopy, grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy. Additionally, the nucleation is studied in function of chemical pretreatment to control the growth and allow selective deposition of SnS, SnSe and Sb_2Se_3.

This particular ALD process offer the growth of high quality and crystalline layers in middle conditions with the use of low cost and environmental friendly precursors.

Y. Wu, D. Döhler, M. Barr, E Oks,M. Wolf, L. Santinacci and J. Bachmann, Nano Lett. **2015**, *15*, 6379

J. Fichtner, Y. Wu, J. Hitzenberger, T. Drewello and J. Bachmann, ECS J. Solid State Sci. Technol. **2017**, *6*, N171

3:15pm **AF1-MoA-8 Flash-Lamp Enabled Atomic Layer Deposition***, **Martin Knaut**, Y. Cui, R. Deltschew, M. Albert, T. Mikolajick,* TU Dresden, Germany

Atomic layer deposition (ALD) processes are widely used in research and development as well as in various production environments. Nowadays, a variety of materials can be deposited using thermal and energy enhanced atomic layer deposition but there are limits that are mainly set by the properties of available precursors and the related processes. Besides the necessity of suitable precursors and chemical reactions to deposit a specific material, there are two major limitations: the thermal self-decomposition of precursor molecules which can be in conflict with the required process temperatures enabling desired film properties, and the typical temperature-related reactivity of precursors and co-reactants with substrate materials. These can affect the initial film growth and can lead to adhesion issues and unwanted interface layers, such as oxides formed by oxidizing agents used during the ALD process.
We developed a novel flash lamp enabled atomic layer deposition (FLE-ALD) process to address these limitations of common ALD processes. The process combines the self-limiting chemisorption of precursor molecules in the first half-cycle with a millisecond flash lamp anneal (FLA) during the second half-cycle. The heat applied during the second process step enables single-source ALD processes by inducing a thermal decomposition of chemisorbed molecules resulting in the desired film material.
This paper demonstrates the FLE-ALD approach for the deposition of oxide and nitride films in single-source processes combining metal organic precursor exposures with flashes of optical light with a duration in the millisecond range to heat a surface for a very short time and to decompose the chemisorbed molecules. The heat induced by the short FLA step is distributed into the substrate's bulk and the process chamber during the subsequent purging step, resulting in a constant substrate temperature and maintaining the self-limiting behavior of the precursor chemisorption.
The process development confirmed the FLE-ALD principle and the ALD typical self-limiting and constant growth per cycle by varying and characterizing process parameters like precursor dose, purge times, flash lamp energy, substrate temperature, and cycle number. Spectroscopic ellipsometry was used to measure the film thicknesses and to investigate the optical properties of the deposited films. The film composition was measured by X-ray photoelectron spectroscopy and scanning electron microscopy was used to analyze step coverage in high aspect ratio structures.

ALD Fundamentals
Room Auditorium - Session AF2-MoA

Simulation, Modeling, and Theory of ALD I

Moderators: Hannah Margavio, North Carolina State University, Bonggeun Shong, Hongik University

4:00pm **AF2-MoA-11 A User Experience Feedback on Numerical Simulation for CVD/ALD Precursor Design & Development***, **Romain Gaillac**,* Air Liquide **INVITED**

Molecular modelling has been a widely used tool in biochemistry or catalysis for decades. More recently, its application to CVD/ALD precursors has been suggested as a way to improve their design and development. We have explored its potential, especially through ab-initio molecular simulations.

In particular, we investigated the relevance of such simulations for the assessment of synthetic pathways and reactions occurring during Atomic

Layer Deposition processes. We also assessed the interest of assisting analytical efforts with molecular simulations, for example for substance identification via spectra simulation.

Our work showed that molecular simulations are a useful tool for the development of new ALD precursors. They can be used to different degrees of accuracy to understand:

- Intrinsic molecule stability, either isolated or in a condensed phase
- Reaction thermodynamics and reaction paths
- Surface adsorption/desorption and reactivity

However the predictive power remains to be improved, and at this point, it should be seen as a useful companion to experimental work. Effective collaboration between the synthetic chemists, ALD/CVD practitioners and molecular modeling theorists accelerates the acquisition of a chemical and mechanistic comprehension of ALD Precursors. Such learning can bring an acceleration to the design and development process.

4:30pm **AF2-MoA-13 From Monolayers to Crystalline Materials in ALD: Simulation and Comparison With Experiments***, **Angel Yanguas-Gil**, J. Elam,* Argonne National Laboratory

Controlling the microstructure of ALD materials is key for many different applications. In some cases, like gate dielectrics in microelectronics, the goal is to achieve materials with good interfaces and that lack grain boundaries to improve leakage and avoid the onset of breakdown. In other cases, applications require the growth of materials with good crystalline quality.

One of the key characteristics of ALD is that its growth conditions (low temperature and pulsed, self-limited nature) are far from those considered in traditional growth models, where the growth of crystalline materials is promoted by either large surface mobilities that allow relaxation or reversible processes close to thermodynamic equilibrium that tend to self-correct defects randomly occurring during growth. In this work, we present a model that explores the evolution of crystallinity and microstructure under self-limited and kinetically limited conditions characteristic of ALD. This model, based on a generalization of the Potts model, tracks the evolution of local coordination environments as a function of the number of ALD cycles, and differs from traditional approaches in the literature by considering the following assumptions: 1) microstructure relaxation takes place only through local rearrangement of atoms 2) relaxation is kinetically limited so that only transitions that lower the energy of the systems are allowed 3) growth takes place in a two-step process involving adsorption of a precursor and reaction with a co-reactant. When these are separated in time, the process is fully self-limited.

The simulation of the evolution of the medium range order, captured in the average size of locally ordered domains, agrees well with experimental results, both ex-situ and in-situ, obtained for a wide range of oxide materials including ZnO, Al_2O_3, and TiO_2. When the probability of local relaxation is high, the material grows from an amorphous interface into crystalline domains of increasing size, demonstrating that local relaxations are sufficient for crystallinity to emerge. This transition can take place in as few as 10 ALD cycles. On the other hand, if the relaxation is too slow or the growth rate is too large, the film reaches a metastable configuration composed of very small domains. These results open up the question of how to use ALD surface chemistry to promote crystallinity by enhancing such relaxation mechanisms. They can also explain some interesting phenomena observed in the ALD literature, such as explosive crystallization.

This research has been funded through Argonne's LDRD program.

4:45pm **AF2-MoA-14 What Is the Reactivity of a Precursor in ALD? - Simulation of Growth and Etch Rates***, **Simon D. Elliott**, A. Chew, Y. An,* Schrödinger, Inc.

In atomic level processing, the most important requirement is reactivity of a precursor towards deposition or etching of the target material; however, it is difficult to quantify reactivity. One possible experimental measure is the growth per cycle (ALD) or etch per cycle (ALE) under conditions where the chemistry is self-limiting. Experimentally measuring reactivity for all possible precursors and target materials is prohibitively expensive, necessitating alternative ways to explore the large design space.In this talk, we examine how to compute precursor reactivity with atomistic modeling.

We discuss long-standing models [1] that use density functional theory (DFT) to simulate ligand exchange in the precursor molecule itself as a measure of reactivity. Advantages of these models are conceptual simplicity, ease of computation and suitability for processing large sets of molecules [2]. Furthermore, these models can extend from oxides/nitrides to metals, approximate temperature effects and deliver formation energies.

However, more information about the multistep reaction mechanism is required to calculate the growth/etch rate of the process.We examine the thermodynamic basis that dictates how many reaction steps the precursor can undergo at the surface, i.e. the 'extent' of the reaction [3].The reaction extent can be converted into a growth/etch rate per cycle if additional information about ligand size and material density is calculated.We propose a high-throughput approach for computing surface reactions with DFT and hence quantifying the reaction extent and the growth per cycle.We then validate our approach against experimental data for commonly used precursors for the ALD of dielectrics.

Finally, we explore the capabilities of machine learning models (ML) to accurately predict the DFT reactivities using structure-property relationships. Since the computational time for running machine learning models is significantly lower than for DFT, an ML approach can enable thousands of ligands to be screened quickly.

These automated modeling approaches enable the quantification of precursor reactivity in terms of growth/etch rates, which will open new opportunities for *in silico* design and process understanding.

[1] P. Hirva et al., Surf. Sci. 220, 137–51 (1989); S. D. Elliott, Surf. Coat. Technol. 201, 9076–81 (2007); T. P. Holme et al., J. Phys. Chem. A 111, 8147–51 (2007); I. Kazadojev et al., Chem. Vap. Depos. 19, 117–124 (2013).

[2] RASIRC® ALD Oxide/Nitride Wizards™ https://www.rasirc.com/ald-oxide-wizard/ https://www.rasirc.com/ald-nitride-wizard/

[3] S. D. Elliott, Comput. Mater. Sci. 33, 20–5 (2005).

5:00pm **AF2-MoA-15 Random Sequential Adsorption and the Consequences for the Growth-Per-Cycle of Atomic Layer Deposition Processes***, **Ilker Tezsevin**, S. Deijkers, M. Merkx, E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) processes are known to deposit a sub-monolayer of material per cycle due to (*i*) steric hindrance effects and/or (*ii*) limited availability of surface sites.[1, 2] Another contributing factor, which has not been addressed in detail, is that molecules arrive one by one at the surface and adsorb at random surface sites, such that the saturation coverage of precursor ligands substantially deviates from closed packing. In this work, the effect of the random sequential adsorption (RSA) mechanism on the saturation of precursor adsorption and hence on the growth per cycle (GPC) of ALD processes is investigated. By systematically varying the precursor radius and the precursor binding sites in the RSA simulations, the surface densities of the adsorbed precursor molecules are modelled. It is found that the random sequential adsorption of the precursor molecules results in a 25% to 68% lower surface density than the (unrealistic) reference case of closed packing of ligands. Moreover, RSA simulations are also used to model the growth-per-cycle values based on the precursor shape and size. Using this RSA model for metallocene precursor adsorption, GPC values of Co, Os, and Ru ALD processes are calculated as 0.28, 0.38 and 0.37 Å/cycle, in agreement with the experimental findings with accuracy of ± 0.08 Å/cycle. [3-5] Therefore, this work clearly demonstrates the importance of the random sequential adsorption mechanism on the ALD growth.

[1] R.L. Puurunen, Chem. Vap. Depos. 9, 249 (2003).

[2] R.L. Puurunen, Appl. Surf. Sci. 245, 6 (2005).

[3] J. Hämäläinen, T. Sajavaara, E. Puukilainen, M. Ritala, and M. Leskelä, Chem. Mater. 24, 55 (2012).

[4] T. Aaltonen, A. Rahtu, M. Ritala, and M. Leskelä, Electrochem. Solid-State Lett. 6, (2003).

[5] J. Yoon, H.-B.-R. Lee, D. Kim, T. Cheon, S.-H. Kim, and H. Kim, J. Electrochem. Soc. 158, H1179 (2011).

5:15pm **AF2-MoA-16 Machine Learning Based Atomistic Modeling of ALD Processes***, J. Schneider, **Suresh Kondati Natarajan**, V. Arcisauskaite, U. Martinez,* Synopsys Denmark*; A. Blom,* Synopsys Inc.

Atomic layer deposition (ALD) of materials has been a key enabling technology for atomically fine-tuned manufacturing of semiconductor devices in the past two decades. As the future brings continued down-scaling of electronic devices, extreme fabrication limits require optimization of existing and development of new deposition setups for maximum process capability and yield, enabled by physical modeling with topography tools, such as Sentaurus Topography.

In this talk, we will show how machine learning (ML) based atomistic simulations of ALD processes can efficiently provide important parameters for topography simulations, which have been historically extracted from experiments. This multiscale modeling approach can be of particular importance when developing new deposition processes where experimental data are unavailable or expensive and time-consuming to obtain. We will demonstrate how to efficiently obtain ALD parameters such as sticking coefficient and maximum precursor coverage by simulating the $HfCl_4$ precursor pulse in the ALD of HfO_2.

ALD atomistic simulations can be computationally very demanding or even unmanageable if performed using *ab initio* density functional theory (DFT) molecular dynamics (MD), whereas computationally cheaper conventional Force Fields are often not available and require a long and error-prone process to be developed, as in the case for $HfCl_4$-HfO_2. This can be overcome by generating and using ML based interatomic potentials (MLIPs). In this work, we efficiently developed and used moment tensor potentials (MTPs), which provide high accuracy with lower computational cost when compared to other MLIPs [1,2]. MTP was trained using reference data from DFT simulations to reproduce *ab initio* quality potential energy surface of the $HfCl_4$-HfO_2 system. MD simulations with such trained MTPs give us DFT quality MD trajectories at a significantly (100x) reduced computational effort. Automated MTP training and MD simulations were performed using the QuantumATK software [3,4] developed by Synopsys.

MD simulations of $HfCl_4$ molecules impacting the HfO_2 (111) substrate reveal that Hf atoms bind to O atoms on the surface as expected, with binding energies being consistent with DFT results. Finally, we show that the sticking coefficient of the precursor decreases as its surface coverage increases and becomes 0 after attaining a maximum coverage at 0.3 monolayers.

[1] A. V. Shapeev, Mult. Model. Sim., 14, 1153 (2016).
[2] Y. Zuo et al., J. Phys. Chem. A, 124, 731 (2020).
[3] S. Smidstrup et al. , J. Phys.: Conden. Matter 32, 015901 (2019).
[4] QuantumATK version T-2022.03, Synopsys QuantumATK (https://www.synopsys.com/silicon/quantumatk.html)

5:30pm **AF2-MoA-17 Modelling Ruthenium Deposition in Atomic Layer Deposition of Ru-doped TaN***, **Rita Mullins**, M. Nolan,* Tyndall National Institute, Ireland

The downscaling of semiconductor devices has led to critical issues with the widely used Cu interconnect such as diffusion into the substrate dielectric layer. A Ru-doped TaN surface is a promising combined barrier and liner material that has the liner properties of Ru and barrier properties of TaN. Ru has good adhesion strength with Cu, high thermal stability and can promote direct electrodeposition of Cu. A previous first principles density functional theory study found that Ru doping of TaN produces nucleation sites for Cu growth and promotes formation of conducting Cu films.

Atomic layer deposition (ALD) allows the fabrication of ultra-thin films for a wide range of applications and offers excellent conformity and thickness control. ALD is a self-limiting film growing process distinguished by exposure to alternating precursors that are introduced sequentially. Similar to thermal ALD, plasma-enhanced ALD (PE-ALD) provides potential advantages such as improved film purity and the facility for deposition at reduced substrate temperatures. To avoid oxygen contamination in PE-ALD process for metals, non-oxidative reactants are chosen. Furthermore, PE-ALD of Ru using oxygen plasma can lead to lower growth or even the absence of growth due to oxygen plasma competitive etching of Ru. Replacing oxygen plasma with NH_3 plasma leads to the formation of smooth Ru films.

In this contribution, the chemistry of NH_x (x = 1,2) surface terminations of TaN and their reaction with Ru precursors is studied using first principles density functional theory (DFT) using the $RuCp_2$ precursor. NH_x-terminations of TaN for the post plasma surface are studied to test their coverage and stability. The TaN surface consists of 24 N (1 ML) and 24 Ta (1 ML) sites that could be H/H_2 and NH/NH_2 terminated respectively. Stable coverages of 1 ML H and 0.5 ML H/0.5 ML H_2 terminated were found for the 24 N sites. For the 24 Ta sites, stable coverages of 0.04 ML NH_2/0.46 ML NH and 0.67 ML NH_2 terminated were found. The adsorption of precursor $RuCp_2$ to the stable NH_x terminated TaN surfaces is then examined. The Cp ligands are lost through hydrogen transfer from the NH_x-terminated surface to the Cp ligand in this mechanism. No spontaneous hydrogen transfer was observed on any of the NH_x-terminated TaN upon adsorption of $RuCp_2$. Therefore the hydrogen transfer step must overcome activation barriers which are computed using the nudged elastic band method.

ALD Fundamentals
Room Van Eyck - Session AF3-MoA

Plasma Enhanced ALD

Moderators: Sumit Agarwal, Colorado School of Mines, Andreas Werbrouck, Ghent University, Belgium

1:30pm **AF3-MoA-1 Revisited Thermal and Plasma Enhanced Atomic Layer Deposition Processes of Metal Nitrides***, **Elisabeth Blanquet**,* SIMaP, CNRS , University Grenoble Alpes, France*; A. Mantoux,* SIMaP, University Grenoble Alpes, France*; F. Mercier,* SIMaP, CNRS, University Grenoble Alpes, France*; R. Boichot,* SIMAP, Grenoble-INP, University Grenoble Alpes, France*; I. Nuta,* SIMAP, CNRS, University Grenoble Alpes, France*; C. Jimenez,* LMGP, CNRS, University Grenoble Alpes, France **INVITED**

Metal nitrides films stand out as candidates for many strategic industrial applications as they exhibit superior functional properties such as mechanical, electrical and thermal properties. Complementary chemical vapor deposition techniques from High Temperature Chemical Vapor Deposition (HTCVD) to Thermal and Plasma Enhanced Atomic Layer Deposition (T-ALD and PEALD) have been investigated to fabricate metal nitrides thin films. Coupling or combining these techniques might open new opportunities. In each case, one of the major challenges is the synthesis of high quality, pure (with no oxygen contamination) material. Among ALD developments, efforts have been focused on the exploration of thermal stabilities of different precursor molecules, chemical reactions as well as growth processes sequences and conditions.

In this presentation, the examples of various metal nitride deposition process development with special focus on Aluminum nitride will be presented. AlN is a multifunctional material, which has been widely investigated for many potential applications in recent years, due to its high melting point, excellent thermal conductivity and good chemical stability and behavior towards oxidization and abrasion with respect to other nitrides. It is a semiconductor material with a wide bandgap, offering transparency even in the UV region. Moreover, its oxidation rate is low at temperatures below 1100°C. AlN films are attractive for applications in energy, aeronautics, electronic or optoelectronic devices. For instance, thin films are investigated in piezoelectric based applications, as passivating and protective coatings for metallic architectures, as AlN substrate in high power applications.

We report on the optimizing routes and strategies via coupling deposition processes to obtain the best film properties on various systems.

2:00pm **AF3-MoA-3 Plasma-Enhanced Low-Temperature ALD Process for Molybdenum Oxide Thin Films and Its Evaluation as Hydrogen Gas Sensors***, **Jan-Lucas Wree**, J. Klimars,* Ruhr University Bochum, Germany*; N. Saliha,* Heinrich-Heine University Düsseldorf, Germany*; D. Rogalla,* Ruhr University Bochum, Germany*; K. Schierbaum,* Heinrich-Heine University Düsseldorf, Germany*; A. Devi,* Ruhr University Bochum, Germany

The versatile properties of molybdenum oxide strongly depend on the structural features and in particular on its crystallinity, composition and morphology. This makes it an interesting material class for a variety of applications, i.e., (opto)electronics, (photo)catalysis and gas sensors. Moreover, the performance of these applications is significantly enhanced by the implementation of the active material in thin film form. Therefore, the development of atomic layer deposition (ALD) processes for the fabrication of nanostructured molybdenum oxide thin films has grown steadily in the recent years. As a consequence, the demand for suitable molybdenum precursors with improved physico-chemical properties is rising as the library for appropriate molybdenum precursors is rather small.

In this study, molybdenum oxide thin films were deposited using a new plasma-enhanced ALD (PEALD) process employing the molybdenum precursor $Mo[(N^tBu)_2(^tBu_2DAD)]$, recently developed in our group, and oxygen plasma. The process yielded a growth rate of 0.75 Å/cycle on Si(100), which is in the range of other PEALD processes reported for molybdenum oxide. Furthermore, the linear dependence of the thickness on the number of cycles was confirmed within a temperature window between 100°C and 240°C. X-ray diffraction (XRD) patterns show that on the lower end of the temperature window the films appear to be amorphous while crystallization starts at the higher end (240°C), yielding nanocrystalline β-MoO_3 thin films. Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA) and X-ray photoelectron spectroscopy (XPS) analyses revealed the formation of pure films, while SEM analysis showed the smooth morphology of the films with crystallite formation at higher deposition temperatures. Furthermore, sensor substrates were coated with molybdenum oxide to investigate the resistive hydrogen sensitivity of the thin films with respect to their morphology. This study demonstrates that the recently developed molybdenum precursor is suitable for the utilization in ALD applications. The resistive response of the deposited MoO_x thin films towards hydrogen gas reveals the potential of this material for thin film hydrogen gas sensors. Moreover, the overall quality of the films makes it also promising for implementation in other applications such as catalysis and optoelectronics.

2:15pm **AF3-MoA-4 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Crystalline Tin Disulfide Thin Films***, **Femi Mathew**, N. Poonkottil, R. Karuparambil Ramachandran, B. Zhao, Z. Hens, C. Detavernier, J. Dendooven,* Ghent University, Belgium

Among the layered metal dichalcogenide materials, semiconducting tin disulfide (SnS_2) is a potent candidate for photocatalysis, field-effect transistors, lithium-ion batteries, and gas sensing applications. Hence, there is a demand for a scalable technique to uniformly and conformally deposit SnS_2 thin films, preferably at low temperatures. Here, we present a plasma-enhanced atomic layer deposition (PE-ALD) technique to deposit crystalline SnS_2 using tetrakis(dimethylamino)tin (TDMASn) precursor and H_2S/Ar plasma at temperatures as low as 80°C.

TDMASn precursor was previously combined with H_2S to deposit tin sulfides via thermal ALD.[1] We employed H_2S plasma as the reactant inspired by previous reports demonstrating a significant effect of using plasma on the ALD growth characteristics and material properties.[2] The new PE-ALD process is self-limiting with a growth per cycle of 0.45-0.15 Å/cycle in a temperature range of 80 –180 °C. **(Fig. 1)** In contrast to the thermal ALD process which deposits amorphous SnS_2 thin films at 80°C and a mixture of SnS and SnS_2 phases at 180°C, crystalline SnS_2 thin films are deposited with the PE-ALD process in the temperature range of 80-180°C.**(Fig. 2)** Moreover, scanning electron microscopy analysis shows an evolution in thin-film morphology from grain-like structures with size in the range of 30-50 nm to out-of-plane oriented structures for SnS_2 deposited by the PE-ALD process at 80°C and 180°C, respectively. **(Fig. 3)** Optical transmission measurements detected an indirect bandgap in the range of 2.1-2.3eV in all the as-deposited SnS_2 thin films. **(Fig. 4)**

SnS_2 nanostructures with different morphologies have been previously investigated as anode materials in lithium-ion batteries to counter the problems of poor capacity retention associated with significant volume changes during cycling. Thus, we compared the electrochemical performance of SnS_2 thin films with three different morphologies as anode material in Lithium-ion batteries. The SnS_2 thin films with out-of-plane orientation structures exhibit better cycling stability with a capacity retention of 77% in contrast to the amorphous films which show 34% capacity retention after 100 cycles. **(Fig. 5)** We assume these out-of-plane orientation sites facilitate the diffusion of Li^+ ions thus limiting the pulverization and retaining the capacity.

9. Ham, G.; Shin, S.; Park, J.; Choi, H.; Kim, J.; Lee, Y.-A.; Seo, H.; Jeon, H., *ACS Applied Materials & Interfaces* **2013,***5* (18), 8889-8896.
10. Kuhs, J.; Dobbelaere, T.; Hens, Z.; Detavernier, C., *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2017,***35* (1), 01B111.

2:30pm **AF3-MoA-5 Leveraging Non-Saturated Oxidation Conditions in Plasma-Enhanced Atomic Layer Deposition for Tuning Functional Properties of CoO_x Catalyst Layers***, **Matthias Kuhl**, A. Henning, L. Haller, L. Wagner, C. Jiang, V. Streibel, I. Sharp, J. Eichhorn,* Technical University Munich, Germany

Electrocatalysts often suffer from poor stability under operating conditions due to (electro)chemical susceptibilities and/or poor adhesion to the support structure. For the realization of highly active and stable catalytic layers, catalyst-support integration and interface engineering play important roles. Interface engineering is also decisive for the integration of electrocatalysts with semiconductor light absorbers for solar-to-chemical energy conversion. For designing surfaces and interface layers of energy conversion devices, plasma-enhanced atomic layer deposition (PE-ALD) has emerged as a powerful method. These processes are typically developed with the aim of ensuring saturated surface oxidation reactions. However, exploring less aggressive process parameters opens new opportunities to precisely tailor the functional properties of active catalysts.

Here, we elucidated non-saturated oxidation of cobaltocene precursor by varying the plasma exposure time and plasma power to precisely control structural, mechanical, and optical properties of biphasic CoO_x thin films, thereby tailoring their catalytic activities and chemical stabilities.[1] Short pulses and low plasma power facilitate the formation of porous, unstable $Co(OH)_2$ layers with high electrochemical activity, while long pulses and high power yield stable, inactive Co_3O_4 layers. The best combination of stability and activity is observed for intermediate plasma exposure times leading to the formation of biphasic films consisting of a $Co(OH)_2$ surface and Co_3O_4 interface layer. The underlying reason for the formation of a porous $Co(OH)_2$ surface layers is the incomplete decomposition of the precursor at either short pulse durations or low plasma power, which also leads the incorporation of carbon impurities. The corresponding change in the chemical composition is reflected in the respective growth chemistry, which is characterized by reduced precursor adsorption and changes in the growth per cycle. The gained mechanistic insights were applied in a two-step growth process to intentionally engineer bilayer films consisting of a stable Co_3O_4 interface layer with a catalytic $Co(OH)_2$ surface exhibiting improved electrochemical performance without sacrificing chemical stability. This work highlights that unsaturated oxidation allows access to different material phases with tailored properties for engineering active catalysts and their interfaces.

[1]. Kuhl, M. *et al.* Designing multifunctional CoO_x layers for efficient and stable electrochemical energy conversion, *chemrxiv,* DOI:10.26434/chemrxiv-2022-23ck4 (2022).

2:45pm **AF3-MoA-6 Low-temperature HfO_2/SiO_2 Gate Stacked Film Grown by Neutral Beam Enhanced Atomic Layer Deposition***, **Daisuke Ohori**,* Tohoku University, Japan*; B. Ge,* Tohoku University, China*; Y. Chen,* National Yang Ming Chiao Tung University, Taiwan*; T. Ozaki,* Tohoku University, Japan*; K. Endo,* National Institute of Advanced Industrial Science and Technology, Japan*; Y. Li, J. Tarng,* National Yang Ming Chiao Tung University, Taiwan*; S. Samukawa,* Tohoku University, Japan

Fabrication of the high-quality insulating film with reduction of the thermal budget in a process is required for the metal-oxide-semiconductor (MOS) transistor fabrication with next-generation semiconductor material such as Ge and SiGe. Hafnium dioxide (HfO_2) is one of the promising candidate materials due to its high dielectric constant (high-k-value), thermal stability, and a high-quality interface between HfO_2 and SiO_2 for reduction of the gate leakage current with miniaturization of fabrication scale. To deposit a high-quality gate dielectric film on a high aspect ratio channel, the atomic layer deposition (ALD) method has been adopted with high coverage and thickness control. We have already successfully deposited high-quality SiO_2 films using defect-free neutral beam enhanced ALD (NBEALD) at low substrate temperature (30 ºC).In this study, we demonstrated a high-quality amorphous HfO_2/SiO_2/Si structure using low-temperature NBEALD.

The NBEALD was carried out in a large chamber for an 8-inch diameter. A precursor and carrier gases were Tetrakis(ethylmethylamino)hafnium (TEMAH) and Ar, respectively. The Si(100) substrate was cleaned with sulfuric acid hydrolysis (4 sulfuric acid:1 hydrogen peroxide) and 1% hydrofluoric acid, and then high-quality SiO_2 with a thickness of 1.6 nm could be initially formed after oxygen NB irradiation. After that, samples were grown under the following ALD growth conditions: gas supply (5 sec), purge (5 sec), oxygen NB irradiation (20 sec), oxygen gas purge (5 sec). Oxygen plasma for oxygen neutral beam was discharged at 1300 W, while the bias was not applied, and the stage temperature was at the room temperature, 30 ºC. Different thicknesses of HfO_2 films were deposited by using 50, 100, 150, and 200 cycles to evaluate the film characteristics. The surface roughness and crystalline state of deposited HfO_2 films were evaluated by atomic force microscopy (AFM) X-ray diffraction (XRD) measurements. The surface roughness increased from 0.3 to 1.1 nm with increasing growth cycle. XRD results were measured by the θ-2θ scan. Any typical diffraction peaks were not observed for all the samples. Therefore, we could successfully form high uniformity amorphous HfO_2/SiO_2 thin films even at low temperatures in an in-situ environment. It is suggested that this technique can contribute to the development of the MOS transistor fabrication process with a small heat budget in the future. Finally, we can discuss the electrical characteristics of nano-devices.

3:00pm **AF3-MoA-7 Effect of O_2 Plasma Exposure Time During Atomic Layer Deposition of Amorphous Gallium Oxide*, Florian Maudet,*** Helmholtz Zentrum Berlin, Germany*; H. Kröncke, S. Banerjee, K. Nair, C. Van Dijck,* Helmholtz-Zentrum Berlin, Germany*; S. Wiesner, J. Albert, V. Deshpande,* Helmholtz Zentrum Berlin, Germany*; C. Dubourdieu,* Helmholtz-Zentrum Berlin, Germany

Crystalline gallium oxide is an attractive ultrawide bandgapsemiconductor, which can be intentionally donor-doped with a large range of accessible electron carrier densities. Amorphous gallium oxide, on the other hand, has been comparatively less studied although it can demonstrate benefit for applications in photovoltaics and electronics. We have investigated the ability to self-doped amorphous gallium oxide thin films grown by atomic layer deposition (ALD) to tune their electrical properties from insulating to semiconducting.

Amorphous gallium oxide (GaOx) thin films were grown at 200 °C by plasma-enhanced ALD on (100) silicon substrates from trimethylgallium $Ga(CH_3)_3$ precursor and O_2 plasma. The effect of O_2 plasma exposure time during ALD cycles on the optical and electrical properties was investigated with the help of *in situ* and *ex situ* spectroscopic ellipsometry and electrical characterization. The O_2 plasma exposure time was varied from 1s up to 30 s. We will first discuss the regrowth of the interfacial SiO_x during the plasma-enhanced ALD. We will then present the effect of the O_2 plasma exposure time on the optical index, extinction coefficient, dielectric constant and leakage currents. An increase in the O_2 plasma exposure time during each ALD cycle up to 30 s - well beyond the time needed to reach a constant growth per cycle - leads to a drastic decrease in the leakage current density by more than five orders of magnitude (for 30 nm films). Interestingly, a concomitant increase in the dielectric constant is observed, reaching a value of $\varepsilon_r \sim 14.2$, larger than that of the single crystalline β-Ga_2O_3. At O_2 plasma exposure times below 8 s, the presence of oxygen vacancies is evidenced with an increasing amount as the exposure time decreases. Finally, we will discuss the information gained from the analyses of *in situ* spectroscopic ellipsometry in the very first stages of the growth (first 10 cycles). A method was developed to unambiguously determine the thickness and optical properties of the growing oxide. We will discuss the change in thickness as a function of time for each of the four steps of the ALD cycles. The change in optical properties, determined after each step within one cycle and for all cycles, give information on the evolution of the film until a “bulk-like” gallium oxide film is reached.

Our study highlights the crucial role of O_2 plasma exposure time during PEALD of amorphous gallium oxide films in the control and tuning of their electrical properties. The ability to self-doped this material can be used to design e.g. semiconducting a-GaO_x channel field-effect device.

ALD Fundamentals
Room Van Eyck - Session AF4-MoA
Surface Science

Moderators: Annelies Delabie, IMEC, Virginia Wheeler, U.S. Naval Research Laboratory

4:15pm **AF4-MoA-12 Thickness Matters: Sintering Inhibition of Pt Nanoparticle Catalysts via Sequential Control of MgO Overcoats*, Zhiwei Zhang*,** *M. Filez, M. Minjauw, J. Li, C. Detavernier, J. Dendooven,* Ghent University, Belgium

Overcoating of metal nanoparticles (NPs) to modulate the performance and thermal stability of catalysts has been proven as an effective method.[1] However, most studies focus on the catalytic effects that overcoats bring to the table, while researching their deposition processes is rare, but crucial to tailoring their properties. Here, atomic layer deposition (ALD) of magnesium oxide (MgO) overcoating on platinum (Pt) NPs is developed and investigated. The thickness of the MgO overcoat is precisely controlled by ALD. The prime function of the overcoat is to prevent rapid NP coarsening during the catalyst lifetime, here simulated by high-temperature annealing. During annealing, the NP properties are monitored in real-time by in-situ grazing incidence small angle X-ray scattering (GISAXS)[2,3].

$Mg(EtCp)_2$ and H_2O are used as Mg precursor and reactant of the MgO ALD process, respectively, while both 150 ℃ and 200 ℃ deposition temperatures were compared. The ALD process of MgO is initially more selective to Pt than to SiO_2 when using bare SiO_2 and sputtered Pt reference substrates. Via *ex-situ* XPS after MgO ALD on Pt NP-decorated SiO_2, the evolution of the relative Mg intensity as the function of the number of ALD cycles is shown (Figure 1). It is found that MgO shows a higher growth per cycle at 150 ℃ compared to 200 ℃, consistent with previous work. [4] In addition, during the first cycles, MgO mainly covers the Pt NPs, since the Pt signal decreases while the Si contribution remains constant. During the subsequent cycles, the Si intensity also decreases in XPS, suggesting MgO is now grown on the SiO_2.

In-situ GISAXS during annealing (from 25 ℃ to 800 ℃) is adopted to study the influence of MgO overcoating on the Pt NP coarsening behavior. A clear sintering delay is observed for both 150 ℃ and 200 ℃ sample sets with increasing number of MgO ALD cycles. However, the very first cycles (e.g. 1-3) do not contribute too much to the anti-sintering behavior which suggests that decorating the Pt NPs with MgO alone is insufficient for catalyst protection (Figure 2a). The sintering onset temperature is significantly delayed as the number of MgO cycles increases beyond the first cycles, which indicates the NPs thermal stability is mainly enhanced once MgO coats the SiO_2 substrate. This trend is generally applicable for both deposition temperatures, clearly showing a critical amount of MgO is necessary to prevent catalyst coarsening (Figure 2b).

[1] Brandon. J. O’Neill, et al. ACS Catal. 2015, 5, 1804.

[2] Jolien. D, et al. Nat. Comm. 2017, 8, 1074.

[3] Eduardo. S, et al. Nanoscale 2020, 12, 11684.

[4] Burton. B. B, et al. J. Phys. Chem. C 2009, 113, 1939.

4:30pm **AF4-MoA-13 Route to Low Temperature Area-Selective Atomic Layer Deposition of Ni*, Himamshu Nallan,*** *X. Yang, J. Ekerdt,* The University of Texas at Austin

Nickel and nickel oxide are utilized within various device heterostructures for chemical sensing, solar cells, batteries, etc. Recently, the increasing popularity of flexible electronics to enable ubiquitous as well as large-area consumer electronics such as next-generation displays and sensors has driven interest in the development of low temperature fabrication processes for the integration of inorganic devices with polymeric substrates. Given the thermal constraints of the substrate as well as the desire for high-throughput and large-area scalability, ALD is a suitable fabrication method. Here we investigate the low temperature area-selective ALD (AS-ALD) of Ni by reduction of preformed NiO. Area-selective deposition of NiO is performed at 100 °C using bis(N,N'-di-t-butylacetamidinato)nickel(II) and water on SiO_2. NiO grows two dimensionally and without nucleation delay on oxide substrates; pre-patterned sp^3 carbon-rich resists inhibit the nucleation of NiO. In this way, first, carbon-free NiO may be patterned. Subsequent thermal reduction of NiO to Ni was investigated using H_2 (50 mTorr) and thermally-generated H atoms (2.5×10^{-6} Torr chamber pressure). Due to relatively high surface energy, Ni films undergo dewetting at elevated temperatures when solid-state transport is enabled. Reduction of NiO to Ni is demonstrated at 100 °C and below using atomic hydrogen. *In-situ* x-ray photoelectron spectroscopy is used to determine oxidation state and *ex-situ* x-ray reflectivity and atomic force microscopy are used to probe the film thickness and surface morphology, respectively.

4:45pm **AF4-MoA-14 Hydrogen Plasma-Assisted Atomic Layer Deposition of sub-Nanometer AlO_x for Low-Impedance Contacts to GaN*, Maximilian Christis,*** *A. Henning,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany*; J. Bartl,* Walter Schottky Institute, Physics Department, and WACKER-Chair for Macromolecular Chemistry, Department of Chemistry, Technical University of Munich, Germany*; A. Zeidler,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany*; B. Rieger,* Department of Chemistry, WACKER-Chair for Macromolecular Chemistry, Technical University of Munich, Germany*; M. Stutzmann, I. Sharp,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany

To achieve low-impedance tunneling contacts, wet-chemical pretreatments are usually required to prepare the semiconductor surface by removing the native oxide layer. Following this step, it is critical to produce continuous sub-nanometer thin coatings, which are challenging to achieve by atomic layer deposition (ALD) due to surface inhomogeneities and precursor steric interactions that result in island growth during film nucleation. Here, we report a novel atomic layer deposition process that alleviates the need for wet chemical etching and achieves full encapsulation of *c*-plane gallium nitride (GaN) with an ultimately thin (~3 Å) AlO_x monolayer, which is enabled by the partial transformation of the GaN surface oxide into AlO_x. This is accomplished using repeated cycles of trimethyl aluminum (TMA) and hydrogen (H_2) plasma exposure in a commercial plasma-enhanced ALD reactor (Ultratech Fiji G2). The introduction of ultra-thin AlO_x significantly modifies the physical and chemical properties of the surface, decreasing the work function and introducing new chemical reactivity [1][2]. Electrochemical cyclic voltammetry (CV) measurements show that the ultra-thin film poses a significantly smaller tunneling barrier to charge carrier transport than the thinnest homogenous AlO_x coatings achievable with the conventional TMA/H_2O ALD process.

Depending on the H_2 plasma parameters, the GaO_x surface oxide on GaN can be fully converted into AlO_x, reducing surface band bending and Schottky barrier height at the n-GaN/metal interface. Titanium-contacted n-doped GaN with an ultra-thin interfacial AlO_x layer shows a low contact resistance value and Ohmic behavior even before annealing. Unlike conventional Ohmic contacts to n-type GaN, this annealing-free contact allows for the integration of GaN with other semiconductors such as Si, for which the thermal budget is relatively low (≤ 400 °C). Given the high reactivity of TMA with surface oxides, the presented monolayer AlO_x deposition scheme likely can be extended to other dielectrics and III-V-based semiconductors, with significant relevance to applications in optoelectronics, chemical sensing, and (photo)electrocatalysis.

[1] A. Henning, J. D. Bartl, A. Zeidler, S. Qian, O. Bienek, C.-M. Jiang, C. Paulus, B. Rieger, M. Stutzmann, I. D. Sharp, *Adv. Funct. Mater.* 2021, 31, (33), 2101441.

[2] J. D. Bartl, C. Thomas, A. Henning, M. F. Ober, G. Savasci, B. Yazdanshenas, P. S. Deimel, E. Magnano, F. Bondino, P. Zeller, L. Gregoratti, M. Amati, C. Paulus, F. Allegretti, A. Cattani-Scholz, J. V. Barth, C. Ochsenfeld, B. Nickel, I. D. Sharp, M. Stutzmann, B. Rieger, *J. Am. Chem. Soc.* 2021, 143, (46), 19505–19516.

5:00pm **AF4-MoA-15 Tunable Ti^{3+}-Mediated Charge Carrier Dynamics of Atomic Layer Deposition Grown Amorphous TiO_2**, ***Jesse Saari***, *H. Ali-Löytty,* Surface Science Group, Tampere University, Finland*; M. Kauppinen,* Competence Centre for Catalysis and Department of Physics, Chalmers University of Technology, Sweden*; M. Hannula,* Surface Science Group, Tampere University, Finland*; R. Khan,* Photonic Compounds and Nanomaterials group, Tampere University, Finland*; K. Lahtonen,* Faculty of Engineering and Natural Sciences, Tampere University, Finland*; L. Palmolahti,* Surface Science Group, Tampere University, Finland*; A. Tukiainen,* Faculty of Engineering and Natural Sciences, Tampere University, Finland*; H. Grönbeck,* Competence Centre for Catalysis and Department of Physics, Chalmers University of Technology, Sweden*; N. Tkachenko,* Photonic Compounds and Nanomaterials group, Tampere University, Finland*; M. Valden,* Surface Science Group, Tampere University, Finland

Amorphous titania (am.-TiO_2) has gained broad interest in the field of photocatalysis due to its exceptional disorder-mediated optical and electrical properties compared to crystalline TiO_2 [1–3]. For instance, Ti^{3+} defects within am-TiO_2 can enable essential charge carrier transport through a protective am-TiO_2 photoelectrode coating in photoelectrochemical (PEC) cells [1], and Ti^{3+}-mediated visible light active amorphous “black” titania is regarded as a potential material for photocatalytic applications [2]. Atomic layer deposition (ALD) allows for tuning the defect composition and structure of am.-TiO_2 thin films via precursor choices and process parameters. Recent progress in computational analysis of am.-TiO_2 [3] has provided means to accurately correlate experimental insights with theoretical models, which can be utilized to tailor am.-TiO_2 coatings with desired properties.

This work examines how intrinsic titanium and nitrogen defects in am.-TiO_2 can be tailored in a controlled and elegant manner via tuning the ALD growth temperature between 100–200 °C when using tetrakis(dimethylamido)titanium(IV) (TDMAT) and water (H_2O) as the precursors. X-ray photoelectron spectroscopy (XPS) analysis and density functional theory (DFT) calculations allowed us to identify structural disorder-induced penta- and heptacoordinated Ti^{4+} ions ($Ti_{5/7c}^{4+}$), which are interrelated to the formation of Ti^{3+} defects in am.-TiO_2 without releasing oxygen, i.e., simultaneous formation of oxygen vacancies and interstitial peroxo species leading to defective but stoichiometric am.-TiO_2. When changing the ALD growth temperature from 100 °C to 200 °C, increase in Ti^{3+} concentration results in “black” TiO_2 and electrical conductivity via polaron hopping mechanism. Furthermore, transient absorption spectroscopy (TAS) shows that the high concentration of Ti^{3+} defects in “black” TiO_2 increases the carrier lifetime to the nanosecond time domain comparable to crystalline low-defect TiO_2. These insights into the formation of Ti^{3+} defects in am.-TiO_2 and into tuning the charge transport properties of ALD grown am.-TiO_2 are beneficial in wide range of applications, such as protective photoelectrode coatings.

[1] P. Nunez, M. H. Richter, B. D. Piercy, C. W. Roske, M. Cabán-Acevedo, M. D. Losego, S. J. Konezny, D. J. Fermin, S. Hu, B. S. Brunschwig, N. S. Lewis, *J. Phys. Chem. C* **123** (33), 20116–20129 (2019).

[2] V.-A. Glezakou, R. Rousseau, *Nat. Mater.* **17** (10), 856–857 (2018).

[3] D. Mora-Fonz, M. Kaviani, A. L. Shluger, *Phys. Rev. B* **102** (5), 054205 (2020).

5:15pm **AF4-MoA-16 Temperature-Time-Thickness (Ttt) Topography Maps: A Parameter Space Visualization Approach for ALD Processes**, ***Parag Banerjee***, *N. Berriel, U. Kumar, C. Feit,* University of Central Florida*; A. Arunachalam,* University of Texas at Dallas*; K. Basu,* University of Texas at Dallas, USA*; S. Seal,* University of Central Florida

ALD processes are developed and optimized in a limited, 1D process parameter space. The establishment of a steady growth rate within a temperature ‘window’ occurs via a series of experiments, where the independent variable – temperature is varied while holding pulse time constant. Similarly, saturation curves are obtained by varying the independent variable - pulse time (*i.e.,* dose) of the precursors while holding temperature constant. The demonstration of i) a viable temperature window and, ii) saturation curves constitute the establishment of an ALD process. The limitation of these approaches is that process parameter interdependencies cannot be studied. Thus, it is not possible to study the impact of temperature on dose saturation and *vice versa*. We hypothesize that these interdependencies hold a rich source of undiscovered ALD operation regimes and can lead to efficient process development, robust control and optimization outcomes.

In this talk, we present temperature-time-thickness (TTT) topography maps of ALD processes generated using *in situ* spectroscopic ellipsometry. Based on the methodology shown by our group recently[1], we demonstrate TTTof several ALD processes including, Al_2O_3, ZnO, CeO_2 and TiO_2 and plasma enhanced ALD (PEALD) of TiO_2. The visualization of these processes in 3D is through a combination of temperature and dose times for thermal ALD processes and as temperature and plasma power for PEALD processes. Saturation regimes of growth rates are observed as 2D surfaces i.e., plateaus and valleys. Precursor adsorption kinetics and thermodynamic parameters are extracted assuming ideal Langmuir adsorption behavior. We propose that a comprehensive database of TTT topographic maps can be used for deeper understanding of processes and to enable robust process control and optimization outcomes.

References:

[1]U. Kumar *et al.*, "In situ ellipsometry aided rapid ALD process development and parameter space visualization of cerium oxide nanofilms," *J. Vac. Sci. Technol., A,* vol. 39, no. 6, 2021, doi: 10.1116/6.0001329.

5:30pm **AF4-MoA-17 *in situ* TEM Study to Unravel Dynamic Processes during the Synthesis of Ultrathin Crystalline ALD Nanotubes**, ***Lilian Vogl***, *P. Schweizer, L. Pethö, A. Sharma,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; E. Spiecker,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; J. Michler, I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

By using Atomic Layer Deposition (ALD), amorphous nanotubes can be successfully made of various metal oxides. However, the creation of **high quality crystalline nanotubes** for example made of sapphire is still a challenging process. To control the crystal structure of ALD based systems, it is indispensable to use microscopy techniques to understand the dynamic processes occurring on atomic scale. In this study, we present a universal approach to create **ultrathin crystalline** ALD nanotubes by using a comprehensive annealing process of specific core-shell nanowires. In combination with correlative *ex situ* observations, ***in situ* TEM** heating experiments unravel diffusion processes going on at small scales and give insights about temperature induced changes of the metal-ALD interface. Heating core-shell nanowires (e.g. Cu/ALD-Al_2O_3) at temperatures below 1000°C lead to the creation of hollowed amorphous ALD nanotubes. While the ALD framework is stable, the **diffusion of the metallic core material** is activated. The conformal ALD shell acts as barrier for the material diffusion and forces the core to continuous diffusion towards the cracked end of the nanowire (Figure 1a). As a first heat-induced phenomenon we observe the creation of voids, which is caused by vacancy agglomeration. Vacancies are induced during the growth process of the metal nanowires at elevated temperatures. However, heating for longer time, the voids and therefore the vacancies get compensated. The thermal activation for the material diffusion can be observed *in situ* with **high resolution** imaging (figure 1b).

The energy barrier to release an atom from the bonded state can be overcome by heat treatment and the released atoms diffuse within the inner cavity of the ALD tube. The time for releasing atoms scales directly with the temperature (figure 1c). By holding the temperature, no core material is left within the ALD framework and an amorphous nanotube is created. The nanotubes have a **high aspect- ratio** with lengths up to 40 µm and a wall thickness of 4 nm. At temperatures above 1000°C, a **phase transition** is induced and a crystalline dense microstructure (κ-Al_2O_3) is achieved (figure 1d).
This type of ultrathin nanotubes shows promising optical and mechanical properties and are the ideal candidate for further functionalization processes.

Atomic Layer Etching
Room Baekeland - Session ALE1-MoA
Thermal and/or Isotropic ALE II

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Adrie Mackus, Eindhoven University, Netherlands

1:30pm **ALE1-MoA-1 Chlorination and Ligand Addition for Thermal ALE of Metals***, **Jessica Murdzek**,* University of Colorado Boulder*; A. Lii-Rosales,* Lam Research Corp*; S. George,* University of Colorado Boulder **INVITED**

Thermal atomic layer etching (ALE) is defined by sequential surface modification and volatile release reactions. Thermal ALE of metals is particularly challenging because the oxidation state of the metal must be changed to match the oxidation state of the volatile metal etch product. After changing the oxidation state, the metal then needs to form a stable and volatile complex. In this work, Ni and Co ALE are developed by oxidizing the metal via chlorination using SO_2Cl_2. Subsequently, the metal is etched by addition of an L ligand to the metal center to create a stable, volatile etch product, MCl_xL_y (Figure 1). The L ligands explored in this work were PMe_3 and tetramethylethylenediamine (TMEDA).

The chlorination and ligand-addition approach for metal ALE is based on the Covalent Bond Classification (CBC) method. X ligands are one-electron donors like Cl and other halogens. L ligands are two-electron donors like PMe_3. TMEDA is a bidentate ligand.One TMEDA ligand acts as two L ligands since TMEDA binds to the metal center through the lone electron pairs on the two nitrogen groups.According to the CBC method, nickel complexes typically have NiX_2L_3 or NiX_2L_2 configurations.Likewise, cobalt complexes are typically found in the CoX_2L_4, CoX_2L_2, or CoX_3L_3 configurations. The goal for Ni or Co ALE is to create these volatile metal compounds using sequential SO_2Cl_2 and L ligand surface reactions.

Both Ni and Co ALE have been studied with in situ quartz crystal microbalance (QCM) and X-ray reflectivity (XRR) to determine etch rate.Quadrupole mass spectrometry (QMS) was also employed to determine the volatile metal-containing etch species. Using SO_2Cl_2 and PMe_3, Ni etch rates varied from 0.1-3 Å/cycle at temperatures from 75-200 °C.QMS measurements also identified $NiCl_2(PMe_3)_2$ (NiX_2L_2) as the stable volatile etch product.Cobalt ALE using SO_2Cl_2 and TMEDA displayed etch rates from 1-12 Å/cycle at temperatures from 175-300 °C (Figure 2). QMS measurements also detected $CoCl_2$(TMEDA) (CoX_2L_2) as the stable volatile etch product.In addition, cobalt can be etched using SO_2Cl_2 and PMe_3 from 70-200 °C, with etch rates between 2-4 Å/cycle. These two Co ALE pathways are complementary with TMEDA useful at higher temperatures and PMe_3 useful at lower temperatures.

Many other X and L ligands could define additional halogenation and ligand-addition reactions.Using the CBC method as a guide, this strategy should lead to the development of various other metal ALE processes.

2:00pm **ALE1-MoA-3 Thermal ALE of Molybdenum via Low Temperature Oxidation in Ozone and Wet Chemical Oxide Dissolution***, **Antoine Pacco,*** IMEC, Belgium*; N. Teppei, S. Iwahata, A. Iwasaki,* SCREEN, Japan*; E. Altamirano Sanchzez,* IMEC, Belgium

Over the last decade, isotropic metal recess has received increased attention due to its relevance for both logic and memory applications. Controllable partial recess of metal requires a high level of accuracy, uniformity, and selectivity. In this work, we present atomic layer etching (ALE) of Mo for its application for Mo recess in buried power rail (BPR) [1] and 3D-NAND structures. Given its improved conductivity at sub 20 nm dimensions, Mo could be a possible candidate to replace W [2].

ALE of Mo thin films was achieved using a sequential oxidation in ozone gas followed by the removal of the molybdenum oxide by simple wet chemical etching. Oxidation in ozone gas has a lower activation energy than in oxygen, thereby effectively reducing the temperature budget of the etching process. We found that the molybdenum oxide formed during oxidation was MoO_3. This Mo (VI) oxide is easier to dissolve in aqueous alkaline solutions than WO_3 which has very low solubility in aqueous solutions [3] and requires more complex removal mechanisms [4-5]. Finally, the underlying Mo metal was unaffected in the aqueous alkaline solutions used allowing for a *selective* removal of MoO_3 as required by an ALE method.

Recess of blanket films as well as patterned samples was studied using this cyclic process and the etch per cycle (EPC) was increased by increasing the oxidation temperature. We were able to tune the EPC between 2 and 6 nm by increasing the substrate temperatures from 180 to 290 ºC. No significant differences in EPC were observed between the recess of Mo metal deposited by either plasma vapor deposition (PVD) or atomic layer deposition (ALD). The effect of an annealing step on recess amount was also investigated. Ultimately, roughening of the surface, a typical unwanted effect from conventional *continuous* wet etching of polycrystalline materials [6], was mitigated by this method.

We found that the thermal-wet ALE presented here is capable of recessing Mo isotropically and selectively towards a broad range of materials (Si, SiO_2, SiN, Al_2O_3, ...). Therefore, applications such as next-generation interconnects, BPR and 3D-NAND memory devices could benefit from this cyclic recess etch method.

[1] A. Gupta et al., Buried Power Rail Metal exploration towards the 1 nm Node, IEDM 2021

[2] D. Gall, J. Appl. Phys. 127, 050901, 2020.

[3] M. Anik and T. Cansizoglu, J. Appl. Electrochem. 36, 603–608, 2006.

[4] W. Xie and G. N. Parsons, J. Vac. Sci. Technol. A 38, 022605, 2020.

[5] N. R. Johnson and S. M. George, ACS Appl. Mater. Interfaces, 9, 34435−34447, 2017.

[6] A. Pacco, Y. Akanishi, Q. T. Le, Solid State Phenomena 314, 295-301, 2021.

2:15pm **ALE1-MoA-4 Selective Thermal Atomic Layer Etching of CoFeB Over MgO by Sequential Exposure to Chlorine and Diketone***, M. Konh, **Andrew V. Teplyakov,*** University of Delaware

Thermal atomic layer etching (ALE) is one of the most promising methods to have precise control of the thin film thickness is required for fabrication of microelectronic devices. CoFeB alloy films are commonly used as ferromagnetic layers in magnetic tunnel junction for integrated memory devices, where they are usually separated by an insulating barrier layer such as MgO. It is important to have a method that can selectively reduce the thickness of CoFeB alloy thin film without affecting MgO layer. Here, selective thermal atomic layer etching of CoFeB alloy thin film using sequential exposure to chlorine and acetylacetone (acacH) is investigated. During the ALE process the concentration of each element in the alloy remains constant according to the X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) is used to indicate the surface morphology preservation after the ALE process. The changes in thickness following thermal ALE on the patterned samples are recorded by AFM to deduce the etch rate, and to evaluate the ALE process on MgO patterns deposited on top of the CoFeB alloy films. To uncover the molecular mechanism of the ALE process, temperature programmed desorption (TPD) experiments are performed to detect possible key desorbing fragments.

2:30pm **ALE1-MoA-5 Ligand-Exchange and Etching Reactions between Metal Fluorides and Silane Precursors Containing Different Ligands***, A. Lii-Rosales, V. Johnson, A. Cavanagh,* University of Colorado Boulder*; A. Fischer, T. Lill,* Lam Research Corporation*; S. Sharma, **Steven George,*** University of Colorado Boulder

Metal fluorides can be spontaneously etched by ligand-exchange reactions. During these reactions, the exchange of ligands between the incoming precursor and the metal fluoride leads to the volatilization of the metal fluoride. These ligand-exchange reactions are important in many thermal atomic layer etching (ALE) processes. To test the effectiveness of different ligands for ligand exchange, the spontaneous etching of metal fluorides by silane precursors containing different ligands was investigated using *in situ* quadrupole mass spectrometry (QMS). The metal fluorides were GaF_3, InF_3, ZnF_2, ZrF_4, HfF_4, and SnF_4. The silane precursors were $SiCl_4$, $SiCl_2(CH_3)_2$, $SiCl(CH_3)_2H$, and $Si(CH_3)_4$. These silane precursors provide Cl, CH_3 or H ligands for the ligand-exchange reaction.

The QMS results showed that F/Cl ligand exchange was observed for all the metal fluorides with the chlorine-containing silane precursors. In addition, all the volatile metal etch products were metal chlorides, namely $GaCl_3$, $InCl_3$, $ZnCl_2$, $ZrCl_4$, $HfCl_4$, and $SnCl_4$. Results for $SiCl_2(CH_3)_2$ on GaF_3 are shown in Figure 1. No metal methyl complexes were detected as volatile metal etch products indicating no F/CH_3 exchange. For $SiCl(CH_3)_2H$ as the silane precursor, the observation of $SiF_2(CH_3)_2$ indicated that F/H exchange is also possible in addition to F/Cl exchange. For the various metal fluorides, the dominance of F/Cl exchange led to nearly equivalent onset temperatures for ligand exchange and for etching to yield metal chlorides as displayed in Figure 2.

Thermochemical calculations of the ligand-exchange reactions verified the formation of metal chlorides. All F/Cl exchanges were thermodynamically favorable as demonstrated by the negative changes in Gibbs free energy (ΔG). These experimental and theoretical results provide guidelines for designing thermal ALE processes. After the fluorination reaction to produce metal fluorides during thermal ALE, ligand-exchange reactions using Cl-containing silane precursors should be effective for etching if the metal fluoride has corresponding volatile and stable metal chlorides.

2:45pm **ALE1-MoA-6 Thermal Atomic Layer Etching of Zinc Sulfide (ZnS) Using Sequential Al(CH_3)$_3$ and HF Exposures***, **Taewook Nam**, J. Partridge, J. Murdzek, S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) processes have been developed from many materials including various oxides, nitrides and metals. This study introduces the thermal ALE of a sulfide material - zinc sulfide (ZnS). ZnS thermal ALE was demonstrated using trimethylaluminum ($Al(CH_3)_3$, TMA) and hydrogen fluoride (HF) as the reactants at temperatures from 225 to 300°C. The ALE was performed on ZnS atomic layer deposition (ALD) films that were deposited using diethylzinc ($Zn(C_2H_5)_2$, DEZ) and hydrogen sulfide (H_2S) as the precursors on p-type Si wafers at growth temperatures from 100 to 300°C. The etch rates were determined by monitoring the thickness of the ZnS ALD films using in-situ spectroscopic ellipsometry. Quadruple mass spectroscopy (QMS) was also used to detect the volatile etch products during ZnS thermal ALE to determine the ALE mechanism.

For the ZnS ALD films grown at 100°C, the etch rate varied from 1.4 Å/cycle at 225°C to 2.2 Å/cycle at 300°C. For the ZnS ALD films grown at 300°C, the etch rate was slightly lower and varied from 0.8 Å/cycle at 225 °C to 1.9 Å/cycle at 300°C. The ZnS ALD films grown at 300°C may have slightly higher densities that slow the etch rate. The ZnS ALD films were amorphous according to X-ray diffraction analysis. However, for the ZnS ALD films grown at 300°C, small islands remained on the surface after most of the ZnS ALD film was etched away. After the ZnS thermal ALE, these islands were confirmed as crystalline ZnS particles by XRD.

QMS analysis of the volatile etch products resulting from the sequential $Al(CH_3)_3$ and HF exposures revealed evidence for a conversion mechanism for ZnS thermal ALE as shown in Figure 1. During this conversion mechanism, $Al(CH_3)_3$ converts the top of the ZnS film to an Al_2S_3 surface layer and releases $Zn(CH_3)_2$ as the volatile product. Subsequently, HF fluorinates the Al_2S_3 layer to AlF_3 and releases H_2S as the volatile product. Then $Al(CH_3)_3$ removes the AlF_3 layer by ligand-exchange and also converts more ZnS to Al_2S_3. These reactions release various $AlF(CH_3)_2$ dimers and trimers from ligand-exchange and $Zn(CH_3)_2$ from the conversion. The volatile products measured by QMS during several sequential $Al(CH_3)_3$ and HF exposures are displayed in Figure 2.

3:00pm **ALE1-MoA-7 Requirements Beyond Etch Per Cycle for Thermal ALE in Semiconductor Manufacturing***, **Martin McBriarty**,* EMD Electronics

Isotropic ALE is poised to enter high volume manufacturing (HVM) of semiconductor devices within this decade. Several new process steps enabling more complex logic and memory architectures will incorporate ALE chemistries derived from fundamental research in academic and industrial R&D labs. The rigorous requirements of HVM introduce significant challenges for ALE integration, such as high selectivity, good process control in high aspect ratio features, and extremely low levels of contaminants and residues. Safety and sustainability are also key concerns, as ALE reagents and byproducts are often corrosive, toxic, or have high global warming potential. The choice of candidate chemistries and types of laboratory experiments at the early stages of ALE research can help identify processes which can be more seamlessly integrated into HVM. This presentation aims to clarify some of the semiconductor industry's pressing ALE needs beyond a good etch per cycle, with recommendations for how researchers can strengthen the impact of ALE experiments.

Atomic Layer Etching
Room Baekeland - Session ALE2-MoA

Plasma and/or Anisotropic ALE I

Moderators: Rémi Dussart, GREMI CNRS/Université d'Orléans, Geun Young Yeom, Sungkyunkwan University

4:00pm **ALE2-MoA-11 From Barrel to ALE: A Lifetime in Etch/A Material and System Design Perspective***, **Mike Cooke**,* Oxford Instruments , UK **INVITED**

Plasma etching has accompanied advances in lithography for decades, both necessary to enable higher component density in semiconductor device manufacture. A low-pressure glow discharge can provide both chemically active radicals and directional energetic ion bombardment to a surface, driving chemistry which would otherwise require high temperatures. We will describe the principal formats of plasma etch tool, and their merits for delivering atomic layer etching.

Plasma etching equipment of all formats share some common concerns: avoiding etching the chamber or contaminating the wafer; suppression of unwanted parasitic plasmas; maintaining cleanliness; delivering a uniform process across the substrate and reliably from substrate to substrate; and safe operation. The talk will comment on lessons learned in working with plasma tools for more than 40 years, and on the prospects for evolution of the techniques.

4:30pm **ALE2-MoA-13 Understanding the Self-limiting Behavior in Atomic Layer Etched HfO_2***, **Souvik Kundu**, T. Schram, F. Lazzarino, J. de Marneffe, P. Bezard, S. Decoster, I. Asselberghs,* IMEC, Belgium

For future generation transistor applications, two-dimensional (2D) channel materials have received significant research attention due to their favorable electronic properties. In aggressively scaled devices, selectively removing the top high-k layer from the 2D channel material is not possible by the conventional continuous plasma etching (CE) mainly due to poor etch selectivity between 2D and high-k materials, which leads to unwanted roughness and snap the channel layer below. In this regard, an alternative etching technique is required where the process variability can be controlled precisely, and the preferred layer can be removed using self-limiting reactions without punching through the layer below. The atomic layer etching (ALE) of HfO_2 with BCl_3/Cl_2 radical adsorption followed by low energy Ar+ desorption was investigated to soft-land on its underneath 2D material for Source/Drain *top contacts* formation. Since low ion energies are indispensable to minimize the plasma damage on 2D material, synchronously pulsed (SP) ALE was adopted where the plasma and bias powers were varied synchronously with a 30% duty cycle. The adsorption and desorption times were identified and an ALE window with 0.16 nm etch rate per cycle (EPC), low surface roughness (post-etch), and more than 90% synergy were obtained. Efforts were consecrated to understand the ALE mechanism and the effects of plasma power, bias power, and gas ratio on EPC, and synergy were further studied to understand their roles on ALE window. X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), and atomic force microscope (AFM) were employed to characterize the post-etch HfO_2 surface and interfaces. To realize the efficacy of SP ALE, 10nm HfO_2 was etched from the *10 nm HfO_2/capped seed layer/3mono-layers WS_2/2 µm SiO_2/Si* stacks, where the WS_2 layer is exposed and the signature of non-etched WS_2 layer was confirmed by the results obtained from Raman spectroscopy, XPS, and AFM. In contrast to SP ALE, when a CE process is concerned, it was ascertained that the WS_2 layer is completely ruptured during the HfO_2 etch and eventually lands on the SiO_2 layer below. The challenges of SP ALE and transferring the process on patterned wafers will also be discussed.

4:45pm **ALE2-MoA-14 Area-Selective Atomic Layer Etching of SiO_2 Using Silane Coupling Agent***, A. Osonio, **Takayoshi Tsutsumi**,* Nagoya University, Japan*; B. Mukherjee, R. Borude,* ASM International, Netherlands*; N. Kobayashi, M. Hori,* Nagoya University, Japan

An inherently area-selective atomic layer etching (ALE) process for silicon dioxide (SiO_2) over silicon nitride (SiN) is demonstrated in this study with the use of 1H, 1H, 2H, 2H perfluorooctyltrichlorosilane (POCS), a silane coupling agent. The area-selective adsorption of the chosen silane precursor is leveraged to achieve a substrate-dependent selectivity without the need for surface inhibitors at low substrate temperature (50ºC). A 100 MHz CCP plasma was used for the PE-ALE process. POCS was introduced in gas phase to the vacuum chamber, where the substrate and blanket samples were heated to 50ºC. Low energy Ar^+ bombardment without a bias power followed to remove the modified layer. The changes on the samples' thickness were monitored real-time using *in-situ* spectroscopic ellipsometry (SE) while the changes in the surface functional groups were investigated using *in-situ* FTIR spectroscopy.

Using *in-situ* SE, the area-selective chemisorption of the POCS on SiO_2 over SiN was confirmed from the increase in thickness after dosing which, at the same time, exhibits self-limiting characteristics. *In-situ* FTIR studies confirmed the functionalization of SiO_2 with the CF_2 and CF_3 functional groups and the simultaneous removal of the free OH on the surface during the modification step. After the Ar plasma exposure for the etching step, the removal of the CF_x bonds and the increase in the absorbance of the free -OH peak were found, related to the consumption of the modified layer. Overall, the work shows an alternative course to realize an ideal ALE process that has both self-limiting modification and etching steps. It attempts to address the challenges of stringent parametric control on existing area-selective ALE processes for SiO_2 using other fluorocarbon chemistries.

5:00pm **ALE2-MoA-15 Improving SiO_2 toSiN_x ALE Selectivity with Surface Pre-functionalization for SiO_2/SiN_x Stacks***, **Xue Wang**,* Colorado School of MInes*; R. Gasvoda, P. Kumar, E. Hudson,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

The downscaling of semiconductor devices to sub-7nm generation will require increasingly high etching selectivity with atomic-scale control over the etch profiles in high aspect ratio device structures. Plasma-assisted atomic layer etching (ALE) is a promising technique to tackle these challenges. We previously demonstrated that in ALE, selectivity for SiO_2 over SiN_x can be achieved through the selective pre-functionalization of the SiN_x surface with aldehydes prior to etching. Etching was performed using a cyclic C_4F_6/Ar and Ar plasma ALE process. We used *in situ* attenuated total reflection Fourier transform infrared spectroscopy to monitor the changes in the surface chemical composition on SiN_x and SiO_2. Pre-functionalization of a pristine, plasma-deposited SiN_x surface with benzaldehyde accelerated the formation of a graphitic hydrofluorocarbon layer, which in turn lowered the initial loss of SiN_x prior to an etch stop. However, in technological applications, both SiN_x and SiO_2 surfaces are either exposed to atmosphere or are used as stacks where the underlying SiN_x surface is already exposed to an etching plasma before it can be dosed with the hydrocarbon (see Fig.1a). An atmosphere-exposed SiN_x surface forms a skin layer of SiO_xN_y, and an SiN_x surface exposed to an etching plasma has a layer of residual CF_x. In each case, we discovered that the surface $–NH_x$ groups present after plasma deposition are partially to largely removed. While benzaldehyde does not react with SiO_xN_y and SiO_2 surfaces, it readily reacts with the CF_x reside on the plasma etched SiN_x and SiO_2 surfaces, which prevents selective reaction of aldehydes with the SiN_x surface.

In this presentation, we will also show that on partially etched SiN_x and SiO_2 surfaces, benzaldehyde can be attached selectively to the SiN_x surface after one ALE cycle by minimizing the CF_x residue on the SiO_2 surface. Thus, on the SiN_x surface, we utilize the reactivity of the surface $–NH_x$ groups and the residual CF_x layer to obtain selectivity for reaction to benzaldehyde (see Fig.1b). Our results also show that the selectivity of benzaldehyde attachment reduced with the slow accumulation of carbon-rich residue on both surfaces during ALE process. For SiN_x and SiO_2 surfaces that were pre-etched for one ALE cycle, using 4-wavelength *in situ* ellipsometry, we show that benzaldehyde dosing reduced the amount of SiN_x etched and increased the etch selectivity from 1.7 to 2.1 for 20 ALE cycles (see Figure 2). If we introduced a second dose for benzaldehyde after the 5th ALE cycle, which is prior to significant CF_x accumulation on SiO_2, the selectivity could be further improved from 2.1 to 3.4.

5:15pm **ALE2-MoA-16 Plasma-Assisted Atomic Layer Etching of Silicon Nitride with Unfragmented Fluorocarbons***, **Chon Hei Lam**, M. Carruth,* University of Texas at Austin*; Z. Chen, J. Blakeney, P. Ventzek, S. Sridhar, A. Ranjan,* Tokyo Electron America Inc.*,; J. Ekerdt,* University of Texas at Austin

The self-limiting behavior in atomic layer etching (ALE) processes promise to deliver atomic scale fidelity for three-dimensional device fabrication. ALE processes typically alternate cycles of chemical modification to weaken the surface bonds followed by ion bombardment to remove material with limited amount. ALE may provide fine control over the etch rate and can limit physical damage to the substrate through the layer-by-layer etch process. Since silicon nitride films are a component used in self-aligned multiple patterning schemes, ALE of silicon nitride is an important consideration in process development. ALE using plasma fragmented fluorocarbons can result in undesirable film growth. Ideally, the process should restrict fluorocarbon film build up to avoid taper profiling, clogging or etch stop. We explore ALE of silicon nitride by utilizing undissociated fluorocarbon (CF_4 and CHF_3) adsorption followed by gentle argon ion bombardment. The impact of gas precursors, energetic ion, temperature, and the nature of the surface chemical modification are discussed. We follow the surface chemistry and monitor structural damage during ALE.

Using CHF_3 we illustrate fluorocarbon surface modification and using energetic argon ion bombardment we illustrate changes to the adsorbed layer during bombardment. The ALE steps are performed at 24 °C and 100 °C (Figure 1). The films are characterized by *in situ* using X-ray photoelectron spectroscopy and spectral ellipsometry. The silicon nitride film is exposed to CHF_3 at 30 mTorr for 1 min as the fluorocarbon adsorption step followed by an argon ion bombardment. The F 1*s* peak appears after the (3 min, 100 eV) argon ion bombardment at 24 °C. The energetic argon ions fragment the fluorocarbon and activate the interaction between fluorine and silicon, and lead to the formation of SiF_x (Fig 2a). When the sample temperature is elevated to 100 °C, the SiF_x shoulder appears in the Si 2*p* spectra upon the CHF_3 adsorption step (Fig 2b) demonstrating the reaction between CHF_3 and silicon nitride is thermally activated. An SiF_x feature remains in the Si 2*p* spectra after the ion bombardment. The shoulder from SiF_x is more intense at 100 °C compared to the 24 °C. The ellipsometry result (Fig 1) shows a gradual change of etch rate over the first 5 ALE cycles as the starting surface is partially oxidized and transitions to silicon nitride. After the removal of the oxidized layer, the etch rate increases and corresponds to approximately 1 nm/cycle. The F 1*s* peak intensity remains at the same level after 5 and 10 ALE cycles indicating the residual fluorine on the surface after ion bombardment.

5:30pm **ALE2-MoA-17 Silicon Atomic Layer Etching with Surface Chlorination and Removal with Ar or He Plasma***, **Namgun Kim**,* Sungkyunkwan University, Korea (Republic of)*; D. Shin, J. Kim, C. Lee, K. Yoon,* Samsung Electronics, Korea (Republic of)*; Y. Kim, H. Chae,* Sungkyunkwan University, Korea (Republic of)

Si atomic layer etching (ALE) has attracted a lot of attention in the semiconductor manufacturing industry due to its excellent depth uniformity with precise control and damage-less compared to conventional reactive ion etching (RIE). [1] Si ALE is generally consisted of two steps, Cl2 adsorption and Ar desorption. The desorption step is the key process of transferring energy to the modified surface and is a major step that determines selectivity and uniformity. [2] Ar was mainly used as the sputtering gas for the desorption step, and there were few studies on other inert gases. In previous papers, the ALE window range was enlarged and the etch per cycle (EPC) was lowered when He was used as sputtering gas instead of Ar, but the recent GaN He ALE study showed different results. [3][4] In this work, Cl2 based Si ALE process was performed using He or Ar as sputtering gas in an 300mm inductively coupled plasma (ICP) reactor. The range of the ALE window did not change to 25V in either condition, the EPC increased from 5.96 Å/cycle to 7.02 Å/cycle, and a nonself-limited behavior was observed when He was used as the sputtering gas instead of Ar. The oxygen atomic fraction was increased in He ALE compared to Ar ALE when an x-ray photoelectron spectroscope (XPS) was observed by changing the number of cycles and bias power. Both ALE processes were compared with conventional RIE by measuring selectivity and roughness. In conclusion, Si quasi-ALE was successfully performed using Ar or He as sputtering gas with Cl2 plasma in the conventional plasma etching tool, and the difference in ALE performance according to the sputtering gas was also investigated.

References

[1] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho, J. Vac. Sci. Technol. A 33, 020802 (2015)
[2] G. S. Oehrlein, D. Metzler, and C. Li, ECS J. Solid State Sci. Technol. 4 N5041 (2015)
[3] H. J. Yun, T. H. Kim, C. B. Shin, C.-K. Kim, J.-H. Min, and S. H. Moon, Korean J. Chem. Eng. 24, 670 (2007)
[4] S. Ruel, P. Pimenta-Barros, F. L. Roux, N. Chauvet, M. Massardier, P. Thoueille, S. Tan, D. Shin, F. Gaucher, and N. Posseme, J. Vac. Sci. Technol. A 39, 022601 (2021)

ALD Fundamentals

Room Arteveldeforum & Pedro de Gante - Session AF-MoP

ALD Fundamentals Poster Session

AF-MoP-1 Unearthing Ruthenium Diazadienyls as Precursors for the ALD of Ru Thin Films: Precursor Assessment and ALD Process Development*, **David Zanders**, J. Obenlüneschloss,* Ruhr University Bochum, Germany*; M. Gock,* Heraeus , Germany*; A. Devi,* Ruhr University Bochum, Germany

Ruthenium thin films are garnering significant interest as next-generation interconnects to replace Cu in future nanoelectronic devices. Especially in the back end of line (BEOL) and middle of line (MOL), ongoing scale down towards 2 nm and beyond has motivated alternative metallization approaches such as semi-damascene in which Ru outperforms Cu and Co notably.[1,2]One deposition technique most suitable to provide thin films for challenging interconnect device architectures is ALD.[3] A paramount factor in each ALD process is the choice of precursors and their chemistry that governs layer formation and material quality. A review of the current ALD processes for Ru thin films shows that a considerable number of often closely related precursors with their individual advantages and drawbacks have been employed.[4] Hitherto, none of them could fully satisfy academic and industrial demands alike.

This presentation describes the synthesis and detailed characterization of an alternative Ru precursor class: Ru diazadienyl cymenes [Ru(DAD)(Cym)] and their potential for CVD and ALD applications. Two examples, Ru(tBuDAD)(Cym) and Ru(iPrDAD)(Cym) (Figure 1) were obtained in high yields in a one-pot synthesis and thoroughly assessed in terms of purity (NMR, EA) and structure (SC-XRD). The structures were reproduced by DFT studies and subjected to bond dissociation analysis which rendered them appreciably stable. Thermal stability upon evaporation was evaluated in more detail alongside overall evaporation behaviour in thermogravimetric analyses (TGA) (Figure 2). Vapor pressures of the two complexes were derived and compared to the most often used $Ru(EtCp)_2$. Especially Ru(iPrDAD)(Cym) showed appreciable volatilization and deemed competitive towards the reference compounds.

Thus, Ru(iPrDAD)(Cym) was employed as precursor in a PEALD process with O_2 plasma. Preliminary results demonstrated the growth of thin, pinhole-free, low roughness films on Si(100) at temperatures as low as 120 °C (Figure 3). A full process study investigating typical ALD growth characteristics in terms of saturation, temperature dependency of film growth and thickness scalability was carried out to assess the ALD behaviour. Complementarily, AFM, RBS/NRA and XPS as well as resistivity measurements were performed.

[1]G. Murdoch, et al., in 2020 IEEE IITC 1052020, p. 4.

[2]https://www.imec-int.com/en/press/imec-presents-alternative-metals-advanced-interconnect-and-contact-schemes-path-2nm.

[3]M.-J. Li, et al., in 2021 IEEE IITC 762021, p. 1.

[4]https://www.atomiclimits.com/alddatabase/.

AF-MoP-2 Towards Greener ALD Processes: The Precursor Chemistry Is Key*, **Matthieu Weber**,* LMGP - Grenoble INP , France*; O. Graniel, D. Muñoz-Rojas,* LMGP - Grenoble INP, France*; N. Boysen, A. Devi,* Ruhr Universität Bochum, Germany

ALD is a versatile and emerging technology, allowing for the precise coating of challenging substrates with a nanometer control over thickness. Due to its unique assets, a substantial growth of the ALD market is expected. In the current context of moving towards greener processes, the ALD technique offers the potential to become greener and to tackle environmental challenges. Indeed, the process itself has currently a consequent impact on the environment which should ideally be reduced as the technique is implemented in a wider range of products and applications. Based on a literature overview, our findings show that the duration of the process, the temperature used, and the precursor chemistry are key factors affecting the environmental impact of ALD. The principles of green chemistry are discussed considering the specificities of the ALD process, and different ways to reduce the impact are proposed, in particular the optimization of the processing parameters, the use of spatial ALD (SALD) and the chemical design of greener precursors are shown as efficient routes to lower the ALD environmental impact and improve its sustainability.

AF-MoP-3 An IR Spectroscopy Study of the Degradation of Surface Bound Azido-Groups in High Vacuum*, **Sofie S. T. Vandenbroucke**, M. Nisula, R. Petit,* Ghent University, Belgium*; R. Vos, K. Jans, P. Vereecken,* IMEC, Belgium*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

'Click chemistry' encompasses a set of powerful chemical reactions that have a high yield, are highly selective and specific, proceed under simple reaction conditions, use readily available starting materials, create stable products and harmless by-products.[Kolb, H.C., et al. (2001) *Ang. Chem. Int.*] The azide-alkyne cycloaddition reaction is considered the cream of the crop of the click reactions. Hence, surface functionalization by azido-moieties is often desired for applications in drug discovery, polymer chemistry, materials engineering and biosensor devices. [Lahann J. (2009) *Click chemistry for biotechnology and materials science*] This can be achieved by depositing self-assembled monolayers using azido-containing organosilanes which typically involves liquid-phase protocols. The use of vapour-phase chemistry might be beneficial regarding integration into a high-throughput production sequence and the deposition of high-quality and reproducible coatings on 3D microstructures. [Vos, R., et al. (2018) *Langmuir*] Because vapour-chemistry typically involves the use of high vacuum equipment, the stability of the azido-groups in high vacuum is of utmost importance.

In this work,[Vandenbroucke S.S.T. (2021) *Langmuir*] the stability of azido-containing self-assembled monolayers is monitored in real-time using in situ reflection FTIR at a temperature of 150 °C and a pressure of 1E-5 mbar for 8 h. The data in Figure 1 displays a clear decrease of the asymmetric azide stretching vibration at 2105 cm^{-1} over time in high vacuum, suggesting the degradation of the azido-groups. The degradation is further investigated at three different temperatures and seven different nitrogen partial pressures using ex situ ATR-FTIR. The degradation is found to increase at higher temperatures and lower nitrogen pressures. This is in accordance with the theory that the degradation reaction involves the decomposition into molecular nitrogen and the formation of a highly reactive nitrene.

Many applications in the semiconductor industry require a perfect control over the surface chemistry down to the nanometre level to yield reproducible results. For the condition with the most degradation only 63% of azides are found to remain at the surface after 8 h in high vacuum. This would imply a significant loss in control over the exact surface chemistry. One should therefore always consider the stability of functional groups such as azides when depositing or post-processing functional coatings in high vacuum.

AF-MoP-4 Nucleation of AlOx on ZrOx and ZrOx on AlOx studied by Low Energy Ion Scattering*, **Jan Tröger**,* Tascon GmbH, Germany*; M. Näsi, T. Blomberg,* Picosun Oy, Finland*; R. ter Veen,* Tascon GmbH, Germany

Nucleation is a crucial step in the formation of ALD films. It determines the formation of the first atomic layer of film. Proper nucleation is needed to deposit closed films with a homogeneous thickness. Since the nucleation deals with the formation of the first atomic layer of film, a very surface specific tool is needed to study nucleation: It should be able to distinguish between a closed monolayer and a half-closed double layer.

For common other techniques, such as XRF or XRR, it is not possibly to make this distinction due to a lack of surface specificity. Low Energy Ion Scattering (LEIS), on the other hand, is specific to the very first atomic layer, enabling it to determine the closure of the film (surface fractions of film and substrate), rather than the overall number of atoms per unit area that XRF or XRR provide.

We will demonstrate how LEIS works for the nucleation of AlOx films on ZrOx and the ZrOx films on AlOx. We show the normalized LEIS peak areas for Al and Zr as a function of cycle number for both depositions. The results show that in both cases, the films are almost closed after 20 cycles. In addition, we will present and discuss the following two features: In the deposition of ZrOx on AlOx, the peak area for Zr "overshoots". This indicates that the initial deposition happens with a stoichiometry that Zr-rich compared to ZrO_2 (and has some similarity to that of the Al_2O_3 substrate). In the case of the deposition of AlOx on ZrOx, the peak area for Al "undershoots", indicating that the initial deposition proceeds with an Al-poor stoichiometry compared to that of Al_2O_3 (with some similarity to that of the ZrO_2 substrate).

AF-MoP-5 Characteristics Evaluation of SiO_2 Thin Film Deposited by Organic vs Inorganic Precursor in ALD*, **Jihyeok An**, I. Yang, S. Yoon,* DUKSAN Techopia Co., Ltd, Korea (Republic of)*; I. Park,* Hanyang University, Korea

As semiconductor device highly integrated in a chip, it required a more complex structure at unit devices such as transistor, capacitor, and resistor. The thin film coated in structure needs better thickness controllability and uniformity as well as very smooth surface, especially in the complicated 3D-structure. To fulfill the demand, ALD method, which provided excellent step coverage, has been strongly adopted in the fabrications of metal oxides and metal itself. Silicon oxide(SiO_2) has been the most representative material used for the longest time in semiconductor industry in gate, floating gate, and other processes. The film characteristics of SiO_2 strongly depend on the precursor type and process parameters even though it was made with the same ALD method.

In this work, the process and materials characteristics dependency of precursor type, especially organic or inorganic, have been studied in ALD process and film properties. SiO_2 thin films were deposited by plasma enhanced ALD system with respective organic (tetrakis(dimethylamino)silane, tDMAS) and inorganic (hexachlorodisilane, HCDS) precursor. ALD window region was confirmed for both precursors. The growth rate of SiO_2 films fabricated with tDMAS and HCDS were 0.78 and 0.21 Å/cycle at the deposition temperature of 400℃ and 300℃, respectively. The Si : O ratio of SiO_2 film was 1.9 for tDMAS and 2.0 for HCDS. The density of both films was the same as 2.5. The surface of SiO2 film made with tDMAS, 0.1 nm RMS roughness, is smoother than that with HCDS, 0.5 nm. The MOS devices based on both SiO_2 films were manufactured with Si substrate and TiN metal electrode, and their capacitance properties were analyzed. The dielectric constant of both films showed the same value of 3.9.

AF-MoP-6 Microstructure and Electrical Properties of Conductive Nitride Films Grown by Plasma Enhanced Atomic Layer Deposition with Considerable Ion Bombardment*, I. Krylov,* Tower Semiconductor Ltd., Israel*; **Valentina Korchnoy**, X. Xu, K. Weinfeld, E. Yalon, D. Ritter, M. Eizenberg,* Technion - Israel Institute of Technology, Israel

We investigated electrical properties and structure of conductive nitrides (TiN_x, ZrN_x, TaN_x, HfN_x) deposited by the PEALD process from amide precursors and H_2/Ar plasma. Ion bombardment introduces additional energy to the growing film promoting chemical reactions and film densification. In PEALD process involving H_2/Ar plasma, most of bombardment effects are related to heavier Ar ions which are responsible for obtaining highly crystalline nitride films. Ion energy depends on the pressure inside ALD reactor during plasma half-cycle. Low pressure is favorable for deposition of highly conductive nitrides. The deposited nitrides have different grain size, carbon contamination, and variation of the film density from theoretical value despite same process conditions. Films crystallinity was investigated by the HAADF-STEM (Fig.1). The deposited nitride films differ in film morphology. TiN_x films consist of large columnar grains elongated through the whole film thickness. HfN_x films has columnar-like grains with smaller grain size compared to TiN_x. ZrN_x and TaN_x films consist of small grains. Significant ion bombardment reached in the process results in the growth of (111)-oriented polycrystalline films with low O contamination (Table1). The films are polycrystalline (Fig.2) despite the significant carbon content. Crystallization is stimulated by the ion bombardment effect achieved by the lowing plasma pressure. Carbon contamination correlates with the level of C-content in the precursor molecule.

Electrical resistivity of deposited nitrides is summarized in Fig.3,a. Despite near similar bulk resistivity of TiN, ZrN, and HfN, a significant difference in resistivity was found in the deposited films. Among the investigated films, TiN_x has the highest grain size and lowest resistivity. Density of the deposited nitrides was measured by the XRR. Deviation of the film density from its theoretical values represents the degree of crystallinity at a given film and follows the resistivity trend. Higher deviation indicates the smaller grain size resulting in higher electron scattering at grain boundaries. Film density can serve as a good qualitative parameter predicting the resistivity of transition metal nitride deposited by PEALD. Positive TCR values (metallic) were obtained for TiN_x and ZrN_x films, whereas the deposited TaN_x and HfN_x films have negative TCR values (semiconducting) (Fig.3,b). Negative TCR values are attributed to the presence of nitrogen-rich phases, $MN_x > 1$ in these films. Among the investigated films, TiN_x films have the highest grain size and lowest resistivity. Therefore, TiN_x is proposed as the leading PEALD nitride for conductive applications.

AF-MoP-7 Room-Temperature Atomic Layer Deposition of Iron Oxide and Its Surface Reaction; Explained by *in-Situ* Observation*, K. Yoshida, I. Nagata, K. Saito, M. Miura, K. Kanomata, **Fumihiko Hirose**,* Yamagata University, Japan

Room-temperature (23- 25˚C) atomic layer deposition (RT-ALD) of iron oxide is developed with a precursor of bis(N, N'-diisopropyl-propionamidinate)iron ($(DIPPA)_2Fe$) and plasma excited humidified Ar. Iron oxide such as Fe_2O_3 is examined as a magnetic coating material for pharmaceutical powders in drug delivery. Since the ALD uses saturation of the surface reaction, it is possible to deposit the oxide film on powder surfaces with nanometer precision. We consider that the ALD could be applied to heat-sensitive pharmaceutical drugs, although there were no previous reports on the RT Fe_2O_3 ALD. To find the gas injection conditions in ALD, we investigate the saturation of precursor adsorption and oxidation on the iron oxide surface in this study. The ALD growth is confirmed by quartz crystal microbalance (QCM). We used plasma excited humidified Ar as an oxidizing gas, and $(DIPPA)_2Fe$ as precursors of iron oxide. Any heaters or thermal sources were not installed on the ALD chamber wall. The $(DIPPA)_2Fe$ container and gas delivery pipe were warmed up around 80 °C to promote the precursor evaporation without its condensation. The exposure of Fe precursor in the adsorption step was 2.0×10^5 Langmuir (L). The oxidation time was set at 600 s. The evacuation steps of 300 and 60 s were inserted between the precursor and the plasma excited humidified Ar injections. P-type Si (100) substrates and polyethylene naphthalate (PEN) films were used for the ALD tests. We confirmed the film composition by XPS with a MgKα X-ray source. For the QCM measurement, we used an ALD sensor (#750-717-G2, Inficon) with AT-cut quartz crystals in which the resonance frequency was 6 MHz. The sampling rate was 2 Hz. We examined the iron oxide deposition on Si(100) and PEN. A sample image of the iron oxide coated PEN is shown in figure 1. The sample is colored brown by the interference of iron oxide thin film, but peelings and cracks were invisible. We confirmed Fe 2p narrow scan spectra of the iron oxide on Si(100) and PEN by XPS. Both of the deposited iron oxide Fe 2p peak positions are indicated the film is stoichiometrically close to Fe_2O_3. These suggest the applicability of the present RT-ALD to heat-sensitive materials. To discuss the surface reaction in this process, we picked up a typical mass variation curve, as shown in figure 2. The number of reacted ligands of the precursor adsorption period is estimated as 1 or 2 from a mass variation ratio during one ALD cycle. In the conference, we report the characteristics of deposited iron oxide and discuss the surface reaction of iron oxide RT-ALD.

AF-MoP-8 Simulation of Conformality of ALD Growth Inside Lateral Channels: Comparison between a Diffusion-Reaction Model and a Ballistic Model*, J. Velasco, J. Järvilehto, J. Yim, E. Verkama, **Riikka Puurunen**,* Aalto University, Finland

A number of models have been developed for simulating the conformality of atomic layer deposition processes.[1] Simulation models can be used, for example, for the optimization of process parameters towards improved conformality, and for the extraction of kinetic-related information through fitting the model parameters to experimental data.[2,3]

Three fundamentally different simulation approaches have been described in the literature to simulate the conformality of ALD processes: diffusion-reaction, ballistic, and Monte Carlo models.[1,5,6] In diffusion-reaction models, transport inside a feature is described by a diffusion equation that includes an adsorption loss term.[1,6] Ballistic models describe particle transport in the molecular flow regime and are based on a balance of particles to compute fluxes at different locations inside a feature.[5] In Monte Carlo models, the path of each particle at a time is simulated.[1]

In this work, we compared the conformality of ALD growth inside lateral channels predicted by two fundamentally different models: a diffusion-reaction model (Model A)[6,7] and a ballistic model (Model B).[5,8] The effect of different operating conditions on the conformality of ALD is studied in the free molecular flow regime.

For all the parameters studied, the main trends of the obtained saturation profiles were similar for both models (Fig. 1 of the supp. info). However, penetration depth at half-coverage predicted by the ballistic model was greater than that predicted by the diffusion-reaction model while the predicted slope at half-coverage was greater with the diffusion-reaction model (Fig. 2 of the supp. info). The ballistic model predicted a sudden increment of coverage when the profile reaches the end of the channel. The reasons and consequences of the differences will be discussed.

This work was supported by the Academy of Finland (ALDI consortium, grant No. 331082). An earlier version of this work was presented at the 21st Int. Conf. on Atomic Layer Deposition, ALD 2021.

References

1. V. Cremers et al., Appl. Phys. Rev., 2019, 6, 021302.

2. K. Arts et al., J. Vac. Sci. Technol. A, 2019, 37, 030908.

3. J.R. van Ommen, A. Goulas, and R.L. Puurunen. Atomic Layer Deposition. In Kirk-Othmer Encycl. Chem. Technol., John Wiley & Sons, Inc., 2022.

4. A. Yanguas-Gil and J.W. Elam, Chem. Vap. Deposition, 2012, 18, 46.

5. A. Yanguas-Gil and J.W. Elam, Theor. Chem. Acc., 2014, 133, 1465.

6. J. Yim and E. Verkama et al., submitted. Preprint DOI:10.33774/chemrxiv-2021-2j4n1

7. M. Ylilammi, O. Ylivaara, and R.L. Puurunen, J. Appl. Phys., 2018, 123, 205301.

8. Machball software, available at: https://github.com/aldsim/machball (accessed: Jan. 25, 2022).

AF-MoP-9 Chemisorption of Aminosilane Precursors on OH-terminated SiO$_2$ Surfaces during ALD of SiO$_2$

Heeju Son, *k. Khumaini, H. Roh, H. Kim, W. Lee,* Sejong University, Korea (Republic of)

Understanding the surface reaction mechanism is required to design and improve the atomic layer deposition (ALD) process. The ALD reaction mechanism can be studied by simulating the chemisorption of silicon precursor by density functional theory (DFT) calculation, which agrees well with the experimentally observed results [1]. The ALD SiO$_2$ using an aminosilane-type precursor, such as DIPAS ($SiH_3(N^iPr_2)$), BDEAS ($SiH_2(NEt_2)_2$), or TDMAS ($SiH(NMe_2)_3$), is being used in various dielectric deposition and patterning processes. DFT studies simulated the chemisorption of the Si precursor, assuming that dialkylamino ligands combine with H atoms of OH groups to form amine molecules as the byproduct. However, there was no report considering the type and distance of the hydroxyl groups on the surface. Also, comparative studies with experimental results are lacking. Therefore, in this study, we compared the chemisorption of aminosilane-type precursors on various OH-terminated SiO$_2$ surfaces modeled with different hydroxyl types and distances by DFT simulation. We also compared the chemisorption mechanisms of the precursors having different numbers of dialkylamino ligands. Reaction energies were calculated for all possible reaction pathways, assuming the release of amine or H$_2$ as the byproduct, and then the activation energies were obtained for exothermic pathways. The surface species predicted by DFT simulation well explains the experimental results from in-situ quartz crystal microbalance (QCM) and Fourier-transform infrared (FTIR) spectroscopy.

[1] H. Roh et al., Appl. Surf. Sci. 571 (2022), 151231.

AF-MoP-10 Volatile Adducts of Cobalt and Nickel Halides

Timo Hatanpää, *A. Vihervaara, M. Ritala,* University of Helsinki, Finland

Volatile metal halides in general are good ALD precursors as they are simple, cheap, readily available, thermally stable, reactive with many non-metal precursors and small in size allowing good growth rates. Unfortunately, halides of many metals are not volatile or they possess only low volatility. Many of such metal halides can, however, be rendered more volatile by adding proper adduct ligands to the metal coordination sphere.

Earlier we have introduced diamine adducts of cobalt and nickel to ALD. While pure halides of Co and Ni have polymeric solid-state structures, high melting point and low volatility, the diamine adducts have monomeric structure and volatility that is among average for known Co and Ni precursors. Under reduced pressure these compounds sublime intact and have sufficiently large temperature window between the sublimation and decomposition temperatures. These compounds have also been shown to perform well in ALD.[1]

For metal films low deposition temperatures are desired to minimize agglomeration and thereby obtain smoother films that are continuous at lower thickness. High volatility of the metal precursor is therefore needed. Here more adducts of the transition metal halides, especially phosphine adducts, were synthesized and studied. While diphosphine adducts of Co and Ni are thermally exceptionally stable, their volatility is low. In contrast, monophosphine adducts of the same are highly volatile but the thermal stabilities are low. For example $NiCl_2(PEt_3)_2$ sublimes already at 80 °C under vacuum, but signs of thermal decomposition are also seen already around 130 °C. The temperature window is still large enough to allow ALD usage as demonstrated by Ni metal film deposition using this precursor (another ALD2022 presentation).[2] Monophosphine adducts of Co have lower volatility than the Ni counterparts so that the temperature window between efficient evaporation and thermal decomposition is narrower.

In this presentation the thermal properties of cobalt and nickel halides with different neutral ligands including amines and phosphines are presented and compared. Among other things, it has been found that the thermal stability mainly increases from chlorides to iodides and the trend seems to be more pronounced with cobalt. The increasing molecular weight from chlorides to iodides causes only small decrease in volatility.

[1] K. Väyrynen (2019), Academic Dissertation, University of Helsinki, http://ethesis.helsinki.fi

[2] A. Vihervaara, T. Hatanpää, M. Ritala, ALD2022 abstract (to be published).

AF-MoP-11 Fabrication of Aluminum Nitride with 160 °C Atomic Layer Deposition using Plasma Excited Ammonia

Kentaro Saito, *K. Yoshida, M. Miura, K. Kanomata, B. Ahmmad, S. Kubota, F. Hirose,* Yamagata University, Japan

Aluminum nitride (AlN) has been attracting much attention since it is also expected to be used as a passivation layer for AlGaN/GaN high electron mobility transistors. In the conventional technologies, AlN depositions were examined by atomic layer deposition (ALD), although these were performed at a temperature of 200 °C and higher. To suppress solid-phase diffusion of the passivation layer, a low-temperature deposition is demanded. In this study, the low-temperature ALD of AlN using trimethylaluminum (TMA) and plasma-excited ammonia is examined. We evaluated chemical composition in the AlN films deposited at 160 °C by secondary ion mass spectrometry (SIMS) and cross-sectional transmission electron microscope (cross-sectional TEM), respectively. To confirm its applicability to a gas barrier, we try to deposit AlN on PET.

TMA was used as an Al precursor. Plasma-excited ammonia was used as a nitridation gas. For its generation, 4.2 sccm ammonia and 1.8 sccm argon were mixed, followed by being excited with an RF power of 250 W and a frequency of 13.56 MHz. TMA was introduced with an exposure of 1×10^5 L (1L=1× 10^{-6} Torr・s). The nitridation time was 180 s.

We observed the interface layer to examine if the film was deposited on the substrate without solid phase diffusion. The chemical composition was evaluated to measure impurity in the AlN film. Fig 1. shows a cross-sectional TEM image obtained from the AlN with the 150 cycles ALD. We see the polycrystalline AlN film on the starting surface without damage to the Si substrate. To propose the application to a gas barrier, we examined to deposit AlN on PET. Fig. 2 shows an image of an AlN deposited PET sample. From Fig.2, it is considered that the AlN deposition on PET is performed without the thermal deformation of the film. The water barrier characteristics are going to be disclosed in the conference for the further discussion.

AF-MoP-12 On the Underestimation of the Low-Temperature Limit for ALD of MoO$_x$ from Mo(CO)$_6$ Precursor

Kees van der Zouw, *T. Aarnink, A. Kovalgin,* University of Twente, Netherlands

Dependencies of the growth rate per cycle (GPC) as a function of the temperature (T), and the so-called precursor saturation curves, are standardly observed for atomic layer deposition (ALD) and reflect its self-limiting nature. Such curves are considered as an indication of the ALD window and required to demonstrate the occurrence of ALD at various circumstances. Plotting GPC versus T is expected to be system independent, meaning that the fundamental features of the GPC curve should be similar between one reactor system and another. It looks feasible to underestimate the limits of the ALD window if there is no universal method to determine the GPC. Based on our experimental findings, we propose an underestimation of the ALD temperature window to occur in the literature study on the (self-limiting) chemisorption of Mo(CO)$_6$ while depositing molybdenum oxide (MoO$_x$) and molybdenum oxide compounds.

According to the literature, the use of Mo(CO)$_6$ as precursor and O$_3$ or O$_2$-plasma as co-reactant results in the self-limiting chemisorption of Mo(CO)$_6$ roughly between 150 and 175 ^{o}C. The GPC is mentioned to quickly decay for temperatures below 150 °C, with hardly any deposition at T<130 °C [1,2]. According to the experimental observations in this work, the deposition of MoO_x on a silicon substrate can indeed hardly start at T<130 °C, due to the practically inappropriate long incubation time. However, the deposition of MoO_x, once enabled at T=130 °C or higher, naturally continues at 80 °C with a reasonable GPC. The growth per cycle decreases only from 0.028 nm/min at T= 175 °C to 0.020 nm/min at T= 80 °C.

In our presentation, an extended look into these experimental findings including film characterization will be given. We further would like to draw attention of the ALD community to a need for verifying the methodology of ALD window determination for scientific experiments.

[1] J. Mater. Chem., 2011, 21, 705-710

[2] Appl. Mech. Mater., 2014, 492, 375-379

AF-MoP-13 $ZnO_{1-x}S_x$ Layer Growth and Composition by Thermal and Plasma ALD

***Stefanie Spiering**, D. Bagrowski, T. Magorian Friedlmeier, W. Hempel, T. Wohnhaas, J. Becker,* Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Germany

$ZnO_{1-x}S_x$ alloys are wide-bandgap materials with high transmittance in the short-wavelength region. This makes them promising candidates as the n-type conducting buffer layer for different absorber types in thin-film photovoltaic devices. In this work, we studied the growth behaviour and composition of ternary $ZnO_{1-x}S_x$ on Si wafer substrates at a fixed deposition temperature of 150°C using a thermal ALD process with diethylzinc (DEZ), H_2O and H_2S as precursors, and additionally a mixed thermal/plasma-enhanced ALD process with DEZ, H_2S and O_2 plasma. The growth rates and the composition of the films were analysed by spectral ellipsometry and EDX (energy dispersive x-ray spectrometry).

With thermal ALD we processed layers over a wide range of different H_2O:H_2S pulse ratios. The cycle ratio for H_2S is defined here as $CR_{H2S}=k*100\%/(k+l)$ with k being the number of H_2S pulses and l being the number of H_2O pulses in a cycle, respectively. In contrast to former works on $ZnO_{1-x}S_x$ by ALD, not only the smallest possible bilayer period P=1*(k+l) for a certain CR_{H2S} was applied, but also larger bilayer periods P=a*(k+l) were examined (e.g. a=1,2,…,7 for CR_{H2S}=50% (k:l = 1:1) à P=2,4, …,14).EDX measurements showed a significant influence of the bilayer period on the sulphur content in the resulting films. Furthermore, we observed a linear relationship between the resulting S/(S+O) ratio in the film and the number of H_2S pulses for a fixed number of H_2O pulses, and vice versa. Therefore, it is possible to estimate the S/(S+O) ratio for a given pulse ratio by extrapolation. We discuss a few exceptions to the linear behaviour, e.g. for H_2O:H_2S ratio 1:1, 1:l and k:1.

$ZnO_{1-x}S_x$ films grown in a mixed thermal-/plasma-enhanced ALD process showed a very different layer growth in comparison to the thermal deposition. With the purely thermal process we deposited layers with S/(S+O) ratios in a wide range from about 10 to 90 % applying moderate $H_2S/(H_2O+H_2S)$ pulse ratios, even a higher S-content in the layers was achieved compared to the theoretically expected one. In contrast, by application of oxygen plasma (O_2Pl) as reactant for the ZnO cycle, a very high H_2S pulse fraction was necessary to reach S/(S+O) ratios >30%. With an O_2Pl:H_2S ratio of 1:24 (CR_{H2S}=96%) a S/(S+O) ratio of 60 % was measured.

AF-MoP-14 Effect of Precursors on Properties of Atomic Layer Deposited Cr-Ti-O Thin Films

***Mahtab Salari Mehr**,* University of Tartu, Institute of Physics, Estonia*; L. Aarik,* University of Tartu, Istitute of Physics, Estonia*; T. Jõgiaas, A. Tarre, H. Mändar,* University of Tartu, Institute of Physics, Estonia

Abstract:

Chromium oxide coatings are technologically important due to their good mechanical, chemical, magnetic, catalytic and optical properties. It has been shown that the properties of Cr_2O_3 coatings can be considerably changed if it is doped with an appropriate element. Chromium containing ternary oxide thin films have previously been grown by chemical vapor deposition or magnetron sputtering methods resulting in hard (hardness 31 GPa) [1]orsuper-hard (40 GPa) coatings [2] or showing good photocatalytic properties [3]. In this work chromium containing ternary compound (Cr-Ti-O) thin films were grown on Si (100) substrates using two different precursor combinations: CrO_2Cl_2 -CH_3OH:$TiCl_4$-H_2O, and $Cr(thd)_3$-O_3:$TiCl_4$-$O_3$by atomic layer deposition offering precise control over the concentration of dopant elements in the composition. Film density, roughness, phase composition, refractive index, hardness and Young's modulus were studied in variation of Ti concentration in the thin films. Thin films with average thickness of 115 nm deposited using CrO_2Cl_2-CH_3OH and $TiCl_4$-H_2Oprecursors exhibited crystalline α-Cr_2O_3 (eskolaite) phase with density from 4.8 to 5.2 g/cm^3. By increasing the number of $TiCl_4$ -H_2O cycles compared to CrO_2Cl_2-CH_3OH cycles, the total intensity of eskolaite reflections decreased. The films with average thickness of 45 nm deposited using $Cr(thd)_3$-O_3 and $TiCl_4$-O_3showed crystalline TiO_2 anatase phases with density from 4.0 to 4.7 g/cm^3 (Fig. 1). As the growth rate of the Cr_2O_3 deposited using $Cr(thd)_3$-O_3 (50 pm/cycle) was remarkable lower than that for CrO_2Cl_2-CH_3OH process (70 pm/cycle), the change of the $Cr(thd)_3$-O_3:$TiCl_4$-O_3 cycle ratio from 1:30 to 1:1 only decreased the amount of the anatase phase in the film.

References:

[1] Bahrami, Amin, et al. "Structure, mechanical properties and corrosion resistance of amorphous Ti-Cr-O coatings." Surface and Coatings Technology, 374 (2019) 690-699.

[2] Mohammadtaheri, M., et al. "An investigation on synthesis and characterization of superhard Cr-Zr-O coatings." Surface and Coatings Technology, 375 (2019) 694-700.

[3] Chen, Yang, et al. "Synthesis of core-shell nanostructured Cr_2O_3/C@ TiO_2 for photocatalytic hydrogen production." Chinese Journal of Catalysis 42 (2021) 225-234.

AF-MoP-15 Ligand Exchange with a Novel Cyclic Alkyl Amido Plumbylene and Transition Metal Complexes

***Kieran Lawford**, G. Bačić,* Carleton University, Canada*; J. Masuda,* St. Mary's University, Canada*; S. Barry,* Carleton University, Canada

Lead-containing precursors are an active field of study for the deposition of PbS (DOI: 10.1021/acs.chemmater.0c01887), PbO (DOI: 10.1149/1.2789286), and other lead-containing films.During our efforts to find new Pb(II) ALD precursors, we found that the acyclic diamido plumbylene lead(II) bis(*N-tert*-butyltrimethylsilylamide) (**0**) undergoes facile thermal decomposition into the homoleptic cyclic (alkyl)(amido) plumbylene (caaPb) bis(*N-tert*-butyl-2-aza-3,3-dimethyl-1-plumba-3-silacyclobutane) (**1**). Our interest in compound **1** pivoted toward the novel nature of the ligand and the potential to use it to synthesize new ALD precursors. We hypothesised that salt-metathesis between **1** and metal chlorides would produce similar heterocycles (caaM, M=metal). Lead is a good candidate for salt metathesis due to the thermodynamic driving force of the formation and precipitation of $PbCl_2$, driving the reaction to completion. Additionally, the high yield of the caaPb, cheap starting materials, and recyclability of the $PbCl_2$ by-product makes this synthetic methodology appealing, economical, and green. We tested the metathesis with $ZnCl_2$ because, if the salt metathesis is possible with zinc, then less electropositive metals should also undergo in the ligand exchange. During our test, we isolated $PbCl_2$ indicating that the metathesis was successful. Quantum chemical studies suggests the analogous reaction with other metal chlorides should also proceed.

There are early examples of titanium, zirconium, and hafnium complexes with a similar heterocyclic system ($CH_2Si(Me_2)NSiMe_3$), and the heterocyclic $Cp_2TiCH_2Si(Me_2)NSiMe_3$- was even used as a titanium-ceramic CVD precursor.[1,2] However, the synthesis of these is unreliable.[2] We can now prepare similar metal complexes using ligand exchange from **1** with higher yields. Additionally, we expect to see a change in thermal properties after exchanging the trimethylsilyl group for a t-butyl group appended to the heterocycle, since the trimethylsilyl moiety is thermally active. A variety of complexes will be vetted to determine which work best as vapour-phase precursors with respect to volatility and thermal stability.

1. Planalp, R. P.; Anderson, R. A.; Zalkin, A. Dialkyl Bis[bist(trimethylsilyl)amido] Group 4A Metal Complexes. Preparation of Bridging Carbene Complexes by γ Elimination of Alkane. Crystal Structure of $\{ZrCHSi(Me)_2NSiMe_3[S(SiMe_3)_2]\}_2$. *Organometallics***1983** *2*, 16-20.

2. Simpson, S. K.; Anderson, R. A. Reaction of the Metallocene Dichlorides of Titanium(IV) and Zirconium(IV) with Lithium Bis(trimethylsilyl)amide. *Inorg. Chem*. **1981**, *20*, 3627-3629.

AF-MoP-16 Diaminosilane Precursors for the Atomic Layer Deposition of Iron Metal

***Molly Alderman**, S. Barry,* Carleton University, Canada

Currently there are few processes for the atomic layer deposition of iron metal thin films, and none without significant limitations—either by CVD or relying on very specific substrates with growth terminating after the initial substrate is covered. With an appropriate precursor, iron films could provide the basis for ferromagnetic coatings and to enable a range of iron alloy films – like stainless steel thin films – with desirable properties.

Geminal diaminosilane (gDAS) ligands are N,N′ κ^2 chelates with silicon bridging the coordinating nitrogen centres (Figure 1). We have previously reported a range of first row transition metal complexes with the gem-diaminosilane ($(^tBuNH)SiMe_2NMe_2$) [2]. Transition metal gDAS precursors possess better volatility and thermal stability than their amidinate analogues while still avoiding problematic metal-oxygen bonds (compared to alkoxides) and with added stability from the chelate effect.

Here we report our initial study of new iron complexes which improve on the previously reported acetamidinate and α-imino alkoxide precursors [1]. We have synthesized, characterized, and evaluated the thermal characteristics of several Fe(II) and Fe(III) complexes containing monoanionic and dianionic gDAS ligands which show promise as precursors for the ALD of iron. Preliminary deposition studies using the previously reported $Fe(gDAS)_2$ monitored by quartz-crystal microbalance, as well as microscopy and initial compositional analysis will also be discussed.

[1] Kalutarage, L. C.; Martin, P. D.; Heeg, M. J.; Winter, C. H. Volatile and Thermally Stable Mid to Late Transition Metal Complexes Containing α-Imino Alkoxide Ligands, a New Strongly Reducing Coreagent, and Thermal Atomic Layer Deposition of Ni, Co, Fe, and Cr Metal Films. *J. Am. Chem. Soc.***2013**, *135* (34), 12588–12591. https://doi.org/10.1021/ja407014w.

[2] Griffiths, M. B. E.; Zanders, D.; Land, M. A.; Masuda, J. D.; Devi, A.; Barry, S. T. (TBuN)SiMe2NMe2—A New N,N′-K2-Monoanionic Ligand for Atomic Layer Deposition Precursors. *Journal of Vacuum Science & Technology A***2021**, *39* (3), 032409. https://doi.org/10.1116/6.0000795

AF-MoP-17 Low-temperature Epitaxy of β-Ga_2O_3 Films via Hollow-cathode Plasma-assisted ALD*, Saidjafarzoda Ilhom*, *A. Mohammad, D. Shukla, B. Willis,* University of Connecticut*; A. Okyay,* Stanford University*; N. Biyikli,* University of Connecticut

Gallium oxide (Ga_2O_3) is an emerging ultrawide-bandgap (UWBG) semiconductor attracting significant interest for high-power and high-frequency electronics that features comparable electrical properties (larger bandgap ~4.9 eV, high dielectric constant 6-8 MV/cm) to wide-bandgap GaN and SiC. However, growing device-level high-quality (Ga_2O_3) films have been mainly possible at high substrate temperatures (700 – 1000 °C) using complex reactor settings, which substantially increases the production cost and limits the application space.

In this work, we report on low-temperature as-grown crystalline β-Ga_2O_3 films on Si, glass, and sapphire via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD). The films were deposited using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Growth experiments have been performed at 240 °C substrate temperatures and 50 W rf-power level. Additionally, eachunit ALD-cycle was followed by an in-situ Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both in-situ and ex-situ ellipsometry were employed to measure the thickness and optical properties of the films. The samples exhibited enhanced growth-per-cycle (GPC) values around 1.3 Å. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial Ga_2O_3 film signature with monoclinic β-phase. On the other hand, GIXRD of the samples grown on Si and glass displayed polycrystalline β-Ga_2O_3 films. High-resolution transmission electron microscopy (HR-TEM) revealed the epitaxial relationship of the Ga_2O_3 layers grown on sapphire substrates. X-ray photoelectron spectroscopy (XPS) measurements shed light on the elemental composition and provide additional understanding on the nature of chemical bonding states within β-Ga_2O_3 layers. Our results demonstrate the effectiveness of in situ Ar-plasma annealing process within a customized HCPA-ALD reactor setting to transform amorphous wide bandgap oxide semiconductors into epitaxial films at substantially reduced substrate temperatures.

AF-MoP-18 Higher Effective Dielectric Constant of Hafnium Oxide When Grown with Hydrogen Peroxide Compared to Water Vapor*, Jeffrey Spiegelman*, RASIRC*; H. Kashyap, A. Kummel,* University of California at San Diego

As high-k gate dielectrics continue scaling in the sub 1nm EOT range, the low-k interfacial layer that is pre-formed or formed during the dielectric deposition process is increasingly problematic since it reduces the effective k-value of the dielectric layer(1) . For Hafnium Oxide grown on silicon, the EOT is a combination of the silicon dioxide interface and the quality of the hafnium oxide. Consiglio (1) reported reduced thickness of the silicon dioxide interface layer with hydrogen peroxide gas when compared to ozone. In this study hafnium oxide was grown on HF cleaned silicon with either water vapor or H2O2 gas. The Keffective was improved by 27% H2O2 grown HfO2. The film grew 50% faster with H2O2 than water. Vt was 0.18V for H2O2 and -1.3V for water. Additional data will be presented to clarify if the Keffective was due to a thinner SiO2 interface layer or improved HfO2 film quality.

AF-MoP-19 Atomic Layer Deposition of Low-resistivity Molybdenum Nitride Using F-free Mo Precursors and NH_3 Plasma*, Wangu Kang*, *J. Ahn, J. Han,* Seoul National University of Science and Technology, Korea (Republic of)

Molybdenum nitride film (MoN_x) is considered as a promising material in CMOS manufacturing process as gate electrode, contact layer, and diffusion barrier due to its high electrical conductivity, chemical stability, and thermal stability. With the continuous miniaturization of semiconductor devices, the development of atomic layer deposition (ALD) MoN_x process has been demanded to obtain conformal MoN_x film in complex 3-dimensional structure. However, MoN_x ALD using fluorine(F)-containing Mo precursor such as MoF_6showed various issues for example, forming void due to HF fume and degradation of metal or peripheral oxide by HF by-product.
In this study, we have developed the ALD MoN_x films using F-free Mo precursor and NH_3 plasma at the temperature range of 200-400 °C. The characteristics of MoN_x thin films such as crystallinity, chemical binding state, impurity and resistivity were examined by GAXRD, XPS, and 4-point measurement system. The post-annealing by rapid thermal annealing (RTA) at 500-800°C was conducted in H_2/Ar ambient to improve the resistivity of MoN_x films, and consequently the significant decrease in resistivity was observed after RTA due to the reduction of MoN_x into Mo.

AF-MoP-20 Atomic Layer Deposition of Molybdenum Carbides for Advanced Metallization: The Influences of Mo Precursor and Post-Deposition Annealing*, Ji Sang Ahn*, *W. Kang, J. Han,* Seoul National University of Science and Technology, Korea (Republic of)

As the width of metallization wire in semiconductor device decreases, Cu interconnect and W word line does not scale down as fast as linewidth due to its high electron mean free path (EMFP). Meanwhile, molybdenum (Mo) and molybdenum carbides (MoC_x) are considered as promising materials for next-generation interconnect owing to its small EMFP andless resistivity size effect.In order to apply the Mo and MoC_xthin films to the 3-dimensional semiconductor devices, atomic layer deposition (ALD) of Mo and MoC_x has been required. However, Mo and MoC_x ALD using fluorine (F)-containing Mo precursor resulted in various issues such as oxide damage and deterioration of device property due to F contamination and HF by-product. Therefore, it is essential to developMo and MoC_x ALD processusing F-free Mo precursors.

In this study, δ-MoC and β-Mo_2C thin films were depositedby ALD using two different F-free precursors. Rapid thermal annealing (RTA) process was adopted to reduce MoC_x into Mo metal and to increase crystallinity of the film. β-Mo_2C showedimproved crystallinity after RTA process, whereas δ-MoC was reduced into metallic Mo (~46.5 μΩ·cm) after post-reduction annealing. The crystallinity, chemical state, impurity, and electrical characteristics of molybdenum carbide thin films will be compared before and after annealing process and reaction mechanism of the post-reduction annealing will be discussed.

AF-MoP-21 ALD of Niobium Oxide (Nb_2O_5) and Niobium-Doped Titanium Oxide (Nb:TiO_2) for Solar Cell Applications*, Thomas Vincent*, *D. Coutancier, P. Dally,* IPVF (Institut Photovoltaïque d'Île-de-France), France*; M. Bouttemy, M. Frégnaux,* ILV (Institut Lavoisier de Versailles) - IPVF (Institut Photovoltaïque d'Île-de-France), France*; N. Schneider,* CNRS-IPVF, France

Atomic Layer Deposition (ALD) is increasingly contributing to the energy field and more specifically to the engineering of solar cells. Its conformity enables deposition on nanostructured substrates and its low growth temperature allows the deposition on temperature-sensitive substrates such as perovskite.

Niobium oxide, Nb_2O_5, is a wide bandgap semiconductor that has been grown by different methods and has recently been used in solar cells. Its optical and electrical properties depend strongly of the technique used for its growth, opening access to a wide range of application, such as electron transport layer (ETL)or passivation layer [1,2]. It is also used for the doping of titanium oxide (TiO_2), a well-known ETL, to reach a better stability of the complete solar cell.

In this work, we first developed ALD-Nb_2O_5 from tris(diethylamido)(tert-butylimido)niobium (TBTDENb) and water. The growth was studied from 100°C to 200°C, on several substrates (Si, glass, FTO, ITO). The ALD process was first optimized using QCM (Quartz Crystal Microbalance). Annealing studies in different conditions (air/inert atmospheres, up to 600°C) were conducted to understand the evolution of Nb_2O_5 at temperatures which are relevant within the fabrication steps of the solar cell.

Then, niobium-doped titanium oxide was developed using tris(isopropoxide)titanium (TTIP) as titanium precursor, and Nb-doping was applied by a supercycle strategy and tuned by several methods (supercycle ratio, precursors sequences). For both materials, structural, chemical, electrical and optical properties were characterized by XRR (X-Ray Reflectivity), GIXRD (Grazing Incidence X-Ray Diffraction), ellipsometry, SEM (Scanning Electron Microscopy), XPS (X-Ray Photoelectron Spectrometry), XRF (X-Ray Fluorescence), spectrophotometry, 4-points probe.

Finally, those ALD-materials were implemented in perovskite solar cell architectures.

[1] Subbiah, et al (2019). *Energy Technology, 8*(4), 1900878. https://doi.org/10.1002/ente.201900878

[2] Macco et al, (2018). *Solar Energy Materials and Solar Cells, 184*, 98-104. https://doi.org/j.solmat.2018.04.037

AF-MoP-22 Understanding the Grown Mechanism of Al_2O_3 Thin Films Using Plasma-Activated Deionized Water as Oxygen Source on Thermal ALD*, **William Chiappim**,* Aeronautical Institute of Technology, Brazil*; J. Chaves,* Aeronautical Institute of Technology , Brazil*; B. Botan Neto, L. Gonçalves de Lima, M. Shiotani Marcondes, N. Galvão, A. da Silva Sobrinho, R. Sávio Pessoa,* Aeronautical Institute of Technology, Brazil

The atomic layer deposition (ALD) of metallic oxides, mainly alumina (Al2O3), when performed in thermal mode, uses deionized water (DI) as an oxygen source and trimethylaluminum (TMA) as a metal reactant. However, growth per cycle (GPC) of Al2O3 thin films for the reactant and co-reactant mentioned above is limited to 0.1 nm/cycle. This barrier in the GPC is overcome by using plasma technology as an oxygen source. This technique is commonly called energy-enhanced ALD because the plasma oxygen source provides tremendous activation energy during the co-reactant step, which allows for greater efficiency in generating active sites on the substrate surface, promoting thus more reactions between the surface and the metal reactant. This process, called plasma-enhanced ALD (PEALD), is commonly used to replace DI water with O2 plasma as an oxygen source [2]. It is reported in the literature that for the TMA reactant, this replacement of the vapor phase oxygen source (thermal ALD) by a plasma oxygen source (PEALD) generates an increase in the alumina GPC to 0.12 nm/cycle, i.e., a gain of 20%. However, this gain in the GPC has a high cost, as the PEALD uses a source to generate the plasma that uses electrical energy to ionize and dissociate the gas introduced into the chamber. In addition, it is necessary to design a new deposition chamber and design the entire electrical system to turn it into equipment that operates in plasma mode, which significantly increases production costs. The present work presents a cheap alternative to increase the GPC of alumina by 20%. A gliding arc plasma and compressed air were used to activate DI water. Plasma-activated water (PAW) was prepared by a forward vortex flow reactor (FVFR) type with air compressed at atmospheric pressure. The activation times were 10, 30, and 60 min, and it was reached the following pH of 3.5, 3.0, and 2.5. PAWs were characterized by UV-vis spectrophotometer and presented reactive oxygen and nitrogen species (RONS), namely, H2O2, HNO2, NO2-, and NO3-.

After activation, plasma-activated water (PAW) is carried out into a recipient and introduced in the line of oxygen source in thermal ALD. The ALD pulse times were 0.15-30-0.3-30 s, TMA, N2 purge, PAW, and another N2 purge. The number of cycles was fixed at 1000 cycles, and the substrate was the Si (100). Alumina thin films growth was characterized *in-situ* by mass spectrometry and *ex-situ* by an optical profilometer, FT-IR and FEG-SEM.

According to the characterizations mentioned above, the existing RONS in PAW probably contributed to the activation of sites in the Si(100) substrate, thus increasing the GPC of the alumina.

AF-MoP-23 Atomic Layer Deposition of Titanium Phosphate onto Reinforcing Fibers Using Titanium Chloride, Water, and Tris-(Trimethylsilyl)-Phosphate as Precursor*, **Pauline Dill**, X. Ren, H. Hintersatz,* University of Technology Chemnitz, Germany*; M. Franz,* Fraunhofer Institute of Electronic Nano Systems ENAS, Germany*; D. Dentel, C. Tegenkamp, S. Ebert,* University of Technology Chemnitz, Germany

Thermal ALD process for depositing titanium phosphate on carbon fiber bundles and flat silicon substrates using the novel precursor system titanium tetrachloride, water, and tris-(trimethylsilyl)-phosphate was studied. We observe a linear growth per cycle of 0.22 nm/cycle. Compositional analysis of the coating was investigated using energy-dispersive X-ray spectroscopy (EDXS), and X-ray photoelectron spectroscopy (XPS). The thermal behavior up to 900 °C and the changes compositional were investigated via infrared spectroscopy (IR). With oxidation of coated carbon fibers in the thermogravimetric analysis (TGA) we could show that the coating also increases the onset temperature of oxidation of the fibers.

The coated fibers will be embedded in a ceramic matrix to give a fiber reinforced ceramic matrix composite (CMC). In this CMC the coating has the role induce the deflection of cracks that run through the matrix and to provide oxidation resistance.

P. Dill, X. Ren, H. Hintersatz, M. Franz, D. Dentel, C. Tegenkamp, S. Ebert, *J.Vac. Sci. Technol. A* 40 (**2022**); doi: 10.1116/6.0001514

AF-MoP-24 Amorphous Carbon(a-C) Atomic Layer Deposition using CBr_4 Precursor*, **Tae Hyun Kim**, M. Kim, S. Park, S. Chung, H. Kim,* Yonsei University, Korea

Phase change memory (PCM) is attracting attention as the need for high-performance memory semiconductors that can process large amounts of data quickly increases with the development of the 4th industry, such as big data and artificial intelligence. At the same time, research on 3dimensions cross-point (3D X-point) memory using memory cells and selectors in the area where word lines and bit lines intersect in 3D to create a highly integrated PCM is also being conducted. However, the most important factor for high efficiency and integration of these PCM devices is to reduce the current required for device operation. Recently, studies have been actively conducted to increase the joule heating efficiency by increasing the specific resistance of the electrode. In this respect, carbon, which exhibits various resistivities (conductor (graphite, sp^2 bond) – insulator (diamond, sp^3 bond)) [1], [2] depending on the state of atomic bonding, is an attractive material as a PCM electrode. So far, PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition) processes have been used to deposit carbon thin films. However, it is difficult to deposit a uniform carbon thin film on a three-dimensional structure with the conventional method, and it is difficult to control the physical properties of carbon. Therefore, in this study, a carbon process using ALD (Atomic Layer Deposition) was developed. Furthermore, the analysis of the carbon thin film properties according to the process conditions (reactant, temperature, pressure, time, etc...) was analyzed, and the corresponding mechanism was studied.

AF-MoP-25 Al_2O_3 Nanowire Growth on WSe_2 Flake by Using Low-temperature ALD*, **Chi-Chung Kei**, C. Su, B. Liu,* Taiwan Instrument Technology Institute, National Applied Research Laboratories, Taiwan*; Y. Su,* Department of Electrophysics, National Yang Ming Chiao Tung University, Taiwan*; T. Lee, C. Cheng, H. Wang, I. Radu,* Corporate Research, TSMC, Taiwan*; W. Chang,* Department of Electrophysics, National Yang Ming Chiao Tung University, Taiwan

Transition metal dichalcogenide (TMD) has been considered a promising material for the channel material of electronics due to remarkable electrical characteristics.Atomic layer deposition (ALD) is a promising method to deposit film for TMD-based device fabrication. However, lack of dangling bond on TMDs leads to a chemically inert surface for the chemisorption of ALD precursors.Physisorption of ALD precursors is considered to form seeding or reactive sites on chemically inert surface of TMDs. In this work, WSe_2 flakes were used as the substrate to grow Al_2O_3 by using ALD. 90^{o}C was chosen as the working temperature to allow the physisorption of ALD precursors on WSe_2 substrates. Atomic force microscopic image (AFM) in **Fig. 1(a)** shows the triangular WSe_2 flakes were grown on mis-cut sapphire substrates after meta-organic vapor deposition. WSe_2 surface, shown in **Figs. 1(b)** and **(c)**, exhibits terrace morphologies and is similar to mis-cut sapphire substrate. Terrace width and step-height are estimated to about 80 nm and 0.3 nm, respectively. In the Al_2O_3 ALD, trimethyl aluminum (TMA) and water were used as the sources of aluminum and oxygen, respectively. One ALD cycle for growing Al_2O_3 started with 0.1 s TMA pulse, followed by 18 s N_2 purge to remove excess precursor and by- products, then 0.1 s water pulse, and finally another 18 s N_2 purge. After 20 cycles of Al_2O_3 ALD, nanowire-like structure was formed on the surface of WSe_2 flake, as shown in **Fig. 2(a)**. According to the line-scan data in **Figs. 2(b)** and **(c)**, the width and height of nanowires are estimated to be about 40 and 6 nm, respectively. The peak-to-peak spacing between nanowires, about 80nm, is consistent with the terrace width of WSe_2 surface. This suggests that Al_2O_3 preferentially nucleates and grows along the valley of terrace structure. This can be attributed that the energy barrier to form a stable physisorbed embryos on a concave valley is lower than that on a flat surface. The growth per cycle (GPC) of about 0.3 nm/cycle also suggests that Al_2O_3 growth was both contributed from the physisorption and chemisorption of ALD precursors.

**AF-MoP-26 Comparison of Atomic Layer Deposited ZrO2 Thin Film using Cp-based Zr Precursor and Newly Synthesized Cp-based Zr Precursor*, Hyemi Han,* *S. Park, S. Na, S. Chung, H. Kim,* Yonsei University, Korea (Republic of)

As the dynamic random access memory (DRAM) has been continuous downscaling, zirconium oxide, a high-k dielectric material, is widely used as a substitute for conventional SiO2. Because it has a relative high dielectric constant (15~22), a high breakdown field (15–20 MV/cm), a large band gap (5–7 eV), and a good thermodynamic stability up to 800 ℃ when in contact with the silicon substrate.[1]

Among the various methods of deposition, ALD has been recognized as the leading candidate to process the high-k dielectrics owing to characteristics such as self-limiting reaction, excellent conformality, easy controlled thickness, and large area uniformity.[2]

The choice of precursor is very important because the film properties are totally different depending on which kinds of precursor is used. For instance, in case of halide ligand precursor, it has been widely used since there is no carbon incorporation into the films. However there is limitation like low volatility, particle issue and harmful byproduct. Also alkoxide ligand having a strong metal-oxygen bonding is required a relatively high temperature and it is easily decomposed by heat and contains high concentration of carbon impurity in the thin film. [3] Among various types of precursors, ZrO2 thin film using Cp ligand precursor have been widely used recently due to their good thermally stable allowing deposition temperature above 300℃ and excellent crystallinity. However it has disadvantage in that the growth rate is decreased due to its bulky size.[4]

Like this, several kinds of precursors have been studied for ALD of ZrO2 thin film but it is still needed for research on precursors. In this paper, new linked-Cp zirconium precursor ((linked CpZr(N(CH3)2)3)) was synthesized for ALD of ZrO2 thin film and compared with the commonly used (CpZr(N(CH3)2)3) precursor in terms of growth characteristic and film property. For ALD ZrO2 process, oxygen plasma was used as the oxidant.

Various experimental methods, including spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), X-ray Reflectivity (XRR) and density functional theory calculations (DFT)) were used for analyzing growth characteristic and film property. Additionally for the analysis electrical property, capacitance-voltage (C-V) and current-voltage (I-V) measurements were conducted.

[1] M. Balog, M. Schieber, Thin Solid Films 1977, 47, 109

[2] H. J. Kim, H. -B. -R. Lee, Thin Solid Films 517, 2563–2580 (2009)

[3] J. Niinistö, K. Kukli, Advanced Engineering Materials vol. 11 223–234 (2009)

[4] J. –S. Jung, S. –K. Lee, Thin Solid Films. Thin Solid Films.Volume 589 831-837 (2015)

AF-MoP-27 Thermal Atomic Layer Deposition of in_2O_3 Thin Films Using a Homoleptic Indium Triazenide Precursor and Water*, Pamburayi Mpofu,* Linköping University, Sweden

Indium oxide (In_2O_3) has received much attention for a wide range of applications, including in optoelectronics as a transparent conducting material. We report ALD of In2O3 using a recently reported indium(III) triazenideprecursor[1] together with water. The deposition process was studied between 150 and 520 °C using a homebuilt crossflow ALD reactor at 50 hPa with indium(III) triazenide pulsed for 4s, and water pulsed for 3s as precursors and purging with nitrogen for 10s in between. The deposition process is self-limiting at ~1.0 Å/cycle and temperature window between 270 and 385 °C. XRD analysis shows that the films are polycrystalline with a preferred (222) orientation. The films are substoichiometric with have low levels of C impurities. Optical transmittance is high, >70% in visible light, and the resistivity was found to be low signifying high conductivity. These results are on par with the current state-of-the-art reported for thermal ALD of In_2O_3 from a formamidinate precursor.[2] We make a direct comparison between the indium triazenide precursor and the indium formamidinate precursor in the same reactor and show that they render very similar temperature windows and film quality optical transparency, and conductivity of the deposited films.

Refs.:

11. O'Brien et al. *Chem. Mater.*, **2020**, *32*, 4481.
12. Kim et al. *Chem. Eur. J.,* **2018**, *24*, 9525.

AF-MoP-28 Nanoindentation of Amorphous Aluminium and Tantalum Oxide Nanolaminates*, Helle-Mai Piirsoo,* *T. Jõgiaas, P. Ritslaid, K. Kukli, A. Tamm,* University of Tartu, Institute of Physics, Estonia

Ta_2O_5-Al_2O_3 nanolaminates are potentially applicable as high dielectric strength insulators [1], resistive switching media [2] and corrosion resistant coatings [3]. For most applications the mechanical properties of the thin films have a significance on the reliability of the devices. Double- and triple-layer amorphous Al_2O_3-Ta_2O_5 laminates with an overall thickness of about 70 nm were atomic layer deposited while changing the sequence of the layers from surface to substrate. Hardness and elastic modulus of the laminates were measured with nanoindentation and influence from the layer thickness and sequence on the mechanical properties were analysed.

Figure 1 depicts the change of hardness along the depth of the films for double-layered laminates. Layered structure caused an uneven rise in hardness with depth dependent on the sequence of Al_2O_3 and Ta_2O_5. Figure 2 describes the hardness of triple-layered laminates, showing an even incline for the laminate with a middle Ta_2O_5 layer surrounded with Al_2O_3 whereas the laminate with middle Al_2O_3 between Ta_2O_5 layers resembled the double-layered laminate behaviour. An additional quadruple-layered laminate was measured and showed a steady increase of hardness with depth. The elastic modulus for all the laminates was similar, steady along the depth and fell between 145 – 155 GPa.

It can be concluded that the hardness of layered films is affected by both the thickness of the layers and their sequence. Lowering a single constituent layer thickness can smoothen the difference in hardness along the film depth which could reduce internal stresses, defects, and delamination. Adding an extra layer to a thin film could increase its mechanical resilience in a cost-effective way.

References:

[1] B.V.T. Hanby, B.W. Stuart, M. Gimeno-Fabra, J. Moffat, C. Gerada, D.M. Grant, Appl. Surf. Sci. 492, 328 (2019) https://doi.org/10.1016/j.apsusc.2019.06.202.

[2]W. Song, W. Wang, H.K. Lee, M. Li, V.Y.-Q. Zhuo, Z. Chen, K.J. Chui, J.-C. Liu, I.-T. Wang, Y. Zhu, N. SinghAppl. Phys. Lett. 115, 133501 (2019) https://doi.org/10.1063/1.5100075

[3] B. Díaz, E. Härkönen, J. Swiatowska, A., V. Maurice, M. Ritala, P. Marcus, Corr. Sci 82, 208 (2014) http://dx.doi.org/10.1016/j.corsci.2014.01.024

AF-MoP-29 Experimental and ReaxFF MD Studies for Boron Nitride ALD Growth from BCl_3 and NH_3 Precursors*, Naoya Uene,* *T. Mabuchi,* Tohoku University, Japan*; M. Zaitsu,* Japan Advanced Chemicals Ltd., Japan*; Y. Jin,* Japan Advanced Chemicals Ltd., Japan, China*; S. Yasuhara,* Japan Advanced Chemicals Ltd., Japan*; A. van Duin,* Pennsylvania State University, USA*; T. Tokumasu,* Tohoku University, Japan

Boron nitride (BN) has been considered a promising dielectric material for 2D material-based electronics. The atomic layer deposition (ALD) technique is a good method to grow conformal and ultrathin materials at relatively low temperatures. However, the growth mechanism is still not clear because the surface events with self-termination resulting from chemical reactions and physical dynamics are complicated. We aim to understand the growth mechanisms of the BN-ALD process from BCl_3 and NH_3 by experiments and simulations using the reactive force-field molecular dynamics (ReaxFF MD).

First, we investigated temperature profiles using a thermal ALD system described in Fig. (a). BN films were grown on the Si(100) surface in a hot walled horizontal reactor through the general ALD cycles as follows; BCl_3 exposure, Ar purge, NH_3 exposure, and Ar purge. Fig. (b) shows the thickness of the grown BN as a function of growth temperature measured on thechamber wall. We obtained a relatively small dependency of growth per cycle on the temperature in the range of 700-900 °C, suggesting ALD growth. The thin film property was characterized using IR spectroscopy as shown in Fig. (c). The remarkable peak at 1367 cm^{-1} is originated from sp^2 BN associated with the in-plane stretching.These experimental results mean proper BN growth on the Si(100) surface by ALD. Second, we started to develop a new force field for the ReaxFF MD, which can simulate the surface events including complicated chemical reactions and physical dynamics. The initial force field is based on the two types of force field; boron nitride nanostructure formation and dynamical crack propagation in silicon, by Lele et al. and Buehler et al., respectively. The initial force field is mainly trained for boron chloride species and the reaction of BCl_3 on the

OH-terminated Si(100) surface. We simulated one ALD cycle after thermal annealing to relax the initial system shown in Fig. (d). The Ar purge steps are simply replaced as the removals of gas molecules with thermal annealing. The simulations revealed some growth mechanisms: the $-BCl_2$ chemisorbed on the OH-terminated surface in the feed step, $-NH_2$ chemisorbed on the Cl-terminated surface in the reaction step, and HCl was generated with the chemisorption in these two steps. Our simulations are still one ALD cycle, however, these growth mechanisms are chemically straightforward.

We will show you thin film properties such as crystallinity and composition and compare them with the experimental results. The experimental and theoretical study of the ALD can be applied not only to the BN system but also to critical materials such as TiN and GaN in the future.

AF-MoP-30 Enhancement of Graphene-Related and Substrate-Related Raman Modes Through Dielectric Layer Deposition*, **Karolina Pietak**,* Warsaw University of Technology Faculty of Chemistry, Poland*; J. Jagiełło, A. Dobrowolski,* University of Warsaw Faculty of Physics, Poland*; R. Budzich,* Warsaw University of Technology Faculty of Chemistry, Poland*; A. Wysmołek,* University of Warsaw Faculty of Physics, Poland*; T. Ciuk,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland

Enhancement of the Raman signal intensity is currently among the most researched directions in developing Raman-based characterization techniques of all 2D materials as it elevates detection limits of their fine structural properties. The interest in signal intensification is also triggered by the wide range of applications it can benefit, including biochemistry and biosensing, polymer and materials science, catalysis, electrochemistry, the study of high-temperature processes, and detection of hazardous gases.

In this research, we demonstrate a method for the enhancement of Raman active modes in hydrogen-intercalated quasi-free-standing epitaxial Chemical Vapor Deposition graphene and the underlying semi-insulating 6H-SiC(0001) substrate through constructive signal interference within the atomic-layer-deposited amorphous Al_2O_3 passivation. We find that an optimum Al_2O_3 thickness of 85 nm for the graphene 2D mode and 82 nm for the SiC longitudinal optical A_1 mode at 964 cm^{-1} enables a 60% increase in their spectra intensities. We demonstrate the method's efficiency in Raman-based determination of the dielectric thickness and high-resolution topographic imaging of graphene surface [1].

[1] K. Piętak, J. Jagiełło, A. Dobrowolski, R. Budzich, A. Wysmołek, T. Ciuk, Enhancement of graphene-related and substrate-related Raman modes through dielectric layer deposition, accepted for publication in *Applied Physics Letters* (28.01.2022).

Acknowledgements:

The research leading to these results has received funding from the Research Foundation Flanders (FWO) under Grant No. EOS 30467715, the National Science Centre under Grant Agreement No. OPUS 2019/33/B/ST3/02677 for project "*Influence of the silicon carbide and the dielectric passivation defect structure on high-temperature electrical properties of epitaxial graphene*" and the National Centre for Research and Development under Grant Agreement No. LIDER 0168/L-8/2016 for the project "*Graphene on silicon carbide devices for magnetic field detection in extreme temperature conditions*".

Karolina Piętak and Rafał Budzich acknowledge financial support from the IDUB project (Scholarship Plus programme).

AF-MoP-31 Interface Modification of Thermoelectric Materials with Oxide Compounds by Atomic Layer Deposition*, **Shiyang He**, A. Bahrami, K. Nielsch,* Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden e.V., Germany

In thermoelectric materials, phase boundaries are crucial for carrier/phonon transport. Manipulation of carrier and phonon scatterings by introducing continuous interface modification has been shown to improve thermoelectric performance. In this work, a strategy of interface modification based on powder atomic layer deposition (PALD) is introduced to accurately control and modify the phase boundary of pure bismuth. Ultrathin layers of Al_2O_3, TiO_2, ZnO and Sb_2O_x are deposited on Bi powder by typically 1–20 cycles. All of the oxide layers significantly alter the microstructure and suppressed grain growth. These hierarchical interface modifications aid in the formation of an energy barrier by the oxide layer, resulting in a substantial increase in the Seebeck coefficient that is superior to that of most pure polycrystalline metals. Conversely, taking advantage of the strong electron and phonon scattering, an exceptionally large decrease in thermal conductivity is obtained. It's worth noting that a substantial decrease of κ_{tot} from 7.8 to 5.7 $W\cdot m^{-1}\cdot K^{-1}$ was obtained with just 5 cycles of Sb_2O_x layers and a 16% reduction of κ_{lat}. Finally, a maximum figure of merit, zT, of 0.15 at 393 K and an average zT of 0.14 at 300–453 K were achieved after 5 cycles of Al_2O_3-coated Bi. The ALD-based approach, as a practical interfacial modification technique, can be easily applied to other thermoelectric materials to enhance their performance.

AF-MoP-32 Comparative Study of the Growth Characteristics and Electrical Properties for Atomic Layer Deposited HfO_2 Films Using Cp-Based Hf Precursors*, **Seunggyu Na**, S. Park, H. Yoon,* Yonsei University, Korea*; Y. Lee,* Stanford University*; S. Chung, H. Kim,* Yonsei University, Korea

Scaling down of Si-based metal-oxide-semiconductor (MOS) has been main issue for semiconductor industry. With the demand for faster and smaller devices, channel length and thickness of gate dielectric have rapidly shortened. To prevent high leakage current for thin SiO_2, scaling down requires materials with higher dielectric constant. Among many materials, HfO_2 has been widely used for its superior properties. It has appropriate band offset with Si (~1.4 eV) and superb dielectric properties, such as high dielectric constant of about 25. For deposition of gate dielectric HfO_2, atomic layer deposition (ALD) technique has been widely used due to its superior characteristics, including excellent conformality, easily controlled thickness at atomic scale, atomic level composition control, large area uniformity, low impurity, and low growth temperature.

Many kinds of precursors, such as halides, alkoxides, alkylamides, and cyclopentadienyls have been studied for HfO_2 ALD process. Among these various type of precursors, alkylamide precursors are attracting attention due to their superior characteristics. They have relatively weak metal-N bonds, and weaker bond attributes to high reactivity in low temperature. Furthermore, the ligands of alkylamide precursors effectively prevent neighboring precursors from bonding to the metal center, which attributes to low melting point and high volatility. However, their weak metal-N bonds lead to decomposition of the precursors at high temperature. It limits ALD window and results in incorporation of impurities in film at high process temperature. In addition, the upper process temperature limit also prevents the formation of films with higher density and higher crystallinity.

To overcome this low thermal stability issue, heteroleptic precursors including cyclopentadienyl (Cp) ligand were introduced. Cp ligand has been widely employed for enhancing thermal stability and volatility of precursor. To take step further in terms of stability, we studied precursor with linking between Cp ligand and alkylamide ligand. By comparing the two Cp-based heteroleptic precursors with the linking between Cp ligand and alkylamide ligand and the one without, we investigated the impact of linked ligand structure on growth characteristics, chemical compositions, crystallinity, and electrical properties. Furthermore, density functional theory (DFT) calculations were introduced for revealing the reaction energy and pathways.

AF-MoP-33 Role of Ligand Coordination Sphere on the Physico-Chemical Properties of New Mn Precursors: Structural, Thermal and DFT Investigations*, **Martin Wilken**,* Ruhr-Universität Bochum, Germany*; A. Muriqi, M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; A. Devi,* Ruhr Universität Bochum, Germany

The interesting redox chemistry of manganese (Mn), its high abundancy in Earth's crust and additionally the associated unique electronic states make manganese-based materials like its oxides, nitrides or the sulfides suitable for a broad range of applications. In particular, when applied as thin films, Mn-based materials can function as cathodes or components in batteries[1], electrocatalysts for oxygen evolution reaction (OER)[2], dilute magnetic semiconductors (DMS) in spintronics[3] etc. Atomic layer deposition (ALD) is one of the preferred methods to deposit thin films with a high degree of control of film properties. The precursors employed for ALD play an important role. Many of the known Mn precursors namely manganocene's (e.g., $[MnCp_2]$)[4], carbonyls $[Mn_2(CO)_{10}]$[5], or β-diketones (e.g., $[Mn(thd)_3]$)[6] are associated with insufficient vapor pressure, poor shelf life and/or low thermal stability. One particular precursor which potentially overcomes the mentioned drawbacks is the all-nitrogen coordinated manganese tert-butyl-acetamidinate $[Mn(^tBuAMD)_2]$[7]. Motivated by this promising development, we further explored this class of Mn precursors by introducing the structurally related guanidinates and formamidinate ligand systems. This resulted in a series of new Mn complexes, which were thoroughly investigated by means of single-crystal XRD, nuclear magnetic resonance spectroscopy (NMR-Evans method), elemental analysis (EA), mass spectrometry (MS), and infrared spectroscopy (IR). To gain insights into the physicochemical properties, detailed thermal analysis was performed. Owing to the extreme sensitivity and reactivity of the compounds towards moisture and oxygen, density functional theory (DFT) calculations were performed to evaluate the origin of the pronounced reactivity. Based on the interesting results from the DFT studies, we investigated the influence of the manganese coordination sphere moving from all nitrogen to mixed O/N coordinated complexes, to optimize the physicochemical properties. The resulting Mn-ketoiminate class of compounds were successfully isolated and characterized in detail. A direct comparison of the all N- with the mixed O/N-coordinated Mn precursors in terms of the precursor characteristics relevant for ALD applications was performed which will be presented in this contribution.

AF-MoP-34 Surface Reactions During Nitrogen-Based Plasma Irradiation in Plasma-Enhanced Atomic Layer Deposition (PE-ALD) of Silicon Nitride,

Abdullah Y. Jaber, Center for Atomic and Molecular Technologies - Osaka University, Japan*; M. Isobe, T. Ito, K. Karahashi, S. Hamaguchi,* Center for Atomic and Molecular Technologies, Osaka University, Japan

Plasma-enhanced atomic layer deposition (PE-ALD) plays an important role in uniform thin films deposition for semiconductor manufacturing with a large area and high accuracy. Silicon nitride (SiN) thin films are widely used in semiconductor devices. Typical technical challenges of developing PE-ALD of SiN (and any other materials) are to form the films with desired qualities at relatively low surface temperature, and possibly on specific surfaces exclusively (i.e., area selective ALD). In a typical SiN PE-ALD process, Si and chlorine (Cl) containing precursors such as dichlorosilane (DCS) H_2SiCl_2 are adsorbed on the surface in the first half-cycle, and in the second half-cycle, Cl atoms are removed and SiN is formed by nitrogen(N_2) / hydrogen(H_2) or NH_3 plasmas. In the first half-cycle, the adsorption of precursors ends after a monolayer of Si is formed on the SiN surface with bonds terminated with Cl atoms, therefore the half-cycle is self-limiting. In the subsequent half-cycle, the plasma-based process is supposed to replace Cl on the surface with N and H atoms. The goal of this study is to understand the effects of nitrogen ions and hydrogen radicals on the removal of Cl atoms from the surface. We used molecular dynamics (MD) simulations to analyze how the Cl-terminated surface interacts with incident N_2^+ ions and H radicals. The simulation results showed that most Cl atoms are removed with H radical irradiation with and without N_2^+ ions after H dose around $1.3\text{x}10^{16}$ (H atoms/cm^2). Incident N_2^+ ions also remove Cl atoms from the surface while they nitride Si deposited on the surface, but the amount of Cl removed from the surface is limited in this case. In addition, knock-on collisions transfer some Cl atoms to a deeper layer, enhancing the Cl contamination of the surface. Incident NH_3^+ ions also remove more Cl atoms than N_2^+ ions only. This means that H plays an important role in converting desorbed precursors such as DCS to SiN in the N_2/H_2 or NH_3 plasma irradiation step. It was also confirmed that MD simulation results and available experimental observations showed good agreement.

AF-MoP-35 Effects of Oxidant and Substrate on Film Properties and Interlayer Formation of Atomic Layer Deposited ZrO_2 Films,

***Seonyeong Park**, S. Na,* Yonsei University, Korea*; Y. Lee,* Stanford University*; S. Chung, H. Kim,* Yonsei University, Korea

In the early stage of dynamic random access memory (DRAM) development, the thickness of the dielectric SiO_2 has been reduced in the Si based two dimensional structure to obtain high integration density and capacitance. However, as the DRAM devices have been continuously scaled down, thickness of SiO_2 reached a fatal limit of reaching the physical thickness at which leakage current due to tunneling effect occurs. To break through this, SiO_2 was replaced by high dielectric constant (k) materials[1]. Among the various high-k materials, ZrO_2 is one of the promising materials since it has good thermal stability, high dielectric constant (k~30) and wide bandgap (5.16-7.8 eV)[2,3]. However, when high-k thin film is deposited on TiN, which is widely used as an electrode, the electrical properties of the thin film are deteriorated such as increased leakage current density due to the interlayer formed between high-k film and TiN[4,5].

The interlayer formed between the substrate and dielectric film occurs due to the oxidation of the electrode during the film deposition process, which is affected by the potential barrier height of the oxidation reaction[6]. Since the potential barrier height depends on the work function of the metal electrode, proper selection of the electrode is required. Studies have been reported on replacing the top electrode with Pt, Au, Ag, etc.[6], but these have the disadvantages of being expensive, which makes difficult to easily apply to real industry. Recently, Ru is recognized as a promising material because of its good thermal stability, low resistance, high work function, and relatively inexpensive among noble metals[7]. In this study, we used sputtered Ru as a top electrode and compared effects of bottom electrode using Ru and TiN on ZrO_2 film properties. In addition, to find the proper oxidant to reduce the oxidation of the substrate, the film properties using the two oxidants (oxygen plasma and hydroperoxide) were also compared and analyzed. For ultrathin high quality ZrO_2 film, atomic layer deposition (ALD) has been used, which can secure atomic layer controlled ZrO_2 film with high conformality and high uniformity.

*Corresponding author: hyungjun@yonsei.ac.kr

[1] Chemical Reviews 99, 1823-1848 (1999)

[2] Reports on Progress in Physics 69, 327-396 (2006)

[3] Journal of Materials Science 53, 15237-15245 (2018)

[4] Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structure 27, 378 (2009)

[5] Solide-State Electronics 115, 133-139 (2016)

[6] Microelectronic Engineering 87, 98-103 (2010)

[7] Microelectronic Engineering 85, 39-44 (2008)

AF-MoP-36 Zinc Precursor Development for Future ALD Film Applications,

***Atsushi Sakurai**, M. Hatase, M. Enzu, A. Yamashita, Y. Ooe, K. Takeda, R. Fukushima,* ADEKA CORPORATION, Japan

ZnO has attractive physical properties such as being an intrinsically n-type semiconductor, having a wide bandgap and high electron mobility. Recently, we have seen an increasing number of stable p-type ZnO devices. Furthermore, 2T0C (two transistor zero capacitor) configuration using IGZO (indium gallium zinc oxide) transistor has been deemed a strong candidate for future 3D memory devices thanks to extremely low I_{off} of IGZO TFTs [1]. Diethyl zinc (DEZ) is the preeminent zinc precursor used to make many types of Zn-based ALD thin films such as zinc oxide, sulfide and nitride [2]. However, DEZ has poor thermal stability and can leave carbon impurities in zinc-based films grown at elevated temperatures. Furthermore, it has been pointed out that DEZ has an undesirable pyrophoric nature when exposed to air. Over the years, we have synthesized many kinds of zinc precursors (amide, alkyl, alkoxide, β-diketiminato, β-diketonato, etc.) which have a wide range of TGA delivery temperatures (Fig.1) and thermal stabilities in order to be compatible with future ALD applications. One interesting example of a new ALD Zn precursor is $[Et_2NCH_2CH_2CH_2]_2Zn$ named as ZNP-2 whose structure has two zinc-carbon bonds with pendant amines at the ligand terminal. Fig.2 shows the cross-sectional SEM image of the ALD ZnO film which was made using the ZNP-2 precursor and H_2O as the co-reactant at 200℃. In addition to the ZNP-2 precursor, we will introduce more detailed structures and physical properties on the other zinc precursors as well as some ALD film data during the conference.

[1] Attilio Belmonte, IEDM2020, 28.2, [2] Shaibal Sarker, ALD2015

AF-MoP-37 Conformal Deposition of B_xC Thin Films from Triethylboron,

***Arun Haridas Choolakkal**, H. Högberg, J. Birch, H. Pedersen,* Linköping University, Sweden

Boron carbide (B_xC) films enriched in ^{10}B is a promising neutron converter material for the next generation solid-state neutron detectors. Upon neutron irradiation, ^{10}B produce detectable particles by the nuclear reactions $^{10}B + n^0 \rightarrow {}^7Li$ (0.84 MeV) + ^4He (1.47 MeV) + ϒ (0.48 MeV) and $^{10}B + n^0 \rightarrow {}^7Li$ (1.02 MeV) + ^4He (1.78 MeV) that have 94% and 6% probability, respectively. Since the world has a ^3He shortage, ^{10}B solid-state detectors can potentially be a replacement to ^3He detectors in large scale neutron facilities. For the next generation high resolution ^{10}B detectors, films enriched in the ^{10}B isotope must be deposited on pixelated sensor-chip substrates with high aspect-ratio morphologies. For such geometries, the currently employed magnetron sputtering technology is limited which highlight the need for alternative deposition techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). In addition, a low temperature process is required since the detector requires ohmic contacts which needs to be coated before converter layer deposition.

For coating high aspect-ratios, ALD would be the obvious choice, but the lack of ALD carbon precursors as well as carbide processes makes conformal continuous CVD processes a promising synthesis route. From our investigation, we report moderate temperature CVD of B_xC thin films on silicon substrates with 8:1 aspect-ratio morphologies, using triethylboron (TEB, $^{nat}B(C_2H_5)_3$) as single source CVD precursor. Step coverage (SC) calculated from the cross-sectional scanning electron microscopy measurements shows that films deposited at ≤450 °C were perfectly conformal (SC = 1). We attribute this to the low reaction probability at low substrate temperatures enabling more gas phase diffusion into the features. The quantitative analysis using time of flight elastic recoil detection analysis (ToF-ERDA) and X-ray photoelectron spectroscopy (XPS) reveals that the as deposited films at 450 °C deposition temperature are B rich carbide material i.e., around 80% Boron, 15% carbon and 5% impurities, which is a promising B/C ratio for neutron detector application if ^{10}B isotope enriched TEB is used. The density of the material, measured by X-ray reflectometry measurements, varies from 1.9 to 2.28 g/cm^3 for the deposition temperatures varying from 425 to 550 ºC in steps of 25 °C.

This study shows that B_xC can be grown conformally by CVD at temperatures matching the thermal budget for the fabrication process and with a total B content which is on par with current state-of-the-art $^{10}B_4C$ films from neutron converters deposited by magnetron sputtering.

AF-MoP-38 Effect of Insulator-to-Metal Transition (Imt) in Vo₂ Deposited by ALD

Aline Jolivet, *J. Cardin, C. Frilay,* CIMAP Normandie Université, ENSICAEN, UNICAEN, CEA, CNRS, France*; O. Debieu,* CIRIMAT-INPT, France*; P. Marie, S. Duprey, F. Lemarie, X. Portier, B. Horcholles,* CIMAP Normandie Université, ENSICAEN, UNICAEN, CEA, CNRS, France*; P. Bazin,* LCS Normandie Université, ENSICAEN, France*; J. More-Chevalier,* Institute of Physics, Czech Academy of Sciences, Czechia*; P. Fitl,* Institute of Physics, Czech Academy of Sciences, , Czechia*; S. Cichoň, J. Lančok,* Institute of Physics, Czech Academy of Sciences, Czechia*; W. Jadwisienczak,* School of Electrical Engineering and Computer Science, Ohio University*; D. Ingram,* Department of Physics and Astronomy, Ohio University*; C. Labbé,* CIMAP Normandie Université, ENSICAEN, UNICAEN, CEA, CNRS, France

Since its discovery in 1959, vanadium dioxide (VO_2) is well-known for its Insulator-to-Metal Transition (IMT) around 70 °C just above room temperature (RT). Over the last decade, it has gained interest because of its potential applications for resistive switching systems, energy storage in lithium-ion batteries, supercapacitors, infrared detectors, or thermochromic materials[1]. Due to its low-temperature process, Atomic Layer Deposition (ALD) offers a real industrial advantage in the growth of VO_2, allowing to run deposition with low energy consumption and therefore low cost, and on substrates that can be temperature sensitive.

In this context, vanadium oxide films were deposited on both silicon (100) and glass substrates at 240 °C from vanadium tri-isopropoxide (VTIP) and water as an oxidizing agent. Films were grown with different thicknesses, ranging from 30 nm to 120 nm, and then annealed for one hour under forming gas (95% Ar, 5% H_2) at a temperature ranging from 400 °C to 550 °C by 50 °C steps.

According to a structural analysis held by X-ray diffraction (XRD) and transmission electron microscopy (TEM) as-deposited vanadium oxide films were amorphous and change morphology to polycrystalline with an admixture of VO_2 and V_2O_5 phases having crystallites size reaching 300 nm after annealing. The elemental analysis was performed by RBS and XPS studies will also be presented for a deeper understanding of their composition and stoichiometry.

VO_2 films were also characterized electrically and optically using resistivity measurements, and spectroscopic techniques such as Raman, FTIR, ellipsometry. All experimental results show a reversible and reproducible IMT around 70 °C for films annealed at 500 °C. For electrical measurements, the resistivity decreases down to 10^{-1} Ω.cm upon IMT temperature. The optical ones show a particularly interesting result by FTIR spectroscopy on VO_2 films on silicon substrate, with an optical absorbance of 0.1 OD at RT which increases up to 0.9 OD above IMT temperature on a wavenumber range extending from 4000 to 1000 cm^{-1}. The phase transition is also observable in the UV-visible range on VO_2 films on glass substrate and is correlated with the appearance or disappearance of low-temperature VO_2 peaks in Raman spectroscopy.

In conclusion, vanadium oxide films deposited by ALD were analyzed between RT and 100 °C and present promising properties tunable with temperature, especially in the IR range, and paves the way for future applications in thermochromic materials.

1. Atomic layer deposition of vanadium oxides: process and application review. Mater. Today Chem. 12, 396–423 (2019).

AF-MoP-39 New ALD Processes for Y₂O₃ Using Molecularly Engineered Yttrium Formamidinates

Sebastian Beer, *N. Boysen,* Ruhr University Bochum, Germany*; A. Muriqi,* Tyndall National Institute, University College Cork, Ireland*; D. Zanders,* Ruhr University Bochum, Germany*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; A. Devi,* Ruhr University Bochum, Germany

Yttrium oxide (Y_2O_3) thin films have been a subject of intensive research, particularly as an alternative high-k dielectric, due to its high relative permittivity (e_r ~17-20) and large bandgap of 5.5 eV. Furthermore, its high chemical resistivity and mechanical strength facilitate its application as a passivation layer in many fields.

Atomic layer deposition (ALD) has been established as one of the most promising techniques for the growth of high-quality layers for the above mentioned applications. As the precursor selection plays a pivotal role in an ALD process, the development of compounds with an optimal combination of volatility, reactivity and thermal stability is needed.

Besides the established Y precursors, such as β-diketonates or cyclopentadienyls, the all-N coordinated class of the amidinates[1] and guanidinates[2] has emerged as a promising class for the fabrication of yttrium-based materials. Recently, the structurally related formamidinate (famd) ligand class (*N,N'*-dialkyl-formamidinato) was explored, exhibiting a high volatility, reactivity, and stability.[3]

In this study, we focused on the systematic molecular engineering of Y formamidinates to fine–tune the physicochemical properties through a variation of the alkyl side chains. Among the four evaluated precursors, the *tert*butyl-substituted $[Y(^tBu_2\text{–famd})_3]$ showed an increased thermal stability and high reactivity towards H_2O, as revealed by thermal analysis and density functional theory (DFT) studies, respectively.

Subsequently, a thermal ALD process for Y_2O_3 using H_2O as co-reactant was developed, yielding dense *fcc*-Y_2O_3 films on Si substrates with smooth topography. Owing to the appealing structural, compositional and morphological quality of the layers, the process was used to deposit Y_2O_3 as a dielectric component in metal insulator semiconductor (MIS) capacitor structures.[4] The promising electric properties set a strong platform for in-depth studies to understand the interplay between precursor chemistry, ALD process development and integration in capacitor structures.

Literature:

[1] de Rouffignac, P., Park, J.-S., Gordon, R. G., *Chem. Mater.*, **2005**, 17, 19, 4808-4814.

[2] Mai, L., Boysen, N., Subasi, E., de los Arcos, T., Rogalla, D., Grundmeier, G., Bock, C., Lu, H.-L, Devi, A., *RSC Adv*., **2018**, 8, 4987.

[3] Boysen, N., Zanders. D., Berning, T., Beer, S. M. J., Rogalla D., Bock, C., Devi, A., *RSC Adv.*, **2021**, 11, 2565-2574.

[4] Beer, S. M. J., Boysen, N., Muriqi, A., Zanders, D., Berning, T., Rogalla, D., Bock, C., Nolan, M., Devi, A., *Dalton Trans*., **2021**, 50, 12944-12956.

AF-MoP-40 Nb/V-Doped Transparent Conductive TiO₂ Films Synthesized by ALD: Effect of Dopant Content and Growing Conditions

Getaneh Diress Gesesse, CIMAP ENSICAEN, France*; O. Debieu,* CIRIMAT, Université de Toulouse, CNRS, Université Toulouse, France*; A. Jolivet, C. Frilay, S. Duprey, X. Portier, C. Dufour, P. Marie, C. Labbé,* CIMAP Normandie Université, ENSICAEN, UNICAEN, CEA, CNRS, France*; M. El-Roz,* Laboratoire Catalyse et Spectrochimie, CNRS, ENSICAEN, Université de Caen, France*; J. Cardin,* CIMAP Normandie Université, ENSICAEN, UNICAEN, CEA, CNRS, France

Titanium dioxide (TiO_2) is a wide bandgap (3.0-3.20 eV) material that presents high transparency in the visible range; besides, it has a high refractive index. TiO_2 doping is widely investigated to induce structural and electronic modifications that may improve electronic properties and photocatalytic activities. Due to their additional electron compared to Ti and their atomic radius slightly above and below the one of Ti, Nb and V are the most promising candidates among the potential dopants of TiO_2. In this context, this work aims to synthesize Nb/V-doped TiO_2 films by atomic layer deposition (ALD) with various dopant concentrations and growing conditions.

Nb/V-doped TiO_2 films were deposited on Si wafer and glass substrates with water as oxidizing agent using a shared ALD window for precursors niobium (V) ethoxide or vanadium (V) oxytriisopropoxide and titanium isopropoxide, respectively. The dopant content was adjusted by the dopant ratio (R_{Nb} or R_V: range from 0 to 1), which is the number of dopant cycles over the total number of ALD cycles. Films were then annealed in N_2 or forming gas (95% N_2 and 5% H_2) at different temperatures of 400, 500, and 600 °C for 1 hour. To investigate the characteristics of films, various techniques, such as spectroscopic ellipsometry, spectrophotometry, GI-XRD, Raman, FTIR, HRTEM, XRR, and four-probe resistivity were used for the as-deposited and annealed Nb/V-doped TiO_2 films.

It was observed that when introducing Nb or V into the TiO_2 matrix up to a doping ratio of 0.025, the thickness increased slightly compared to the undoped TiO_2 film, and then gradually decreased as the dopant ratio increases further. For both dopants, the refractive index and the electronic density of films were found to evolve similarly and in the opposite way to their thickness. In the as-deposited Nb-doped TiO_2 films with R_{Nb} = 0-0.025, the presence of the crystalline anatase phase was identified, but the peak intensity decreased and progressively shifted as R_{Nb} increased. In the case of the as-deposited V-doped TiO_2 film, only an amorphous phase was obtained which transform into crystalline phase with annealing.

After annealing, the optical transmittance and electrical resistivity of anatase phase crystallized films were measured for Nb/V-doped TiO_2 films. With increasing R_{Nb}, the films showed transmittance ranging from 60 to 80% in the visible range, which increase with the conductivity (~10^2 S.cm^{-1}). The optical and electrical properties of V-doped TiO_2 film are also performed and will be further discussed.

This work highlights the significant role of Nb and V dopants in tuning the structural, optical, and electrical property of TiO_2.

**AF-MoP-42 Atomic Layer Deposition of Tin Oxide Thin Films Using a New Liquid Precursor Bis(methylcyclopentadienyl) Tin*, Makoto Mizui,* *N. Takahashi, F. Mizutani,* Kojundo Chemical Laboratory Co., Ltd., Japan*; M. Inoue, T. Nabatame,* National Institute for Materials Science, Japan

Transparent conductive oxide thin films, including In-Sn-O (ITO), Zn-Sn-O (ZTO), and In-Zn-Sn-O (IZTO) films, have attracted attention for various applications such as flat-panel displays, sensors, and solar cells. We have reported the atomic layer deposition (ALD) of In_2O_3 and ZnO thin films using cyclopentadienyl-based precursors [1, 2]. In order to deposit such transparent conductive oxide thin films by ALD, ALD-Sn precursor is indispensable. This time, we report ALD of tin oxide (SnO_x) thin films using a new liquid cyclopentadienyl-based precursor.

Bis(methylcyclopentadienyl) tin, $Sn(MeCp)_2$, was synthesized as a liquid precursor. Differential scanning calorimetry (DSC) was conducted to measure its thermal decomposition temperature. The decomposition temperature was estimated approximately 220 °C, so the deposition temperature was set to 200 °C, which is the same temperature in the case of ALD of In_2O_3 and ZnO thin films [1, 2]. The vapor pressure of $Sn(MeCp)_2$ was determined by directly measuring equilibrium vapor pressures at several points. From the Clausius-Clapeyron plot for $Sn(MeCp)_2$, the precursor temperature was set to 130 °C, which corresponds to the vapor pressure of approximately 10 Torr.

SnO_x thin films were deposited on 150 mm Si wafers with native oxide films. ALD process was conducted by using $Sn(MeCp)_2$ as a precursor, and remote O_2 plasma as an oxidant. Linear growth of SnO_x thin film was observed when 0.1 s $Sn(MeCp)_2$ and 10 s O_2 plasma pulse times were applied. The growth per cycle (GPC) was approximately 0.06 nm/cycle with this ALD condition. This growth rate was rather slow compared with a previous experiment using tetrakis(dimethylamino)tin (TDMASn) as a precursor and remote O_2 plasma as an oxidant (~0.11 nm/cycle) [3]. One possible reason is that the deposition density was small due to steric hindrance of MeCp ligands. On the contrary, by applying H_2O for 10 s in the place of O_2 plasma, GPC was significantly small (~0.005 nm/cycle).

SnO_x thin films were deposited by ALD using a new cyclopentadienyl-based precursor $Sn(MeCp)_2$, and linear growth of SnO_x thin film was confirmed.

References

[1] F. Mizutani, S. Higashi, M. Inoue, and T. Nabatame, AIP Advances **9,** 045019 (2019).

[2] F. Mizutani, M. Mizui, N. Takahashi, M. Inoue, and T. Nabatame, ALD2021, AF1-10 (2021).

[3] M. A. Martínez-Puente, J. Tirado, F. Jaramillo, R. Garza-Hernández, P. Horley, L. G. S. Vidaurri, F. S. Aguirre-Tostado, and E. Martínez-Guerra, ACS Appl. Energy Mater. **4,** 10896 (2021).

**AF-MoP-43 Growth Rate of Atomic Layer Deposition of Zinc Oxide Thin Films Using Bis(*n*-propyltetramethylcyclopentadienyl)zinc*, Fumikazu Mizutani,* *M. Mizui, N. Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan*; M. Inoue, T. Nabatame,* National Institute for Materials Science, Japan

We have reported the atomic layer deposition of zinc oxide thin films using cyclopentadienyl-based precursors, bis(*n*-propyltetramethylcyclopentadienyl)zinc, $Zn(Cp^{pm})_2$, which is expected to deposit high-purity ZnO thin films [1, 2]. At that time, ZnO thin films were deposited at 200 °C on 150 mm Si wafers with native oxide films, and the ALD process consisted of alternating exposure to $Zn(Cp^{pm})_2$ and oxidants, H_2O followed by an O_2 plasma. However, the growth rate (GPC) was very small, about 0.02 nm/cycle or less. Until then, the precursor was supplied by vapor draw type or Ar assist type, so it was presumed that the reason for the small GPC was the low chemisorption coverage for low supply of the precursor. Therefore, we tried to increase the GPC by supplying the precursor by Ar bubbling type, which can supply a sufficient amount of precursor even at a low vapor pressure.

Other than supplying $Zn(Cp^{pm})_2$ by Ar bubbling, ZnO thin films were deposited on 150 mm Si wafers with native oxide films as before, and the ALD process consisted of alternating exposure to $Zn(Cp^{pm})_2$ and oxidants, H_2O followed by an O_2 plasma. As previously reported, the Clausius-Clapeyron equation for $Zn(Cp^{pm})_2$ is $\log_{10}P$ (Pa) = -2502 / T (K) + 8.84, so the temperature of $Zn(Cp^{pm})_2$ was set to 70 °C where the vapor pressure of $Zn(Cp^{pm})_2$ is 0.3 Torr. The ZnO thin film was deposited for 30 cycles with the H_2O pulse time and the O_2 plasma pulse time fixed at 30 s and 15 s, respectively, and increasing the $Zn(Cp^{pm})_2$ pulse time from 5 s to 30 s. The film thickness of the obtained ZnO thin film increased as the pulse time increased, and was saturated around 20 s. The film thickness was about 7 nm when the Zn pulse time was 20 s to 30 s. Therefore, the GPC is about 0.2 nm/cycle or more, which is an extremely large increase compared to the previous GPC of about 0.02 nm/cycle or less.

Next, when a ZnO thin film was deposited with a $Zn(Cp^{pm})_2$ pulse time of 30 s, an H_2O pulse time of 30 s, and no O_2 plasma pulse, it was deposited without nucleation delay, and the film thickness was about 8 nm. Without the O_2 plasma pulse, the GPC would be slightly larger, as OH groups remained on the surface during the $Zn(Cp^{pm})_2$ pulse, increasing the amount of chemisorption.

Thus, if this $Zn(Cp^{pm})_2$ precursor is sufficiently supplied by Ar bubbling or the like, it can be deposited on a silicon wafer with a native oxide film without nucleation delay, and a large GPC of 0.2 nm / cycle or more can be obtained.

References

[1] F. Mizutani, S. Higashi, N. Takahashi, M. Inoue, and T. Nabatame, ALD2020, AF-MoP70 (2020).

[2] F. Mizutani, M. Mizui, N. Takahashi, M. Inoue, and T. Nabatame, ALD2021, AF1-10 (2021)

AF-MoP-44 Monte Carlo Simulation in a Laptop for Understanding Physical Interaction of Atomic Layer Deposition Precursors*, Bonwook Gu,* Incheon National University, Korea (Republic of)*; N. Le, C. Nguyen,* Incheon National University, Viet Nam*; S. Yasmeen,* Incheon National University, Pakistan*; K. Youngho,* Incheon National University, Korea (Republic of)*; H. Lee,* Incheon National University, Korea (Republic of)

Since the reaction of atomic layer deposition (ALD) strongly depends on surface property, understanding of surface reaction mechanism between substrates and precursors is essential to predict and interpret thin film deposition in ALD. Recently, the many researchers have studied chemical reactions of ALD using density functional theory (DFT) and physical reaction using molecular dynamic (MD). However, DFT is suit for calculating a few of molecule adsorption but not simultaneous multiple adsorptions, and MD is not proper for a large scale simulation due to huge computing resource and long calculation time. In addition, although the steric hindrance effect between the molecules is an important physical factor for simulation of ALD, but it was not considered as a main variable for simulation. In this study, by adopting several assumptions and approximations, we developed a simple simulation method to understand physical steric hindrance effects of ALD precursors by using Monte Carlo (MC) without huge computing resources and applied the method to study surface reaction mechanism of ALD and area selective ALD (AS-ALD). We calculated the areal coverage of precursor on a specific surface used in ALD and AS-ALD using the MC simulation with a random adsorption model. The simulation results show high consistency agreement with experiment data. Based on the 2D model developed first, we extended the MC simulation to 3D system, and obtained reliable results in bulky precursor systems. The simulation method developed in this study could be applied to many of ALD precursors and AS-ALD inhibitor systems just by using a laptop computer.

AF-MoP-45 Atomic Layer Deposition of Tin Monosulfide Films Using a Novel Cyclic Amide Divalent Metalorganic Precursor and H_2S

Mohd Zahid Ansari, School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)*; P. Janicek,* 2Institute of Applied Physics and Mathematics, Faculty of Chemical Technology, University of Pardubice, Czechia*; D. Nandi,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)*; B. Shong,* Department of Chemical Engineering, Hongik University, Korea (Republic of)*; S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Tin (II) sulfide has emerged as an alternative light absorber and optoelectronics material, but its utilization is limited by lacking of purity due to various oxidation states of Sn. In this work, a better quality and stoichiometric SnS thin films were prepared by atomic layer deposition (ALD) using a novel metal-organic liquid precursor, N, N′-di (t-butyl)-2-methyl-1,2-propanediamino tin(II) (Sn (dmpa)) and H_2S. The current ALD system showed distinctive ALD features, such as a self-limited growth, well-defined wide range ALD window between 75 to 175°C, and direct dependency on the number of ALD cycles on the film thickness. Interestingly, the proposed ALD-SnS process shows relatively high growth rate (GPC) value of 0.13 nm/cycle with no incubation delay at 125°C. DFT calculations are performed to investigate the surface reactions and self-limiting nature of the Sn precursor. The surface reactions are found to be feasible even at room temperature with either low- or high-coverage of the thiol group. The obtained films were characterized by several characterization techniques and found that the crystalline SnS films could be grown even at room temperature (25°C) to a high temperature of 250°C on a thermally grown SiO_2 substrate. Mix phase of cubic (π) and orthorhombic (o) SnS films are possible at below 100°C, whereas only orthorhombic phase is stable at above 125°C and SEM verified that the SnS films with different structures have different surface morphologies. The as-grown SnS film's purity was analyzed using Rutherford backscattering spectrometry, and X-ray photoelectron spectroscopy analyses, confirmed the deposition of a stoichiometric tin monosulfide (S/Sn=1) phase with negligible impurities. The optoelectronic properties (band-gap, refractive index, and extinction coefficient) of the SnS films were further evaluated via spectroscopic ellipsometry (SE) analysis. The results from the SE analysis supported the observed change from mixed π-SnS and o-SnS to o-SnS with increasing temperature and allowed the determination of the energy bandgap (~1.1 eV) and a relatively broad semi-transparent window (up to 3000 nm). This newly ALD SnS process may have an immersive range of favorable prospects to utilize in temperatures compatible applications.

Acknowledgments:This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (2021R1A2C1007601). The authors appreciated the financial support from grant LM2018103 by the Ministry of Education, Youth, and Sports of the Czech Republic. The precursor used in this study was provided by Hansol Chemical Co. Ltd., Korea.

AF-MoP-46 Density Functional Theory Study on the Selective Capping of Cobalt on Copper Interconnect

Khabib Khumaini, *R. Hidayat,* Sejong University, Korea (Republic of)*; T. Mayangsari,* Universitas Pertamina, Indonesia*; T. Chowdhury, H. Kim,* Sejong University, Korea (Republic of)*; S. Lee,* DNF Co. Ltd., Korea (Republic of)*; W. Lee,* Sejong University, Korea (Republic of)

As the scaling of Cu interconnect systems continues, electromigration (EM) has emerged as a problem. The EM is mainly due to the movement of Cu atoms through the interface between Cu wire and the dielectric barrier. The selective Co capping on Cu improves the interface, resulting in increased EM lifetime. However, studies on the mechanism of the selective growth of Co on Cu over the inter-metal dielectrics are rare. The chemisorption of $CpCo(CO)_2$ on Cu and SiO_2 substrates was studied by density functional theory (DFT) calculation [1]. However, endothermicity on both substrates cannot explain the experimental reports [2]. Therefore, we studied the mechanism of selective Co growth using $CpCo(CO)_2$ on Cu over SiO_2 by DFT. We attempted to build reliable substrate models and consider all possible reaction pathways. We also investigated the roles of H_2 co-reactant and the silylation treatment of SiO_2. The calculation results show that H_2 plays a critical role on the Cu substrate but acts as a spectator on the SiO_2 substrates. The chemisorption was exothermic on Cu by forming H_2CO or CO, and H_2 lowered the activation energy from +1.09 eV to +0.62 eV. Contrarily, the reaction was endothermic on the –OH terminated SiO_2 releasing CO, which explains the origin of selective growth of Co on Cu. The chemisorption on the $–SiMe_3$ terminated SiO_2 surface showed the activation energy of +1.74 eV, which is higher than +1.35 eV on the –OH terminated SiO_2. Therefore, the silylation treatment can effectively improve the selectivity of $CpCo(CO)_2$ chemisorption on Cu over SiO_2, especially at high temperatures. Our DFT simulation successfully explains the mechanism of experimental observations on CVD Co.

[1] Adamczyk, A. J., et al. Computer Aided Chemical Engineering. 44. Elsevier, 2018. 157.

[2] Ryu, S. W., et al. Current Applied Physics. 16 (2016) 88.

AF-MoP-47 A New Low Temperature PEALD Process for HfO_2 Thin Films

Florian Preischel*, D. Zanders,* Ruhr University Bochum, Germany*; A. Kostka,* Ruhr-University Bochum, Germany*; D. Rogalla, A. Devi,* Ruhr University Bochum, Germany

With its high permittivity and large band gap of E_g = 5.7 eV, HfO_2 is of significant interest for high-*κ* dielectric layers and excellent resistance ratios as well as fast switching speeds are reported for HfO_2 based memristor devices. To realize these microelectronic components, the deposition of pinhole-free thin films with an excellent uniformity and conformality is required. Owing to its saturative growth characteristics, atomic layer deposition (ALD) intrinsically fulfills these requirements. Plasma-enhanced ALD (PEALD) furthermore allows thin film depositions at low temperatures, as required for future flexible electronics, and is thus the method of choice. To enable the beneficial features of ALD, the physico-chemical properties of the precursor need to be carefully fine-tuned in order to optimize its thermal stability, volatility as well as reactivity. Looking for Hf precursors that fulfill these prerequisites, we investigated new heteroleptic Hf complexes. Starting from the parental Hf dialkylamide, we introduced a chelating formamidinate ligand that stabilizes and shields the Hf center, thereby increasing the thermal stability of the resulting complexe while retaining adequate reactivity and volatility. The resulting bis-(dialkylamido)-bis-(formamidinato) Hf(IV) precursor was synthesized on a multigram scale, structurally characterized and evaluated by thermogravimetric analysis and subsequently employed as a precursor for the deposition of HfO_2 in a PEALD process. Using an oxygen plasma, the typical ALD characteristics of precursor saturation, linearity and ALD temperature window were demonstrated with constant growth of 0.7 Å per cycle from 125 °C to 200 °C on Si(100) substrates. The resulting HfO_2 films were further characterized by RBS/NRA, XPS and AFM, revealing the formation of pure and smooth HfO_2 layers. Compared to our previous work [1] with a closely related guanidinate precursor, shorter plasma pulses were sufficient to achieve ALD growth, preventing the formation of an interfacial SiO_2 layer, as revealed by transmission electron microscopy (TEM). By coating polyimide (PI) foils at temperatures as low as 150 °C, there is a potential of implementing the presented low-temperature HfO_2 PEALD process into the development of flexible electronic devices in the future.

[1] D. Zanders et al., *ACS Appl. Mater. Interfaces*, 106 (**2019**) 28407

AF-MoP-48 Density Functional Theory Study on Atomic Layer Deposition of Silicon Nitride using Chlorosilane-type Precursors

Tanzia Chowdhury*, R. Hidayat, K. Khumaini, H. Son, H. Kim, W. Lee,* Sejong University, Korea (Republic of)

Silicon nitride thin film is an essential dielectric material in semiconductor devices. Recently, three-dimensional vertical NAND flash memory devices utilized it as a charge trapping and sacrificial layers. There have been a variety of silicon nitride ALD processes, including thermal and plasma-assisted schemes. Thermal ALD, which benefits from excellent step coverage, is typically achieved with chlorosilane-type precursors, such as dichlorosilane (SiH_2Cl_2) and hexachlorodisilane (Si_2Cl_6), using ammonia (NH_3) as the co-reactant. The reaction mechanism of thermal ALD was reported by experimental and computational studies [1,2]. However, most density functional theory (DFT) studies focused on a single reaction pathway for each precursor. For disilane or trisilane-type precursors having Si-Si bonds, the comparison between multiple reaction pathways is necessary, which is crucial to have a good insight into the film growth and resulting properties. Thus, in the present study, the comprehensive reaction mechanism of ALD silicon nitride using Si_2Cl_6 and Si_3Cl_8 was studied by DFT. The chemisorption of the silicon precursors was modeled and simulated on an NH_2/NH-terminated silicon nitride substrate. Multiple possible reaction pathways assuming the dissociation of a Si–Si or Si–Cl bond were considered, along with different initial orientations of the precursor molecule. For Si_2Cl_6, the most exothermic reaction pathway was the cleavage of a Si-Cl bond to form $–NHSi_2Cl_5$ surface group along with a $–NH_3^+Cl^-$ as the byproduct. For Si_3Cl_8, the most exothermic pathway was the cleavage of a Si–Si bond, forming $–NHSiCl_3$ and Si_2Cl_5H byproduct. The activation energies of exothermic pathways will be calculated and compared to determine the most feasible pathway.

[1] L.L. Yusup et al., Appl. Surf. Sci., 432 (2018) 127.

[2]G. Hartmann et al, Phys. Chem. Chem. Phys., 20 (2018) 29152.

AF-MoP-49 PE-ALD of SiO_2 and Ti-doped SiO_2 in High Aspect Ratio Structures using Low Cost Precursors*, **Véronique Cremers**, G. Rampelberg, A. Werbrouck, J. Dendooven, C. Detavernier,* Ghent University, Belgium

PE-ALD of SiO_2 has been well studied in the past years, and has found a lot of applications as e.g. for advanced lithograpy, dielectric material in microelectronic devices, photovoltaics and optical applications. For these purposes where a high film quality is required in combination with a limited throughput, the use of more expensive precursors is justified. However, in recent years PE-ALD of SiO_2 found its way towards high surface applications as e.g. the encapsulation of OLEDS or deposition of anti-reflective coatings where precursor cost is a much bigger issue.

In this work, the PE-ALD growth characteristics of SiO_2 was investigated using four precursors in a different price setting: Bis(diethylamino)silane (BDEAS), (3-Aminopropyl)triethoxysilane (APTES),Tetraethyl orthosilicate (TEOS) and Hexamethyldisilazane (HMDS) (in order of high to low precursor cost price), in combination with oxygen plasma as a reactant.

Although it was possible to deposit SiO_2 with all four ALD processes, a significant difference in growth rate was observed. The growth rate varied from 1 Å/cycle for BDEAS to 0.2 Å/cycle for the TEOS-based process (Figure 1). Further the conformality of the four processes was investigated using macroscopic lateral structures with an equivalent aspect ratio (EAR) of 22. While BDEAS and APTES showed an excellent conformality, TEOS and HMDS showed a coated EAR of only 1 and 2.5 respectively. Here the coated EAR is defined as the EAR where the deposited film thickness equals 50% of the original film thickness.
In order to enhance the growth rate and conformality of these last two processes, TiO_2 subcycles were added to the TEOS and HMDS- based processes using titanium(IV)isopropoxide (TTIP) as a low-cost precursor. Both $Ti_xSi(1\text{-}x)O_2$ films showed a strong improvement in growth rate, from 0.2 to 0.5 Å/cycle for the TEOS-based process and from 3.5 to 6.2 Å/cycle for the HMDS-based process, using a 1 TTIP :9 TEOS/HMDS subcycle ratio. Besides the growth rate, also a strong improvement in conformality was observed as is shown in Figure 2. The coated EAR for the TEOS-based process increased from 2.5 to 17.5 and for the HMDS based process from 1 to 12 (in both cases for a 1:9 (TiO_2:SiO_2 subcycle ratio)). These results could be promising when (no-pure) SiO_2 films are required for high surface area applications where a low precursor cost is relevant.

AF-MoP-50 Importance of XPS Investigations of ALD Grown 2D Materials*, **Jhonatan Rodriguez Pereira**, R. Zazpe, J. Macak,* University of Pardubice, Czechia

The success of graphene opened a door for an extensive research and utilization of semiconducting 2D transition metal dichalcogenides materials (TMDCs) displaying a range of unique properties [1]. Molybdenum disulphide (MoS2), a TMDCs benchmark material, has been widely studied for multiple applications. In parallel, 2D diselenide and ditelluride analogues, i.e. MoSe2 and MoTe2, have also attracted important interest due to their intriguing properties, such as a higher electrical conductivity than that of MoS2 among others [2, 3].

Recently, we have demonstrated the ALD synthesis of both 2D MoSe2 [4-7] and 2D MoTe2 [8] (using an in-house synthesized precursors), as well as their outstanding performances in different applications. XPS turned a key tool to provide detailed chemical composition analysis of as-deposited 2D Mo-based TMDCs on substrates of different nature. Besides, the post-performance XPS characterization was appealing since the applications of the aforementioned 2D materials involved chemical and/or electronic processes on the surface and it enabled to identify potential chemical composition changes and physico-chemical photo-electro stability of the 2D TMDCs.

This presentation will thus focus on the XPS as key tool for assessment of chemical composition of both as-deposited and post-performance 2D Mo-based TMDCs, recent experimental results as well as the description of some inherent drawbacks that XPS must face during the analysis of the 2D materials.

References:

[1] A. V. Kolobov, J. Tominaga, Two-Dimensional Transition-Metal, Dichalcogenides. Springer Series in Materials Science, Springer International Publishing AG, Switzerland 2016

[2] D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao, Y. Cui, Nano Lett. 2013, 13, 1341.

[3] A. Eftekhari, Appl. Mater. Today 2017, 8.

[4] R. Zazpe et al, FlatChem 2020, 21, 100166

[5] J. Charvot et al, Chempluschem 2020, 85, 576

[6] J. Rodriguez-Pereira et al, Surf. Sci. Spectra 2020, 27, 024006

[7] R. Zazpe et al, ACS Appl. Nano Mater. 2021, 3, 12, 12034

[8] R. Zazpe et al, Appl. Mater. Today 2021, 23, 101017.

AF-MoP-51 Atomic Layer Deposition for Modification of Various 1D Nanomaterials*, **Jan Macak**, R. Zazpe, H. Sopha,* University of Pardubice, Czechia*; M. Rihova,* Brno University of Technology, Czechia*; L. Hromadko, S. Thalluri,* University of Pardubice, Czechia

One-dimensional nanomaterials – materials with one dimension outside the nanoscale, further noted as 1D NMs – represent a class of very important nanomaterials with continuously increasing importance. Due to their intrinsic features, unique properties and diversity of functionalities, they count among the most widely studied materials nowadays. While considerable research efforts have been spent to synthesize various 1D NMs (e.g. nanopores, nanotubes or nanofibers), limited efforts have been devoted to surface modification and property tailoring of these materials.

However, it is their surface that comes into direct contact with various media (air, gases, liquids, solids) and influences the reactivity, stability and biocompatibility of these materials. The surface and aspect ratio (defined as their diameter to length ratio) influence the performance of these materials in various applications. Considering these facts, it is more relevant to tailor the surface of these materials and to be able to influence their properties and reactivity at the nanoscale, rather than to deal with tailoring their own bulk material composition.

The focus of this presentation is on the modification of two types of 1D nanomaterials – nanotubes and nanofibers. Numerous techniques can be utilized for this purpose, such as for example wet chemical or physical deposition techniques. However, it is only the Atomic Layer Deposition (ALD) that is capable of really uniform and homogenous coating of these 1D nanomaterials, in particular those of very high-aspect ratio.

The presentation will be mainly focused on modification of TiO_2 nanotube layers and various nanofibers of different aspect ratios via ALD.

Experimental details and some very recent application examples [1-10] and structural characterizations of these modified materials will be discussed.

13. H. Sopha et al (2017), *Appl. Mater. Today*, *9*, 104.
14. H. Sopha et al. (2018), *Electrochem. Commun.,*97, 91.
15. S. Ng et al. (2017), *Adv. Mater. Interfaces*, 1701146.
16. F. Dvorak et al. (2019), *Appl. Mater. Today,* 14, 1.
17. H. Sopha et al. (2019), *FlatChem* 17, 100130.
18. M. Motola et al. (2019), *Nanoscale* 11, 23126.
19. S. Ng et al. (2020), *ACS Appl. Mater. Interfaces,* 12, 33386.
20. M. Motola et al. (2020) *ACS Appl. Bio Mater.* 3, 6447.
21. M. Motola et al. (2021) *Appl. Surf. Sci.*, 549, 149306.
22. M. Rihova et al. (2021) *Nanoscale Adv*., 3, 4589.

AF-MoP-52 Atomic Layer Deposition of Cobalt(II) Fluoride Thin Films*, **Elisa Atosuo**, M. Mäntymäki, K. Mizohata, M. Chundak, M. Leskelä, M. Ritala,* University of Helsinki, Finland

Cobalt(II) fluoride, among some other first-row transition metal fluorides, is an excellent cathode candidate for lithium-ion and sodium-ion batteries. These metal fluorides have high theoretical potentials and high energy densities compared to the current oxide-based cathodes. However, although ALD is recognized in lithium-ion and sodium-ion battery research in general, the number of ALD processes for fluoride-based battery materials has remained small. Particularly, these first-row transition metal fluorides have been lacking ALD processes. In this work, we present the first ALD process for cobalt(II) fluoride.

CoF_2 was deposited using $CoCl_2TMEDA$* and NH_4F as precursors. The films were characterized with XRD, EDS, XPS, ToF-ERDA, SEM, and AFM. The deposition temperature range studied was 180–300 °C, and all the deposition temperatures resulted in tetragonal CoF_2, as measured by XRD. Also XPS and ToF-ERDA confirm the films to consist of CoF_2. The impurity content measured with ToF-ERDA is low. Most importantly, the amounts of Cl and N, which are constituents of the precursors, are low, for example 0.53 and 0.08 at-% for a film deposited at 250 °C. The combination of a chloride-based precursor and NH_4F thus seems to work well in this case. The saturation of the growth per cycle with respect to pulse and purge lengths was confirmed at 250 °C, and the growth per cycle saturates to ~1.1 Å. In addition, the film thickness is linearly dependent on the number of applied cycles. Like many ALD metal fluorides, these films are rough, as seen in SEM and AFM. At a deposition temperature of 250 °C, for example, a ~60 nm film has a roughness of 12.6 nm.

*TMEDA: N,N,N′,N′-Tetramethylethylenediamine

AF-MoP-53 Mechanistic Aspects of the Indium Nitride Growth under Atomic Layer Deposition Conditions: A Multiscale Modelling Study

__Giane Damas__, IFM, Sweden*; K. Rönnby,* Linköping University, IFM, Sweden*; H. Pedersen, L. Ojamäe,* Linköping University, Sweden

The wurtzite form from Indium Nitride has semiconducting behavior that, combined with advantageous electron transport properties, has offered potential applicability of this material in the field of electronics and light-emitting diodes.[1] The InN thin film is preferentially obtained using atomic layer deposition (ALD) techniques, with lower temperatures that are beneficial for the crystal stability and enable the utilization of ammonia precursor at such conditions.[2] In the process, trimethylindium is a well-known In precursor that might undergo partial decomposition in the gas phase,[3] resulting in the CH_3 radical release that is expected to affect the initial steps of the reaction mechanism. In addition, this precursor usually leads to high level of carbon impurities that is inconvenient for large scale production. Therefore, this project aims at fully understanding the mechanistic aspects of the adsorption and reaction-related processes leading to the In-rich layer formation for InN crystal growth by using a multiscale approach that comprises density functional theory (DFT) and Kinetic Monte Carlo (KMC) computational techniques.

The atomic-scale periodic calculations are carried out within the Perdew–Burke–Ernzerhof (PBE) level of theory in VASP[4]. Initially, the thermal effects are neglected to enable a more extensive investigation of the relevant reaction pathways. Such effects are then added to approximate the model to the actual experimental conditions (T= 593 K, 1 bar). The outcome indicates that the initial decomposition steps whether they occur in the gas phase or at the surface both lead to the final product, *i.e.*methylindium (MI) chemisorbed at the *hcp* site and ethane. However, the N- rich layer leads to an activation of this process that is found to facilitate the precursor dissociation at the surface environment, with an activation enthalpy $\Delta^{\ddagger}H$ <20 kJ/mol for TMI/DMI displacement towards other stable adsorption sites. In a second step, the hydrogen atoms are subsequentially removed through the involvement of two additional precursor molecules to produce low-weight hydrocarbons. The results also suggest the origin of the carbon impurities to be the CH_3 radical released during the process that in turn can form a strong chemical bond with the N-rich layer. From this point, all data necessary for the KMC simulation at the mesoscale level are acquired, which shall also be presented.

References:

1-Bhuiyan, A. et al. *J. Applied Phys*. **94**, 2779 (2003).

2-Deminskyi, P. et al. *J. Vac. Sci. Technol.* A **37**, 020926 (2019).

3-Hwang, J. et al. *J. Electrochem. Soc*., **155**, 2 (2008).

4-Gresse, G. et al. *Comput. Mat. Sci.* **15**, (1996).

AF-MoP-54 Simple Nanoscale Thermal Techniques for the Measurement of ALD Grown Thin Films

__Thomas Pfeifer__, S. Makarem, P. Hopkins, University of Virginia, USA

Measuring the thermal resistances associated with ALD / MBE grown films is critical for their design and use in the semiconductor industry, however traditional measurement techniques such as Time or Frequency Domain Thermoreflectance (TDTR and FDTR respectively) come with complications limiting their widespread adoption.

In these traditional thermoreflectance techniques, two laser beams serve to heat the sample (pump), and subsequently monitor changes in reflectivity (probe), which corresponds to changes in temperature. In TDTR, the beams are pulsed, and the temperature decay over time is measured. This requires the use of a precisely aligned and calibrated delay stage to temporally offset the pump and probe pulses, making this technique impractical for many. In FDTR, a pulsed or CW beam can be used, and the phase offset between sinusoidal heating and a sinusoidal temperature response is monitored. Difficulties in eliminating a frequency-dependent systematic phase offset may make robust use of this technique difficult. in a more recently developed technique, Steady State Thermoreflectance (SSTR), the magnitude of the temperature response is monitored with varying pump intensity. This is limited to the measurement of one single parameter at a time however, and is typically only sensitive to the dominant thermal resistance in the system. SSTR also requires the use of a reference sample with an identical transducer in order to correlate a voltage as measured via the probe's photodetector to a known temperature rise.

We combine the principles behind SSTR (where the magnitude of the temperature response is roughly proportional to the net resistance), with that of FDTR (where the frequency-dependent response of the material system depends on all thermal properties). By examining the magnitude of the reflectivity response at multiple frequencies, we may now simultaneously measure multiple thermal parameters, such as thermal conductivity, volumetric heat capacity or thermal boundary conductance. This also enables the tightening of uncertainty of measured parameters. To validate this approach, we measure a variety of thin ALD-grown films (2-100nm) on several substrates (sapphire, silicon, diamond). All samples have an 80nm aluminum transducer deposited on top, and we measure the net thermal resistance across the ALD-grown film, in addition to the thermal conductivity of the substrate itself. We also measure bulk substrates, demonstrating the simultaneous measurement of thermal conductivity and heat capacity. We include robust uncertainty analysis to establish upper and lower bounds of measured values, and validate these results with an in-house TDTR system.

AF-MoP-55 Investigation of Tris(trialkylsilyl)Phosphides in Atomic Layer Deposition

__Jaroslav Charvot__, University of Pardubice, Czechia*; M. Barr, J. Bachmann,* University of Erlangen-Nürnberg, Germany*; F. Bureš,* University of Pardubice, Czechia

Phosphides are interesting materials among wide variety of scientific fields. InP and GaP are the most profound semiconductors with application in photovoltaics or electronics. Several ALD depositions of metal phosphides were already presented. Apart from one reported reaction of $P(NMe_2)_3$ with $GaMe_3$ affording GaP,[1] PH_3 or its alkylated analogue *t*$BuPH_2$[2]are usually used as a source of P^{-III} ion. Nevertheless, except high toxicity of PH_3, depositions using this precursor are often accompanied with lower reactivity supplemented by plasma activation[3] or laser irradiation.[4] PH_3 may also decompose during the deposition causing high content of phosphorus resulting in non-linear growth.

Trialkylsilyl ligand were utilized in ALD of As,[5] Sb[6] Se[7,8] and Te[7] several times. Its electropositive nature generates negative charge on the deposited atom ensuring high reactivity, while keeping good volatility and thermal stability. For example, tris(trimethylsilyl)phosphide is a favorite precursor for metal phosphide quantum dots. It is fairly volatile and can be distilled even at laboratory pressure. Interestingly, no ALD deposition using this class of precursor has been reported for so far. Therefore, this work aims to investigate tris(trialkylsilyl)phosphides as a potential ALD precursors. Preparation of these molecules will be discussed along with structure/thermal properties relationships and selected phosphides will be tested for thin film deposition in ALD.

[1] E. Graugnard, V. Chawla, D. Lorang, C. J. Summers, *Appl. Phys. Lett.***2006**, *89*, 211102.

[2] N. Otsuka, J. Nishizawa, H. Kikuchi, Y. Oyama, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.***1999**, *17*, 3008.

[3] A. V. Uvarov, A. S. Gudovskikh, V. N. Nevedomskiy, A. I. Baranov, D. A. Kudryashov, I. A. Morozov, J. P. Kleider, *J. Phys. D Appl. Phys.***2020**, *53*, 345105.

[4] M. Yoshimoto, A. Kajimoto, H. Matsunami, *Thin Solid Films***1993**, *225*, 70–73.

[5] T. Sarnet, T. Hatanpää, M. Laitinen, T. Sajavaara, K. Mizohata, M. Ritala, M. Leskelä, *J. Mater. Chem. C***2016**, *4*, 449.

[6] V. Pore, K. Knapas, T. Hatanpää, T. Sarnet, M. Kemell, M. Ritala, M. Leskelä, K. Mizohata, *Chem. Mater.***2011**, *23*, 247–254.

[7] T. Hantapää, V. Pore, M. Ritala, M. Leskelä, *Electrochem. Soc.***2009**, *25*, 609–616.

[8] R. Zazpe, J. Charvot, R. Krumpolec, L. Hromádko, D. Pavliňák, F. Dvorak, P. Knotek, J. Michalicka, J. Přikryl, S. Ng, V. Jelínková, F. Bureš, J. M. Macak, *FlatChem***2020**, *21*, 100166.

AF-MoP-56 Plasma Enhanced Atomic Layer Deposition of Nickel Oxide from Nickelocene: Growth Characteristics and Photoelectrochemical Performance*, **Shane O'Donnell**, F. Jose, M. Snelgrove , C. McFeely , R. O'Connor,* Dublin City University, Ireland

Owing to its relatively low cost and suitable band edge positions, n-type silicon has been widely investigated as a promising candidate for photoelectrochemical (PEC) water splitting photoanodes. However, its PEC performance is hampered due to rapid corrosion from the electrolyte solution rendering the silicon photoanode inoperable within a short period of use. NiO thin films deposited via atomic layer deposition (ALD) have been used as protective coatings to lessen this corrosion in an effort to enhance PEC performance through distancing the oxidation reaction from the n-Si photoanode surface and operating as an oxygen evolution reaction catalyst [1].

We investigate growth kinetics of a plasma enhanced ALD process as well as the PEC performance of NiO thin films fabricated using nickelocene with O2 plasma co-reactant. We compare the performance of as-deposited NiO films with those reduced to Ni metal by including short H2 plasma steps during the deposition recipe, followed by a long H2 plasma anneal. Films are investigated in detail using quasi in-situ x-ray photoelectron spectroscopy (XPS), without vacuum break. PEC performance was measured to link the effects of varying film deposition parameters and processes on photocurrent output and film surface chemistry.

Through the investigation of various NiO film thicknesses and post deposition treatments, post deposition H_2 plasma annealing of all films thicknesses showed a reduction in photocurrent output and sample stability due to susceptibility to etching effects of the plasma treatment. From the work performed on supercycle deposition processes it is observed that the deposition of Ni films in continuous growth conditions with a post deposition H_2 plasma anneal results in films exhibiting greater contributions of Ni metal along with elevated carbon composition resulting from residual ligands being incorporated in the film during growth. Films where H2 exposure takes place during the growth process exhibit a lower relative carbon contribution due to the reduction of remnant ligands distributed throughout the film. The presence of Ni metal is also seen to be lower in sequentially grown films when compared to their post deposition annealed counterparts of the same number of ALD cycles

1 Ke Sun. *etal.* Energy Environ. Sci. 2012, 5 (7), 7872–7877

AF-MoP-57 Computational Investigations of Precursor and Deposition Chemistry in ALD and AS-ALD*, **Ralf Tonner-Zech**,* Leipzig University, Germany

The mechanistic details of many ALD processes are hardly understood. Despite the progress made by seminal work of Elliott and others, the chemical complexity of ALD processes requires the continued investigation of many aspects for the precursors and surface chemistry when the target is a comprehensive understanding by theoretical methods. We will show our recent progress made by applying density functional theory and electronic structure analysis approaches to understand aspects of ALD in more detail. Our aim is thereby always to cover the full periodicity of the growth surface to enable a realistic modelling of the experimental conditions. For selected aspects of the ALD process, gas phase screening approaches are suitable, which has been shown in the past and will be validated for our target systems here. We will also show that these investigations can be extended to area-selective ALD (AS-ALD) processes by small-molecule inhibitors (SMIs) and that theoretical modelling can play a crucial role in precursor and SMI design as well as uncovering the underlying principles.

AF-MoP-58 Epitaxial-like Growth of Ga_2O_3 Films on GaN Substrate by ALD using GaCp and Combinations of H_2O and O_2 Plasma Gas and Annealing Process*, **Toshihide Nabatame**, M. Inoue, S. Soeya, T. Sawada, T. Onaya, A. Ohi,* National Institute for Materials Science, Japan*; M. Takahashi, K. Ito,* Osaka University, Japan*; N. Ikeda,* National Institute for Materials Science, Japan*; K. Tsukagoshi,* National institute for Materials Science, Japan

β-Ga_2O_3 is an attractive semiconductor because β-Ga_2O_3 has a large bandgap of 4.5-4.9 eV and a high breakdown electric field of 8 MV/cm for future power device. Large high-quality single-crystal β-Ga_2O_3 wafers can be generally fabricated by melt growth methods such as the floating zone and Czochralski techniques. Also, Ga_2O_3 films have been deposited on various substrates including Si and Al_2O_3 by sputtering, CVD and ALD methods. In ALD studies, Ga_2O_3 thin films were deposited by using various precursors such as $Ga(acac)_3$, $[(CH_3)_2GaNH_2]_3$, $Ga_2(NMe_2)_6$, $Me_2GaOiPr$ and $Ga(CH_3)_3$. In our previous study, we reported to deposit Ga_2O_3 thin films on Si by ALD using pentamethylcyclopentadienyl gallium (GaCp) and combinations of H_2O and O_2 plasma as oxidant gas [1]. We also found that the Ga_2O_3 thin film had an amorphous structure and negligible small residual carbon. However, there has few report characteristics of ALD-Ga_2O_3 film on GaN.

In this paper, we investigated crystal growth of Ga_2O_3 films on GaN substrates by ALD and post-deposition annealing processes.

Ga_2O_3 films were deposited on 3-inch (0001) c-plane GaN wafer (c-GaN) and (10-10) m-plane GaN with off-cut angles of 5° toward the (0001) (m-GaN) by ALD with GaCp and combinations of H_2O and O_2 plasma gas. ALD was performed at 300 °C and the growth per cycle value was 0.06 nm/cycle. 20-nm-thick Ga_2O_3 films on GaN substrates were annealed at 800 °C in N_2. The structure of as-deposited and annealed Ga_2O_3 films were evaluated using in-plane XRD and XRD pole figure measurement.

The as-deposited Ga_2O_3 film on c- and m- GaN substrates dominantly had an amorphous structure because of negligible small XRD peak. On the other hand, in c-GaN substrate, the annealed Ga_2O_3 film had four sharp peaks. These peaks at 2q = 19.0, 38.4, 59.3 and 82.4° were assigned to (-201), (-402), (-603) and (-804) of β-phase of Ga_2O_3, respectively. From the (-201) pole figure measurement, strong peak was also observed in the center. These indicated that epitaxial-like growth of β-Ga_2O_3 film with (-201) was dominantly formed on 3-inch GaN wafer. The epitaxial-like growth of β-Ga_2O_3 film on m-GaN was also observed.

This work was supported in part by JSPS KAKENHI (Nos. JP20H02189 and JP18J22998).

[1] F. Mizutani et al., J. Vac. Sci. Technol. A 38, 0022412 (2020).

AF-MoP-59 The Impact of Oxygen Reactants on ALD InOx films using novel dimethyl[N^1-(tert-butyl)-N^2,N^2-dimethylethane-1,2-diamine]indium precursor*, **Seong-Hwan Ryu**, T. Hong, S. Choi,* Hanyang University, Korea*; J. Seok, J. Park,* Hansol Chemical, Korea (Republic of)*; J. Park,* Hanyang University, Korea

The oxide semiconductor has been attention due to its high mobility, low growth temperature, and low off-current characteristics (~10^{18} μA/μm). In particular, there are several reports about the indium oxide (InOx) based materials such as IGZO, IZO, IGO, and IGTO, because it has low resistivity due to the large overlap between indium 5s orbitals forming the electron conduction path. Meanwhile, in terms of deposition technique of oxide semiconductor, atomic layer deposition (ALD) is attractive due to excellent control of the thickness and composition control during deposition. In this regard, several studies are reported depositing InOx with ALD, however, there are few studies about the growth mechanism such as precursor ligand and reactant. In this study, we deposited InOx using ALD with novel indium precursor and different reactants. The InOx grown with different reactants exhibits different material properties including crystallinity and electrical properties even at the same low growth temperature. For InOx analysis depending on different growth temperatures with the different reactants, we conducted X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), grazing-incidence wide-angle X-ray scattering (GI-WAXS), X-ray reflectometry (XRR) and Hall measurement.

AF-MoP-60 Development of an Innovative Method to Find New Efficient Gallium ALD Precursors*, P. Pavard,* CNRS-IPVF, France*; C. Gosmini,* LCM, École Polytechnique CNRS, France*; D. Lincot,* CNRS-IPVF, France*; V. Albin, V. Lair, A. Ringuede,* Chimie ParisTech, PSL University, CNRS, France*; A. Auffrant,* LCM, École Polytechnique CNRS, France*; **Nathanaelle Schneider**,* CNRS-IPVF, France

Atomic Layer Deposition (ALD) is a booming technology to deposit thin films and has been applied in several fields. This technique is based on surface-chemical reactions, and relies on the gas phase transport of metal containing molecules into a reaction chamber. However, not any molecule is suitable to be used as precursor, as they must be thermally robust while being sufficiently volatile and chemically labile to react with the surface functional groups. Organometallic chemistry offers an infinite set of options to design new efficient precursors, though predicting their volatility and reactivity in the ALD chamber remains tricky.[1] Establishing a new method to assess the physical and chemical properties of complexes would grant access to new ALD precursors and a better understanding of surface reactions.

This communication focuses on the development of new efficient gallium precursors to be used in the ALD of oxygen-free gallium-containing sulfide thin films.[2] A series of gallium complexes with chelating nitrogen based ligands (guanidinate, amidinate and triazenides) were synthesized and characterized (NMR, XRD) thanks to modular procedures.[3,4] To assess the thermal stability of the reagents and shed light on their transport in ALD, thermal analysis (TGA, DSC) were realized under N_2 and vacuum to mimic transport conditions. Finally, reactivity studies in solution of established ALD precursors and synthesized complexes provide an insight of surface reactions which might take place in an ALD chamber.

References:

[1] S. E. Koponen, P. G. Gordon, S. T. Barry, *Polyhedron***2016**, *108*, 59–66.

[2] N. Schneider, M. Frégnaux, M. Bouttemy, F. Donsanti, A. Etcheberry, D. Lincot, *Materials Today Chemistry***2018**, *10*, 142–152.

[3] A. P. Kenney, G. P. A. Yap, D. S. Richeson, S. T. Barry, *Inorganic Chemistry***2005**, *44*, 2926–2933.

[4] S. Dagorne, R. F. Jordan, V. G. Young, *Organometallics***1999**, *18*, 4619–4623.

AF-MoP-61 Detailed Characterization of Bis(tri-isopropylcyclopentadienyl)strontium(Sr(iPr$_3$Cp)$_2$) for the Understanding of SrTiO$_3$ Atomic Layer Deposition*, Young Jae Park,* Samsung Advanced Institute of Technology, Korea (Republic of)*; J. Park,* Korea Research Institute of Standards and Science, Korea (Republic of)*; J. Han, J. Lim, B. Choi,* Samsung Advanced Institute of Technology, Korea (Republic of)*; S. Kang,* Korea Research Institute of Standards and Science, Korea (Republic of)*; C. Baik,* Samsung Advanced Institute of Technology, Korea (Republic of)

The detailed characterization of Bis(tri-isopropylcyclopentadienyl)strontium(Sr(iPr$_3$Cp)$_2$) precursor was conducted to understand growth mechanism in atomic layer deposition of SrTiO$_3$ thin films. First, the adsorption behavior was studied using an in-situ attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The band of the Sr(iPr$_3$Cp)$_2$ spectrum on the Ge crystal surface was identical to that of the spectrum measured in the gas phase, but peak intensity was different. In addition, the absorption characteristics studies were carried out over the Ge crystal temperature in the range of $40\sim100^{o}$C. Upon increasing the temperature, a reduction of absorption was observed. Second, to investigate the volatility of Sr(iPr$_3$Cp)$_2$, vapor pressure curve was determined using thermogravymetric analysis. This method can reduce both precursor amount and time required for the vapor pressure measurement. Furthermore, molecular simulation was applied to explain the interrelationship between those properties evaluated in this study and molecular structure. Our study to understand the detailed behavior of precursor can be provided as useful information for optimization of ALD process and new precursor design.

AF-MoP-62 New Potential Synthesis Route of Molybdenum Nitride Nanosheets by Nitriding Molybdenum Disulphide Deposited by Atomic Layer Deposition (ALD)*, Julien Patouillard,* SIMAP, Grenoble-INP, CNRS, France

The first syntheses of transition metal nitrides are derived from metallurgical processes and consisted in nitriding a powder of the metal or one of its oxides (Oyama, 1992; Toth, 1971). These nitrides were synthesized under severe conditions (T > 1200 °Cz and had low specific surfaces (Marchand et al., 1996). Subsequently, the development of catalytic applications requiring nitride powders with large specific surfaces made it necessary to use processes with more moderate temperatures (700 °C to 900 °C) (Marchand et al., 1996, 1999). These “softer” synthetic routes have developed and been applied to the formation of nitrides from transition metal sulfides.

Among the transition metal disulfides, molybdenum disulfide (MoS_2)is one of the most widely studied materials in recent years to synthesis molybdenum nitride due to its availability (E. R. Braitwaite & J. Haber, 1994). MoS_2 has a natural two-dimensional structure with the sandwich-like S-Mo-S layers serving as building blocks, in which the atoms in the layer are bonded with strong covalent bonding, while the layers are packed together with weak interlayer forces (Jariwala et al., 2014; Li & Zhu, 2015). In recent years, the emergence of 2D materials and the increase in the demand of metal nitrides nanosheets due to their remarkable physical and chemical properties such as high electrical conductivities, catalytic properties, energy storage, and conversion efficiency aroused a particular interest (Khazaei et al., 2013; Wang & Ding, 2018; Xiao et al., 2017, 2018; Zhong et al., 2016). Thereby, some research group(Sun et al., 2018),(Cao et al., 2020) have demonstrated the transformation of MoS_2 nanosheets exfoliated from bulk material into molybdenum nitride nanosheets with ammonia and urea reactive heat treatments, respectively.

In this work, we proposed a method to transform a well-controlled uniform MoS_2 thin film deposited by Atomic Layer Deposition into molybdenum nitride (MoN_x) nanosheets via an ammonia reactive heat treatment at 700 °C supported by *in-situ* reflectance measurements and *ex-situ* Raman and X-Ray Photoelectron spectroscopy characterizations.

AF-MoP-63 Phase-Transformation of as-Grown Crystalline VOx Films Using Ar-Plasma Annealing During Low-Temperature Hollow-Cathode Plasma-Assisted ALD Monitored via *in-Situ* Ellipsometry*, Adnan Mohammad,* *S. Ilhom,* University of Connecticut*; A. Okyay,* Stanford University*; B. Willis, N. Biyikli,* University of Connecticut

Vanadium oxide films show phase-change properties at different stoichiometries including the famous metal-insulator transition (MIT) for VO_2around 70 °C shifting between monoclinic to tetragonal rutile structure phase with temperature change. Such layers have the potential to be used forlow-power electrical switches. The existing VOx ALD reports demonstrate mainly as-grown amorphous VOx films via thermal atomic layer deposition (ALD) using TEMAV and VTIP metal precursors and water vapor or ozone as co-reactant. These amorphous films are shown to transform in various crystalline phases using post-deposition annealing process at high temperatures (typically higher than 500 °C). However, no significant report is yet found on low-temperature as-grown VO_2 films grown by thermal or plasma-ALD.

In this study we had two major goals: (i) To demonstrate as-grown crystalline VOx films using our customized hollow-cathode plasma-ALD reactor at substrate temperatures lower than 200 °C; (ii) to further improve the crystalline quality and transform the phase structure of the deposited VOx film into the desired VO_2 stoichiometry. We have grown crystalline VOx thin films at substrate temperatures as low as 200 °C using TEMAV as the vanadium precursor and O_2 plasma as the oxygen co-reactant. The resulting as-grown film was crystalline V_2O_5. The recipe for the plasma-ALD experiments was as the following: 0.1 s of TEMAV pulse with 10 sccm of N_2-carrier flow, 50 sccm Ar-purge for 10 sec, 50 sccm O_2 plasma for 10 s, plasma power 50- 300 W, followed by another 10 s of Ar purge. To provide enough TEMAV dose into the reactor chamber, the TEMAV precursor cylinder is heated at 110 °C. The resulting films are crystalline V_2O_5 with a growth per cycle (GPC) value reaching ~2 Å and a refractive index of 2.45. The corresponding growth process has been real-time monitored with *in-situ* ellipsometry depicting the individual chemisorption and ligand exchange surface reactions.

Having accomplished our first goal, our next step is to incorporate *in situ* Ar-plasma annealing process steps to further improve and transform the crystal structure of V_2O_5 films. Ar-plasma annealing parameters including Ar-flow rate, plasma annealing duration, and subsequent purge time will be investigated via *in-situ* process monitoring and *ex-situ* materials characterization.If successful, the resulting VO_2 films will be characterized for their temperature-dependent electrical properties to validate the MIT behavior, paving the way for prototype switch devices.

AF-MoP-64 ALD Process Monitoring and Optimisation by Self-Plasma OES*, Mantas Drazdys,* Centrer for Physical Sciences and Technology, Lithuania*; D. Astrauskyė,* Center for Physical Sciences and Technology, Lithuania*; R. Drazdys,* Center fro Physcial Sciences and Technology, Lithuania*; M. Audronis,* Nova Fabrica Ltd., Lithuania

This work reports on the application of Self Plasma Optical Emission Spectroscopy (SPOES) to perform Process Gas Analysis (PGA) to monitor and optimize thin film atomic layer deposition (ALD) process, carried out using metalorganic precursors and water vapor or oxygen plasma as oxidizers. Depositions were carried out at 150℃ using N_2 or Ar as carrier and purging gas. The ALD cycle consisted of four steps: (a) metalorganic precursor pulse, (b) purge, (c) oxidant pulse, and (d) purge. Purge times varied in the range of 2 – 120 seconds to find the optimal value based on the PGA results. We performed SPOES PGA using Broadband Plasma

Emission Monitoring (2B-PEM) of an inverted magnetron-based plasma reactor attached to the ALD process exhaust. The miniature plasma reactor can operate at pressures 7.5e−7 Torr to 7.5 Torr. The sensor signals derived from SPOES data react instantly to composition changes revealing trace amounts of constituents of the process material. We demonstrate how real-time process diagnostics, pump-down monitoring, process condition recognition and end-point detection, all taking place in parallel, facilitate ALD process yield maximisation and reaction by product residue in thin films prevention. Furthermore, the gas analysis technology demonstrated does not require additional (differential) pumping systems to perform analyses.

AF-MoP-65 Growth of Boron Nitride by Atomic Layer Deposition Using the in-Situ Decomposition of Ammonium Carbamate*, Ana Álvarez-Yenes,* *M. Knez,* CIC nanoGUNE, Spain

Boron nitride (BN) is a binary compound of boron and nitrogen alternatively linked which can exist in various crystalline forms, all of them analogous to the carbon allotropes. In each of its forms, BN presents interesting properties that make it a useful material in different applications, especially remarkable in nanotechnology.

The aim of this work is to develop and characterize a new Atomic Layer Deposition (ALD) process for the growth of boron nitride thin films. So far, this has been achieved by using ammonia as the nitrogen providing precursor in combination with a boron halide at temperatures above 400^{o}C. The interest is to obtain boron nitride thin films at reaction temperatures below 275^{o}C. In this work, ammonium carbamate ($NH_4[H_2NCO_2]$) and boron tribromide (BBr_3) are used as precursors. $NH_4[H_2NCO_2]$ is a solid at room temperature which easily decomposes giving a CO_2/NH_3 mixture that can substitute ammonia, making the laboratory work safer and simpler. This work focuses on the analysis of the dependence of the growth rate of the process on its different parameters, aiming to optimize the deposition and predict the thickness of the grown films.

The thin films deposited using this process have been analyzed by means of X-Ray reflectivity, X-Ray photoelectron spectroscopy and electron energy loss spectroscopy among other techniques to conclude that the material deposited is amorphous boron nitride with a 1:1 stoichiometry.

AF-MoP-66 Modelling Atomic Layer Deposition of Noble Metals*, Sylwia Klejna,* AGH University of Science and Technology, Academic Centre for Materials and Nanotechnolog, Poland

The major challenge in metal ALD is the reduction process to yield the metallic target film from metal source that usually comprise of metal cation surrounded by anionic ligands. Existing strategies involve using reducing agent or, counterintuitively, oxidizing agent as second co-reagent. Using reducer as co-reagent, *e.g.* H_2, can lead to an abbreviated cycle, and reduced rate of deposition, when stable metal hydrides are not available. In process using oxidizing agent, *e.g.* O_2, transient metal oxide surface may be generated and that can greatly facilitate noble metal ALD [1]. In this scenario the reduction of metallic center is a result of precursor decomposition at this catalytic surface. The higher growth rate is thus achieved, because the metallic film forms also in the processes of combustion of ligands by the oxidizing agent, however with the danger of surface poisoning and oxide deposition.

Thus, the second co-reactant role is crucial. It is used to eliminate the surface bound species of the metal pulse and, at saturation, to produce a reactive overlayer – the catalytic oxide surface, which is characteristic for a particular noble metal. We therefore first investigate the thermodynamics to understand the self-limiting surface chemistry of the oxidizing co-reagent. We use density functional theory (DFT) to establish order of reactivity as a function of temperature and pressure of noble metals (Ru, Rh, Pd, Ag, Os, Ir, Pt, Au) to form oxides. Next, we examine the thermodynamics of ALD process that includes the transient generation of noble metal oxide.

Finally, we investigate reaction steps involved in the metal nucleation on the example of Pt ALD from $MeCpPtMe_3$ and O_2. We evaluate whether the nuclei of the catalytic surface can be formed during the O_2 co-reactant pulse, i.e. when oxidizing agent is introduced into the ALD chamber to combust hydrocarbon-based ligands into the volatile by-products (*e.g.* CO_2, H_2O). We discuss the possibility of production of transient surface bound OH groups predicted in previous study [2] and other by-products, *e.g.* CH_4 identified in the experiment [3]. The factors that facilitate nucleation are examined. This will allow to propose appropriate reagents and chemical processes to control and improve efficiency of the atomic layer deposition of noble metals.

23. *The Journal of Chemical Physics*, 2017, **146**, 052822.
24. *Langmuir*, 2010, **26**, 9179-9182.
25. *Physical Chemistry Chemical Physics*, 2018, **20**, 25343-25356.

AF-MoP-67 Effect of the N-Source on the Growth and Quality of Pe-ALD Tin Thin Films*, Clémence Badie,* Aix-Marseille University, France*; M. Barr, J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; T. Defforge, G. Gautier,* GREMAN, CNRS, Univ. Tours, France*; L. Santinacci,* Aix-Marseille University, France

The thermal ALD of TiN is a well-documented process. The common precursors combination is $TDMAT/NH_3$, for thermal as well as for plasma-enhanced ALD (PE-ALD). However, PE-ALD offers a larger variety of co-reactant (N-sources): N_2, H_2 and N_2/H_2. Building the ALD window of TiN using the recipes from our manufacturer, the PE-ALD processes exhibit a longer cycle duration associated to a slower GPC regarding to the thermal ALD one. This is unexpected since the plasma should enhance the production of reactive species and then promote the deposition process. The GPC should therefore be higher. The aim of this work is to optimize the PE-ALD recipes using two different N-sources: NH_3 and N_2. In addition to shorten the deposition duration, the effects of those N-sources as well as their dilution in Ar and the plasma power on the final properties of the films are also studied. The influence of those parameters has been monitored by in situ characterizations (ellipsometry and optical emission spectroscopy, SE and OES, respectively) and by ex situ characterizations (morphology, composition, crystalline structure and electric properties).

The recipe parameters are adjusted to limit the recombinations of the reactive species generated between the remote plasma source to the substrate. For instance, a large Ar dilution of both N_2 and NH_3 limits the film growth (lower GPC). A gas ratio of 1:1 for N-source and Ar flow is set to the optimal values. This is correlated with the OES spectra presenting that in diluted condition, the intensity of the Ar pics is predominant compared to the N-sources one. This suggests that high Ar dilution hinders the generation of N-reactive species leading to a reduction of the number of reactive species involved in the deposit growth and then, to lower GPC, mainly for N_2 plasma. The applied power (50 to 300 W) has no significant effect on the GPC with NH_3 plasma while, for N_2-based plasma, the GPC is maximum at the highest power. This is consistent with the expected low reactivity of N_2 (inert without plasma activation) as compared to highly reactive NH_3. Note that using NH_3, a thermal contribution cannot be discarded. Those results indicate that producing less active species facilitate their transport by limiting recombinations.

The films grown from both N-sources have a similar roughness, composition and morphology. However, the conductivity, conformality on high aspect ratio substrates (1:25) and the growth rate are better using NH_3-based plasma. The N_2 plasma process exhibits an acceptable film quality and it should be considered as well since it uses a non-harmful gas.

AF-MoP-68 Silicon Nitride Grown by VHF (162 MHz) Plasma Enhanced Atomic Layer Deposition With Floating Multi-Tile Electrodes Using Di(Isopropylamino)Silane and N_2 Plasma*, You Jin Ji,* *H. Kim, K. Kim, J. Kang, D. Kim,* Sungkyunkwan University (SKKU), Korea (Republic of)*; K. Kim,* Massachusetts Institute of Technology, Korea (Republic of)*; D. Kim,* Sungkyunkwan University (SKKU), Korea (Republic of)*; A. Ellingboe,* Dublin City University, Ireland*; G. Yeom,* Sungkyunkwan University (SKKU), Korea (Republic of)

To satisfy the requirements for applications of silicon nitride (SiN_x) at the highly scaled logic and memory devices, high quality films (i.e., low contamination, low roughness, etc.) with high conformality at low temperatures are demanded. To meet the stringent requirements for SiN_x applications, plasma enhanced atomic layer deposition (PEALD) is being extensively investigated as the deposition technique. However, the minimization of plasma damage and lowering the process temperature still remain as issues for SiN_x PEALD processes. In this work, the properties of PEALD SiN_xfilms deposited at a low process temperatureof100^{o}Cwithdi(isopropylamino)silane(DIPAS)andN_2plasmaexcitedbyveryhighfrequency(VHF,162MHz)capactivelycoupledplasma (CCP) sources with a floatingmulti-tile type electrode and a conventional diode type electrode are investigated and compared in addition to the plasma characteristicsofbothplasmasources. ThePEALDSiN_xfilmdepositedusing thefloating multi-tile electrodeexhibitedhighergrowthrate(~0.6Å/cycle),morestoichiometricfilm (N/Si~0.98), andhigherconformalityinatrenchcomparedtothosedepositedbytheconventi onal VHF CCP.Inaddition,theimprovedelectricalcharacteristicscouldbeobtainedwiththefloatingmulti-tile electrode.The improved properties are believed to be related to the higher plasma density, higher radical density, and lower ion energy bombarding the substrate observed for the multi-electrode type through the enhanced power coupling efficiency between the pairs of multi-electrodes in the plasma source.

AF-MoP-69 Computational Fluid Dynamics Study of ALD Processes: Benchmarking and Validation*, **Gizem Ersavas Isitman**, D. Izbassarov, R. L. Puurunen, V. Vuorinen,* Aalto University, Finland

Computational fluid dynamics study of ALD processes: Benchmarking and Validation

Gizem Ersavas Isitman[1] , Daulet Izbassarov[1] , Riikka L. Puurunen[2] , Ville Vuorinen[1]

1. School of Engineering, Department of Mechanical Engineering, Aalto University

2. School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Aalto University

Atomic layer deposition (ALD) is an advanced gas-phase deposition technique [1]. ALD technology is exceptionally effective for obtaining high-quality and conformal coating on high aspect ratio structures e.g in microelectronics, nano-materials, etc. These applications often require high manufacturing costs. Numerical methods provide a great opportunity to optimize the manufacturing process.

In this research, the purpose is to better understand ALD using computational fluid dynamics (CFD) in a porous medium by investigating how the reactive gas flow interacts with the catalytic surface. The ALD process is modeled using a CFD tool called aldFOAM [2]. The surface reactions are based on the irreversible Langmuir kinetics. The approach is validated against standard benchmark problems for non-reacting and reacting cases. First, the solver is validated against non-reacting flow past a single particle and tube banks (e.g Fig.1). Next, the irreversible Langmuir surface kinetics model in aldFoam solver is validated against reference data [3] for high aspect ratio structures. After the validation, the method is applied to investigate the surface coverage on different 2D and 3D shapes (e.g Fig.2) under a range of parameters such as pressure and Reynolds number (Re). It is found that the time to fully cover the surface decreases with increasing partial pressure and Re.

References

[1] J.R. van Ommen, A. Goulas, and R.L. Puurunen, “Atomic layer deposition,” in Kirk Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 2021, 42 p. https://doi.org/10.1002/0471238961.koe00059

[2] A. Yanguas-Gil, J.A. Libera, and J.W. Elam, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 39, 062404 (2021).

[3] M. Ylilammi, O.M.E. Ylivaara, and R.L. Puurunen, Journal of Applied Physics 123, 205301 (2018).

AF-MoP-70 Feature-Scale Conformality of Atomic Layer Deposition from Continuum to Free Molecular Flow: How Knudsen Number Influences Thickness Profile Characteristics*, J. Velasco, **Christine Gonsalves**, G. Ersavas Isitman, J. Yim, E. Verkama, D. Izbassarov, V. Vuorinen, R. Puurunen,* Aalto University, Finland

Atomic layer deposition (ALD) is often chosen over other techniques for thin film growth or surface modification because of its conformality, which originates from the self-terminating nature of the reactions used [1]. It is of paramount importance to understand how the conformality in high-aspect-ratio (HAR) surface features evolves with time and depends on process parameters and chemistry. Many simulation frameworks are available to model ALD growth in HAR features [2,4]: diffusion–reaction models, Monte Carlo models and ballistic models. Most simulation frameworks work in the free molecular flow conditions, where kinetic information of the reactions can be extracted from an experimental thickness profile by a simple slope method [3,4].

As seen in Figure 1, the thickness profile characteristics such as the half-thickness penetration depth $x_{50\%}$ and the slope at this half-thickness penetration depth, strongly depend on the Knudsen number in other diffusion conditions than free molecular flow. While $x_{50\%}$ can be taken as a simplistic measure for “conformality”, the slope carries information of reaction kinetics, specifically of the sticking coefficient. To make interpretations on kinetics from experimental thickness profiles, understanding the flow conditions is of central importance. Specifically, assuming Knudsen flow when it is in reality not valid, would lead to incorrect (too high) interpretation of the sticking coefficient.

Recently [4], we showed that the way the process parameters affect the simulated thickness profile in HAR structures, depends on the diffusion regime: free molecular flow (Knudsen number Kn >> 1) has partly different trends than transition flow (Kn ~1). In this work, we extend the simulations to continuum conditions (Kn << 1). In addition to the previously used 1d diffusion–reaction model [4,5], in this work we also use computational fluid dynamics (CFD) calculations to investigate the processes in 3d.

This work was supported by the Academy of Finland (ALDI project).

References

[1] J.R. van Ommen, A. Goulas, and R.L. Puurunen, “Atomic layer deposition,” in Kirk Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 42 p, (2021).https://doi.org/10.1002/0471238961.koe00059.

[2] V. Cremers et al., Applied Physics Reviews, 6(2), 021302, (2019).

[3] K. Arts et al., J. Vac. Sci. Technol. A, 37, 030908, (2019).

[4] J. Yim and E. Verkama et al., Phys. Chem. Chem. Phys., in press,

https://doi.org/10.1039/D1CP04758B

[5] M. Ylilammi, O. Ylivaara, and R.L. Puurunen, J. Appl. Phys., 123, 205301, (2018).

AF-MoP-71 Nucleation Studies of Copper ALD on SiO_2 and Si_3N_4*, **Krzysztof Mackosz**,* Empa - Swiss Federal Laboratories for Materials Science and Technology , Switzerland*; A. Szkudlarek,* AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Poland*; I. Utke,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Nucleation of ALD metal layers shows several key problems, among others, are nucleation delay and island growth, which prohibit the formation of thin compact metal films. To shed more light on the process of nucleation, we have performed a comprehensive electron microscopy study of the early growth stages of copper films prepared by means of the ALD protocol reported by the group of Karppinen [1] optimized for a hot-wall reactor.

$Cu(dmap)_2$ and HQ were used to grow copper by varying the growth temperature in the range of 120-160°C. Films were grown on Si substrates of different orientations covered with native oxide, on Si/SiO_2 substrates with different thicknesses of oxide layer, and Si_3N_4 membranes. We have observed island growth irrespective of substrate type for a few hundreds of ALD cycles. Moreover, the growth mechanism is influenced by other factors such as the temperature of the substrate as well as the precursor flux. We will report on the coverage density, distribution of island size and chemical composition differs depending on growth conditions. We have resolved mixed compositions varying from metallic copper to copper oxide based on TEM studies. Both, Cu(I) and Cu(II) oxides are present in all the films studied. It is uncertain whether the oxide phase was deposited, or it is formed upon exposure to air during samples transfer from ALD reactor to TEM experimental chamber.

[1] D. J. Hagen, et al., Dalton Trans., 2018,47, 15791-1580

AF-MoP-72 Photocatalytic Degradation of Harmful Pollutants to Improve Indoor and Outdoor Air Quality*, Tobias Graumann*, *S. Pleger, C. Jacobs, C. Beyen, V. Sittinger,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

The application of photocatalytic materials in air treatment and air-borne pollutant remediation has been well established. Photocatalytically active materials used in urban areas on a commercial base can include paints, tiles, and concretes which mainly utilize TiO_2 as the photocatalyst material. Feasibility studies demonstrated the potential of those materials for the use of mineralizing organic compounds into carbon dioxide, water and corresponding mineral acids. Of special interest is the decomposition of nitrogen oxides with a main focus on NO and NO_2. A review of the photocatalytic effectiveness for outdoor applications is not always possible due to the simultaneous variation of other parameters, such as traffic density and weather conditions. Therefore, for the simulation of air pollutants numerical models for the release calculation in the atmosphere, the transport of pollutants in the gas phase, and the interaction with solid surfaces are used.

The determination of the deposition rate of available photocatalytic materials is currently limited to examining those embedded in matrices and formulations, e.g. for concrete surfaces, roof tiles or plaster, since these currently have the largest commercial proportion of photocatalytically active products. An evaluation of other, especially vacuum-based, coating processes for the deposition of TiO_2 layers has not yet taken place. To create a basic understanding of the essential process parameters influencing photocatalytic NO oxidation thermal atomic layer deposition is used.

In this work suitable process windows for the deposition of photocatalytic TiO_2 are identified and evaluated with a main focus on the precursor combinations $TiCl_4/H_2O$, $TiCl_4/O_3$, $TTIP/H_2O$, $TTIP/O_3$ and $TiCl_4/TTIP$. Process parameters affecting the crystallinity of the TiO_2 layers and thus the photocatalytic effectiveness and the process-related layer properties with different process temperatures and layer thicknesses are determined.

For a cross-method and unified comparison of the TiO_2 layer properties the photocatalytic oxidation of methylene blue in aqueous solution and the degradation of nitrogen monoxide in a photoreactor are compared with each other as well as the kinetic modelling which was observed and simulated during NO degradation.

AF-MoP-73 High Vacuum Chemical Vapour Deposition: High Growth Rate ALD-Like Film Synthesis and Epitaxial CVD for Integrated Photonics*, Wojciech Szmyt*, *J. Geler-Kremer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; S. Abel,* Lumiphase AG, Switzerland*; J. Fompeyrine,* Lumiphase, AG, Switzerland*; P. Hoffmann,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

In high-vacuum chemical vapour deposition (HV-CVD), heated substrates are exposed to continuous precursor fluxes from orifices in the precursor delivery system. Owing to the HV conditions, the precursor trajectories are ballistic, therefore the fluxes can be evaluated analytically. By blocking of individual effusion orifices, a range of different combinations of precursor fluxes can be explored in a single synthesis, which vastly accelerates the process optimization for the desired film properties. This approach is referred to as combinatorial deposition.

Moreover, due to HV conditions the probability of gas-phase collisions between precursor molecules is negligible, and thus, the chemical reactions occur strictly on the substrate surface. This characteristic allows for ALD-like synthesis of the films at a higher growth rate than ALD, provided that the substrate temperature is below the pyrolysis threshold of the precursors. In one of the previous works of our group (Reinke *et al*., J. Phys. Chem. C, 2015, 119, 50, 27965–27971), we presented HV-CVD of TiO_2 using ALD precursors TTIP and H_2O at typical ALD temperatures 175-225°C, achieving growth rates of up to 2nm/min. The growth was demonstrated to follow ALD chemistry and kinetics. The combinatorial HV-CVD allowed to extract a range of kinetic parameters of the precursor system under study, thus proving the HV-CVD highly valuable as a tool for the fundamental study of ALD processes. Moreover, it shows that ALD processes can be adapted in the HV-CVD system for higher growth rates.

Owing to the negligible gas-phase reactions, in the CVD mode of HV-CVD, highly crystalline films are attainable. The HV-CVD-grown films rival the quality of molecular beam epitaxy results, achieved at lower temperatures, and providing much-improved process scalability and cost-efficiency. Our recent efforts have been focused on the epitaxial growth of $BaTiO_3$ on $SrTiO_3$-buffered substrates for integrated electro-optical devices using $Ba(iPr_3Cp)_2$, TTIP and O_2 as precursors (Borzì *et al*, Materialia, 2020, 14, 100953). Employing the combinatorial mode of growth, we have established the optimal precursor fluxes for the correct stoichiometry, validated by Rutherford backscattering and Elastic recoil detection elemental analysis. We also demonstrated the films to be epitaxial by XRD as well as <0.5nm root mean square roughness, as shown by AFM, both of which being crucial for the application.

Emerging Materials
Room Arteveldeforum & Pedro de Gante - Session EM-MoP

Emerging Materials Poster Session

EM-MoP-2 Calcium and Vanadium Mixed Oxides With ALD*, Fabian Krahl*, *K. Nielsch,* Leibniz Institute for Solid State and Materials Research Dresden, Germany

Ternary oxides can show a wide range of very interesting physical properties and several have already been successfully deposited with ALD[1]. One that, to our knowledge, hasn't yet been reported with ALD is $CaVO_3$, ALD-processes for calcium and vanadium oxides have been reported already in the early 1990s and 2000respectively[2,3].

$CaVO_3$ is a correlated metal. These materials with strongly correlated charge carriers hold promise for a new type of transparent conductor (as opposed to highly doped wide bandgap materials like indium tin oxide)[4]. VO_2 and $CaVO_3$ also show a metal-insulator transition depending on film thickness which could make it an interesting phase change material[5–7].

An ALD process of $CaVO_3$ could therefore be a great step towards the utilization and further research of this material because ALD is scalable and has great control over the thickness and composition of the deposited films. Here we want to present the status of our work with the ALD of CaO, V_xO_y and the mixed $Ca_xV_yO_z$ Oxides.

References

[1] A.J.M. Mackus, J.R. Schneider, C. MacIsaac, J.G. Baker, and S.F. Bent, Chem. Mater. **31**, 1142 (2019).

[2] J. Aarik, A. Aidla, A. Jaek, M. Leskelä, and L. Niinistö, Applied Surface Science **75**, 33 (1994).

[3] J.C. Badot, S. Ribes, E.B. Yousfi, V. Vivier, J.P. Pereira-Ramos, N. Baffier, and D. Lincotb, Electrochem. Solid-State Lett. **3**, 485 (2000).

[4] L. Zhang, Y. Zhou, L. Guo, W. Zhao, A. Barnes, H.-T. Zhang, C. Eaton, Y. Zheng, M. Brahlek, H.F. Haneef, N.J. Podraza, M.H.W. Chan, V. Gopalan, K.M. Rabe, and R. Engel-Herbert, Nature Mater **15**, 204 (2016).

[5] S. Beck, G. Sclauzero, U. Chopra, and C. Ederer, Phys. Rev. B **97**, 075107 (2018).

[6] M. Brahlek, L. Zhang, J. Lapano, H.-T. Zhang, R. Engel-Herbert, N. Shukla, S. Datta, H. Paik, and D.G. Schlom, MRS Communications **7**, 27 (2017).

[7] G. Rampelberg, M. Schaekers, K. Martens, Q. Xie, D. Deduytsche, B. De Schutter, N. Blasco, J. Kittl, and C. Detavernier, Appl. Phys. Lett. **98**, 162902 (2011).

EM-MoP-3 Atomic Layer Deposition of Highly Pure Metals for Memory Devices Preparation*, Haojie Zhang*, *B. Kalkofen, S. Parkin,* Max Planck Institute of Microstructure Physics, Germany

Solid-state non-volatile memory devices have been seen as one of the most promising candidates to replace the stat-of-the-art data storage media (e.g. hard disk drives). The expansion of memory devices from two-dimensional (2D) to three-dimensional (3D) can further increase the capacity and storage density of memory devices. Therefore, atomic layer deposition (ALD) of highly magnetic metals films is crucial for the design and preparation of 3D memory devices. In this work, we develop ALD recipes to deposit highly pure and smooth metals layers, including Pt, Co, and Ni. The deposited metal layers with optimized ALD recipes exhibit superior conductivity and magnetic property. Our developed recipes have huge potential to be used for other applications, such as batteries, renewable energy conversion.

EM-MoP-4 Liquid Atomic Layer Deposition of Cu_2 (Bdc)$_2$ (Dabco) Through 3D-Printed Microfluidic Chips*, **Octavio Graniel**, D. Muñoz-Rojas,* University Grenoble Alpes, CNRS, Grenoble INP, LMGP, France*; J. Puigmartí-Luis,* Departament de Ciència dels Materials i Química Física, Institut de Química Teòrica i Computacional, ICREA, Catalan Institution for Research and Advanced Studies, Spain

In recent years, liquid atomic layer deposition (LALD)[1] has emerged as a much simpler and versatile strategy to overcome some of the current constraints of its gas phase homolog for the deposition of metal-organic frameworks (MOF) thin films (e.g. thermal decomposition of precursors at high temperatures, poor control over the crystallinity).

This work describes the automated deposition of Cu_2 (bdc)$_2$ (dabco) thin films on silicon and glass substrates using a 3D-printed microfluidic chip. Films with preferred (001) and (100) orientations were obtained by changing the temperature of the reaction, the concentration of the reactants, and the dimensions of the microfluidic reactor as demonstrated by GIXRD measurements. In addition, the area of the thin film was successfully controlled by changing the flow rates of the precursors in a continuous flow mode.

1O. Graniel, J. Puigmartí-Luis and D. Muñoz-Rojas, *Dalt. Trans.*, 2021, **50**, 6373–6381.

EM-MoP-7 Atomic Layer Deposition of Yttrium Iron Garnet (YIG) for 3D Spintronics*, **Michaela Lammel**,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science, Germany*; D. Scheffler,* Institut für Festkörper- und Materialphysik, Technische Universität Dresden, Germany*; D. Pohl,* Dresden Center for Nanoanalysis (DCN), cfaed, Technische Universität Dresden, Germany*; P. Swekis,* Max-Planck Institute for Chemical Physics of Solids, Germany*; S. Reitzig,* Institut für angewandte Physik, Technische Universität Dresden, Germany*; S. Piontek,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science, Germany*; H. Reichlova, R. Schlitz,* Institut für Festkörper- und Materialphysik, Technische Universität Dresden, Germany*; K. Geishendorf,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science, Germany*; L. Siegl,* Universität Konstanz, Germany*; B. Rellinghaus,* Dresden Center for Nanoanalysis (DCN), cfaed, Technische Universität Dresden, Germany*; L. Eng,* Institut für angewandte Physik, Technische Universität Dresden, Germany*; K. Nielsch,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science, Germany*; S. Goennenwein,* Universität Konstanz, Germany*; A. Thomas,* Institut für Festkörper- und Materialphysik, Technische Universität Dresden, Germany

During the last decade, three-dimensional (3D) nanostructures have gained increasing interest in the field of nanoscience. On the one hand, this development is driven by the desire to create ever denser microelectronic circuit structures. Truly 3D nanostructures will be key to go beyond stacked planar layers, which are commonplace in today's chip architectures. These structures then have electronic functionality in all three spatial directions, enabling for example ultra-high density memory concepts such as racetrack memory. On the other hand, nanoscale 3D structures bring along novel magnetization configurations and interesting physical effects arising from their "non-flat" geometry. Atomic layer deposition (ALD) is ideally suited for the fabrication of such truly 3D magnetic nanostructures due to its conformal coating capability.

We here demonstrate the fabrication of the ferrimagnetic insulator yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) via atomic layer deposition. YIG is a prototypical magnetic insulator used in the field of spintronics, since it combines a small coercive field, a large spin diffusion length and very low magnetization damping. We realize the ALD-based fabrication of YIG thin films by a supercycle approach based on the deposition of nanolaminates and show that our ALD-YIG films exhibit excellent structural and magnetic properties - comparable to those of high quality YIG thin films obtained by conventional, directional deposition methods. By validating the conformal 3D deposition of the ALD-YIG thin films, we highlight the usability of our ALD process for the fabrication of 3D nanostructures consisting of high quality YIG. Our findings provide the foundation for a variety of novel experiments on magnetic nanostructures using one of the best suited materials.

EM-MoP-13 ALD of Sulfide- and Selenide-Based Layered 2D Materials*, **Samik Mukherjee**, K. Nielsch,* Leibniz IFW Dresden, Germany

Layered two-dimensional (2D) materials exhibit many exotic physical, chemical, and electronic properties,[1] which allows them to create exciting new opportunities as a test-bed for many fundamental theories of materials science,[2,3] as well as pave the path for a wide variety of applications, such as optoelectronic and nanoelectronic devices,[4–6] clean energy harvesting,[7] catalysis materials,[8] bioengineering,[9] and others. As an additional paradigm, a precise layering of quasi-2D building blocks of different materials in well-controlled sequences can provide an additional degree of complexity in terms of materials design and harnessing novel nano- and quantum-scale phenomena.

This work will discuss the current progress regarding the ALD synthesis of sulfides and selenides of tin, molybdenum, and tungsten on bare silicon and oxide-capped silicon (001) substrates. A comparative study, in terms of the structure, the morphology, and the growth rate of the films, for chloride and dimethylamido-based metallic precursors, will be presented. Some of the initial results of the ALD synthesis of 2D multi-layered films will be discussed. The work will also highlight the alteration to the crystal structure, morphology, and orientation of the as-grown films, brought about by post-growth annealing treatments.

Reference:

[1] S.Z. Butler, S.M. Hollen, L. Cao, Y. Cui, J.A. Gupta, H.R. Gutiérrez, T.F. Heinz, S.S. Hong, J. Huang, A.F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R.D. Robinson, R.S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M.G. Spencer, M. Terrones, W. Windl, and J.E. Goldberger, ACS Nano **7**, 2898 (2013).

[2] X.X. Zhang, Y. You, S.Y.F. Zhao, and T.F. Heinz, Phys. Rev. Lett. **115**, 257403 (2015).

[3] C. Jin, E.C. Regan, A. Yan, M. Iqbal Bakti Utama, D. Wang, S. Zhao, Y. Qin, S. Yang, Z. Zheng, S. Shi, K. Watanabe, T. Taniguchi, S. Tongay, A. Zettl, and F. Wang, Nat. 2019 5677746 **567**, 76 (2019).

[4] J. Cheng, C. Wang, X. Zou, and L. Liao, Adv. Opt. Mater. **7**, 1800441 (2019).

[5] J. Li, L. Niu, Z. Zheng, and F. Yan, Adv. Mater. **26**, 5239 (2014).

[6] Y. Jin, D.H. Keum, S.J. An, J. Kim, H.S. Lee, and Y.H. Lee, Adv. Mater. **27**, 5534 (2015).

[7] M.J. Lee, J.H. Ahn, J.H. Sung, H. Heo, S.G. Jeon, W. Lee, J.Y. Song, K.H. Hong, B. Choi, S.H. Lee, and M.H. Jo, Nat. Commun. 2016 71 **7**, 1 (2016).

[8] D. Deng, K.S. Novoselov, Q. Fu, N. Zheng, Z. Tian, and X. Bao, Nat. Nanotechnol. 2016 113 **11**, 218 (2016).

[9] M. Xu, D. Fujita, and N. Hanagata, Small **5**, 2638 (2009).

EM-MoP-14 Plasma Enhanced Atomic Layer Deposition of Scandium Nitride*, **Thomas Larrabee**, G. Rayner,* Kurt J. Lesker Company*; N. Strnad,* U.S. Army Research Laboratory*; N. O'Toole,* Kurt J. Lesker Company

Scandium nitride is a III-V semiconductor from group III and group XV, with properties distinct from those of more common III-Vs from group XIII and group XV.(1)Among the most important applications of ScN, however, is when it is alloyed with AlN to form $Al_{(1-x)}Sc_xN$.Thin films of $Al_{(1-x)}Sc_xN$ have shown enhanced piezoelectricity(2), and recently ferroelectricity(3), enabling novel electronic devices, such as FE-FETs(4).While ScN has been deposited by a variety of techniques including hybrid vapor-phase epitaxy (HVPE), magnetron sputtering, MBE, and MOCVD, an ALD technique would have advantages for CMOS integration --- including low temperature, wide-area uniformity, 3D conformality, precise thickness control, etc.While Sc_2O_3 ALD has been reported(5), to the best of our knowledge, this represents the first example of ScN by an ALD technique.

Scandium nitride was deposited at 250 °C from tris(N,N'-di-isopropylformamidinato)scandium(III) (Sc(amd)$_3$) and N_2/Ar plasma in a Kurt J. Lesker ALD150LX plasma-enhanced ALD reactor.The Sc(amd)$_3$ was delivered from a source held at 160 °C.XPS results demonstrate 1:1 Sc to N composition, with a small amount of carbon (3.8%) and very low oxygen in the bulk of the film (~1%).In nitride PEALD, ultra-high purity (UHP) process conditions have been shown to be necessary to obtain low oxygen content in readily oxidizable thin films, such as TiN(6), which we believe is critical to low-impurity ScN PEALD.Grazing incidence X-ray diffraction (GIXRD) shows evidence of polycrystalline ScN at this growth temperature from a film grown on Si (with native oxide), with peaks corresponding to the (200), (220), (311), and (222) peaks of reference cubic ScN.A UHP process for ScN with compatible temperature window for PEALD of AlN, such as this, is anticipated to enable ultra-thin ALD-grown $Al_{(1-x)}Sc_xN$ for applications in 3D piezoelectric MEMS devices and/or ferroelectric memory which would be difficult or impossible to achieve via existing non-ALD deposition techniques.

[1]Biswas, B.; and Sava, B. *Physical Review Materials***3**, 020301 (2019).

[2]Akiyama, M.; et al.*Adv. Mater.***21**, 593 (2009).

[3]Ficktner, S.; Wolff, N.; Lofink, F,; Kienle, L.; and Wagner, B.*J. Appl. Phys.***125**, 114103 (2019).

[4]Liu, X.; et al. *Nano. Lett.***21**, 3753-3761 (2021).

[5]Wang, X.; et al. *Appl. Phys. Lett.***101**, 232109 (2012).

[6]Rayner, Jr., G.B.; O'Toole, N.; Shallenberger, J.; Johs, B. *J.Vac. Sci. Technol. A***38**, 062408 (2020).

EM-MoP-15 Yttrium Fluoride Coatings*, **Carlo Waldfried,*** Entegris, Inc.

There is a desire to produce ALD coatings of yttrium-fluoride materials, such as YOF and YF_3, but the implementation of such coatings is challenging and requires special considerations in the choice of precursor chemicals and reactants as well as ALD tool designs due to the corrosive nature of these processes.We will be presenting an approach to produce thin films of ALD-based YOF and YF_3 by depositing ALD Y_2O_3 and then converting the oxide film into YOF and/or YF_3 with a post-coat chemical vapor (non-plasma) conversion process. Utilizing this method YF_3 and YOF layers with thicknesses of more than 100nm have been produced and applied to high aspect ratio structures.

Film structure, composition, chemical bonding arrangement and morphology have been studied using techniques such as XPS, XRD, EDAX, and FIB SEM. It is believed that the fluoride is formed by an O-> F exchange reaction, converting the Y_2O_3 into YF_3 or YOF.

Furthermore, we will discuss how blends of YF_3 and YOF, with a gradual transition of the composition from YF_3 to YOF and Y_2O_3 can be obtained and how that may be advantageous for the implementation of such fluoride coatings.

Hybrid Materials & Infiltration
Room Arteveldeforum & Pedro de Gante - Session HM+EM+NS-MoP
Hybrid Materials & Infiltration Poster Session

HM+EM+NS-MoP-1 Converting Electrospun Polymer Fibers Into Metal Oxide Nanofibers, Nanobelts, and Core-Shell Fibers via Sequential Infiltration Synthesis*, R. Azoulay, M. Barzialy, I. Weisbord, R. Avrahami, E. Zussman,* Israel Institute of Technology, Israel*; **Tamar Segal-Peretz,*** Technion- Israel Institute of Technology, Israel

Sequential infiltration synthesis (SIS) has emerged in the past decade as a powerful technique for growth of inorganic materials within polymers through ALD chemistry. In SIS, ALD precursors diffuse into the polymer and interact with it, leading to inorganic materials growth within the polymer's free volume. If desired, the polymer can later be removed, yielding polymer-templated inorganic structures.

Here, we utilize SIS for high precision fabrication of AlO_x, ZnO, and AlO_x-ZnO core-shell fibers, with programmable dimensions, morphology, and surface structure. Designed growth profiles within the fiber are achieved through control over the precursors' diffusion depth within the polymer fibers. Long precursor diffusion times lead to moderate growth gradients and result in spherical fibers after polymer removal, while short precursor diffusion times lead to sharp growth gradients and result in fiber buckling into nanobelt morphology. To move towards complex inorganic fiber architectures, we extend single metal oxide SIS into spatially-controlled, multi-material SIS and demonstrate AlO_x-ZnO core-shell fibers with tunable core and shell thicknesses. The core-shell fibers are fabricated in a single SIS process, where the location of each metal oxide is controlled by its diffusion time. By harnessing the additional degrees of freedom of SIS, *i.e.* ALD-based growth within 3D polymer volume, we were able to achieve complex fiber morphologies.

HM+EM+NS-MoP-2 First Principles Modelling of Growth of Hybrid Organic-Inorganic Films*, **Arbresha Muriqi,** M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Density functional theory (DFT) has proven to be a powerful tool to investigate the reaction mechanisms in hybrid film growth, predict the most suitable precursors and address aspects of the molecular layer deposition (MLD) experiments.

In our work, we use first principles density functional theory calculations to examine key steps in the mechanism of hybrid film deposition through MLD by modelling precursor-surface and precursor-precursor reactions and challenging the proposed reaction mechanisms in hybrid films. We explore the growth mechanism of aluminium, magnesium and titanium containing hybrid films known as alucones, magnesicones and titanicones, respectively. For alucones we investigate in detail the chemistry of the MLD process between the post-TMA ($Al(CH_3)_3$) pulse methyl-terminated Al_2O_3 surface with ethylene glycol (EG) and glycerol (GL). Double reactions of organic molecules with the alumina surface are also explored. We show that while both organic precursors react favorably with TMA fragments, EG and GL lie flat and create double reactions through the two terminal OH groups. For EG this phenomenon removes the active OH groups from the surface and growth will be less favorable while for GL the third OH group is available and growth can proceed. [1] Because of the double reaction phenomenon of aliphatic molecules EG and GL, we proposed new aromatic molecules which due to their stiff backbone avoid the unwanted double reactions and lead to thicker and more flexible hybrid films.[2] As the infiltration phenomenon of TMA into the growing film is another common practical issue in alucone film growth, we consider DMAI ($(CH_3)_2Al(OC_3H_7)$)as an alternative to TMA. DFT calculations show that the reactivity of DMAI is sufficient for DMAI to take part in the MLD reactions. Combined with the fact that DMAI is a bulky molecule that avoids infiltration into the alucone film, DFT studies provide motivation to develop an MLD process using DMAI as inorganic precursor.

We also investigate the growth mechanism of titanicones grown using $TiCl_4$ and TDMATas metal source and EG or GL as organic reactants. We found that compared to $TiCl_4$, TDMAT adsorbs more favorably on the anatase-TiO_2, rutile-TiO_2 and Al_2O_3 surfaces and reacts more favorably with the organic species. Therefore, TDMAT is a more suitable precursor for titanicone film growth.

1. A. Muriqi, M. Nolan, First principles study of reactions in alucone growth: the role of the organic precursor, Dalton Trans., 2020, 49, 8710 – 8721.

2. A. Muriqi, M. Karppinen M. Nolan, Role of terminal groups in aromatic molecules on the growth of Al_2O_3-based hybrid materials, Dalton Trans., 2021, 50, 17583-17593.

HM+EM+NS-MoP-3 Hybrid Organic-Inorganic Isoporous Membranes with Tunable Pore Sizes and Functionalities for Molecular Separation*, Z. Zhang,* Helmholtz-Zentrum hereon GmbH, Germany*; **Assaf Simon,** T. Segal-Peretz,* Technion IIT, Israel*; V. Abetz,* Helmholtz-Zentrum hereon GmbH, Germany

Block copolymers (BCPs) are considered promising materials for various membrane applications ranging from water treatment to protein separation due to their ability to self-assemble into highly ordered structures with uniform pore size and high pore density. Typically, the pore's size and surface interactions are controlled by the BCP chemistry. However, simultaneous control over both properties is difficult to achieve. In particular, reaching nanometric pores which will allow for molecular separation through the BCP chemistry is considered a major challenge.

In this study, we tailor the size and chemistry of BCP based ultrafiltration membranes by selectively growing metal oxides within and on the pores. Poly (styrene-*b*-4-vinyl pyridine) (PS-*b*-P4VP) was used to create ultrafiltration membranes in a process combining self-assembly with non-solvent induced phase separation (SNIPS). This results in one integral but asymmetric membrane, with ordered pores at the top of the membrane and sponge-like mechanically robust support layer at the bottom of the membrane. Sequential infiltration synthesis (SIS), an atomic layer deposition-based technique that enables selective growth of metal oxides inside the polar domains of BCP, was used to grow Al_2O_3 inside the P4VP domains of the BCP films. By incorporating metal oxides in the pores, the pore size can be reduced. By modifying the number of SIS cycles and/or the metal oxide we use, we can achieve control over the pore size while laying grounds for further membrane functionalization.

Functionality is achieved *via* straightforward scalable gas/liquid-solid interface reactions, where the hydrophilicity/hydrophobicity of the membrane is significantly changed by introduction of functional groups. The functionalized membranes reveal a superior selectivity and permeability to separate small organic molecules and fractionate similar-sized proteins based on size, charge and hydrophobicity.

This demonstrates the great potential of combining BCP and metal oxide growth for high-performance membranes for molecular separation. These membranes could be used in chemical and pharmaceutical processing as well as in other nanofitlation applications.

HM+EM+NS-MoP-4 Surface Functionalization of Porous Carbon Fibers by Vapor-Phase Methods for CO_2 Capture*, Stephan Prünte,* Eindhoven University of Technology, Netherlands*; G. van Straaten, D. van Eyck, J. van Dijck, H. de Neve,* Carbyon, Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

The removal of excess CO_2 from the atmosphere will play a major role in the mitigation of global warming. While CO_2 sequestration at fossil fuel power plants is primarily achieved via wet chemical routes, CO_2 capture from ambient air is much more challenging. Solid-state adsorbents, consisting of CO_2-binding functional amine groups on porous supports, can deliver high CO_2 capture capacities with low energy requirements[1].

In this contribution, we report on the functionalization of porous carbon fibers by self-limiting vapor-phase techniques. Functionalization was carried out either via i) exposure to a cyclic azasilane molecule (2,2-dimethoxy-1,6-diaza-2-silacyclooctane) to introduce amine functionalities or ii) ALD of Al_2O_3 based on cycles of trimethylaluminum and H_2O followed by exposure to the azasilane molecule. Given the high specific surface area of the carbon fibers exceeding 1400 m^2/g with a bimodal distribution of pore diameter (0.5-0.6 nm and 0.8 nm), the above-mentioned precursors were dosed in multi-pulses.

The self-limiting nature of the two processes was verified by weight gain measurements. The increase in weight relative to the pristine sample saturated at 23% for direct amine functionalization. For case ii), the weight gain saturated at 11% for Al_2O_3 ALD and at 3.1% upon azasilane exposure relative to the pristine sample. The lower amine loading in case ii) with respect to case i), i.e. 0.14 mmol/g vs. 0.97 mmol/g, respectively, may result from clogging of smaller pores by ALD of Al_2O_3. XPS analysis confirmed amine functionalization, while EDX mapping of fiber cross-section revealed an homogenous distribution of Al and Si.

CO_2 capture capacities of 0.18 and 0.13 $mmol/g_{sorbent}$ were measured under simulated ambient conditions by mass spectrometry for case i) and ii), respectively. The capture capacities were in the same range as those reported for amines grafted on SiO_2[2,3]. However, the capture capacity with respect to amine loading for case ii) was 5-fold exceeding case i). This indicates that the functionalization of carbon fibers by ALD of Al_2O_3 and azasilane exposure leads to an efficient utilization of amine groups for CO_2 capture.

The presented research demonstrates the potential of modifying porous carbon fibers by grafting CO_2 adsorption functionalities via vapor-phase methods on the fibers' internal surface. Future engineering of porous materials by ALD and vapor-phase functionalization may pave the way towards realizing efficient direct air capture.

[1] N. McQueen *et al.*, Prog. Energy, **2021**, 3, 32001

[2] J.A. Wurzbacher *et al.*, Energ. Environ. Sci., **2011**, 4, 3584–3592

[3] S.A. Didas *et al.*, Chem. Sus. Chem., **2012**, 5, 2058–2064

HM+EM+NS-MoP-5 Mechanical Behavior of Hybrid Organic-Inorganic Thin Films Fabricated by Sequential Infiltration Synthesis (SIS)*, Shachar Keren,* *T. Segal-Peretz , N. Cohen,* Technion, Israel

Hybrid organic-inorganic materials have drawn increased interest in the last decades due to their synergic properties. Control over the mechanical properties of hybrid organic-inorganic nanomaterials is central to their implementation in a wide range of applications, including energy absorbing materials and protective coatings. In recent years, sequential infiltration synthesis (SIS) has emerged as a promising new technique for fabricating hybrid materials with nanoscale precision. In SIS, inorganic materials are grown within polymers from vapor phase precursors using atomic layer deposition (ALD) chemistry. Several studies have demonstrated the potential of SIS to tune the mechanical properties of polymers. However, a full understanding of the relationship between the nanoscale structure and composition and the nanostructure mechanical behavior is still an ongoing effort.

In this research, we study the mechanical response of pristine and hybrid thin films fabricated via SIS using a combined experimental and theoretical approach. Hybrid thin films were fabricated by growing AlO_x within PMMA films via SIS process, using trimethylaluminum and H_2O as precursors. *In-situ* FTIR measurements were used to evaluate the interaction between the inorganic AlO_x and the polymer chains, and *in-situ* microgravimetric measurements were used to assess the inorganic mass gain. The mechanical responses were studied with nanoindentation combined with scanning electron microscopy (SEM). In addition, we developed a microscopic model which accounts for the hybrid organic-inorganic microstructure profile and correlates between the hybrid structures and their mechanical properties.

HM+EM+NS-MoP-6 Plasma Enhanced-MLD Processes of Phosphorus-Containing Thin Films*, Justin Lomax,* University of Western Ontario, Canada*; E. Goodwin, P. Gordon,* Carleton University, Canada*; C. McGuiness,* Solvay, Canada*; S. Barry,* Carleton University, Canada*; C. Crudden,* Queen's University, Canada*; P. Ragogna,* University of Western Ontario, Canada

Since the introduction of Molecular Layer Deposition (MLD), many compounds have been employed as a precursor to generate thin films of materials on the angstrom scale. Examples include amides, ureas, thioureas, azomethines, ethylene terephthalates, and ester precursors for thin film construction.[1] MLD films have been prepared with relatively few elements other than C, N, O, and S, leaving vast areas on the periodic table open for investigation. The Ragogna group has developed a method of preparing robust phosphorus polymer networks that in the bulk phase show excellent surface adhesion, barrier properties (O_2; H_2O), optical transparency (visible) and thermal stability (up to 400 °C).[2] This known method of generating polymer networks rich in phosphorus content was translated into an MLD process. By using plasma-enhanced MLD on Si/SiO_2 and Al_2O_3 substrates, film generation using the commercially available 1° phosphine $i\mathrm{BuPH}_2$ paired with a known volatile siloxane precursor (tetramethyltetravinylcyclotetrasiloxane) was explored. Thin film construction (10-100 nm) used an Ar radical source to facilitate P-H addition to the vinyl functionalities on the siloxane precursor and yielded a growth rate of 0.6 - 1.45 Å per cycle. Films were characterized by XPS, AFM and ToF-SIMS.

(1) Meng, X. An Overview of Molecular Layer Deposition for Organic and Organic–Inorganic Hybrid Materials: Mechanisms, Growth Characteristics, and Promising Applications. *J. Mater. Chem. A***2017**, *5* (35), 18326–18378. https://doi.org/10.1039/C7TA04449F.

(2) Guterman, R.; Rabiee Kenaree, A.; Gilroy, J. B.; Gillies, E. R.; Ragogna, P. J. Polymer Network Formation Using the Phosphane–Ene Reaction: A Thiol–Ene Analogue with Diverse Postpolymerization Chemistry. *Chem. Mater.***2015**, *27* (4), 1412–1419. https://doi.org/10.1021/cm504784e.

HM+EM+NS-MoP-7 Al_2O_3 Dot and Antidot Arrays Fabricated by Sequential Infiltration Synthesis in Hexagonally Packed PS-*b*-PMMA Block Copolymer Thin Films*, Gabriele Seguini,* *A. Motta, M. Bigatti, F. Caligiore,* CNR, Italy*; G. Rademaker, A. Gharbi, R. Tiron,* CEA/LETI-University Grenoble Alpes, France*; G. Tallarida, E. Cianci, M. Perego,* CNR, Italy

Sequential infiltration synthesis (SIS) is a three-dimensional (3D) growth process derived from atomic layer deposition (ALD) on polymers. SIS permits to grow inorganic materials into polymeric films. SIS into self-assembled block copolymers (BCP) offers the possibility to fabricate inorganic nanostructures starting from nanostructured organic templates. The fine-tuning of the dimensions of the resulting nanostructures can be achieved by proper selection of the SIS process conditions. In particular, the sequential reaction steps of the SIS process allow tuning the dimensions of the nanostructured material adjusting the number of SIS cycles. This capability to achieve a fine tuning of the dimensions of the resulting inorganic nanostructures is fundamental to make this technology suitable for the different target applications. At the same time, this step by step growth of the inorganic nanostructures allows to obtain information about the progressive mass uptake of the inorganic component into the polymer matrix and to delve into the growth mechanism.

In this work, Al_2O_3 dot and antidot arrays were synthetized by infiltration of trimethylaluminum and water precursors into out of plane cylinder forming poly(styrene-block-methyl methacrylate) (PS-b-PMMA) BCP thin films. The evolution of the characteristic dimensions of these inorganic nanostructures were investigated as a function of the SIS cycle number. Collected data provided information about the mechanism governing the effective incorporation of Al_2O_3 into the PMMA component of the BCP thin films. Accordingly, mass uptake of Al_2O_3 into the PMMA component of self-assembled PS-b-PMMA thin film is significantly enhanced compared to mass uptake in pure PMMA thin films, due to the presence of additional paths for diffusion of precursor molecules into the not reactive PS component and to their sorption at the PS/PMMA interface. Mass uptake is directly proportional to the surface of the PMMA nanodomains suggesting that in this specific BCP system the incorporation of Al_2O_3 into the PMMA component is essentially sorption limited. From the technological point of view, collected data demonstrate that SIS provides accurate control on the characteristic dimensions of the Al_2O_3 dot and antidot arrays.

This research was partially supported by the project “IONS4SET” funded from the European Union’s Horizon 2020 research and innovation program (Grant No. 688072).

HM+EM+NS-MoP-8 Flexible and Conductive Zinc oxide – Zincone Nanolaminate Thin Films Deposited using Atomic and Molecular Layer Depositions*, Seung Hak Song*, *B. Choi,* Korea University, Korea (Republic of)

The combination of atomic layer deposition (ALD) and molecular layer deposition (MLD) enables the fabrication of various functional organic-inorganic composite thin film structures. By adjusting ALD and MLD cycles ratio, the structure of organic-inorganic thin films can be controlled. Therefore, the properties of the thin films can be tuned through the combination of various nano layers. Flexibility can be improved by inserting organic layers between thicker inorganic thin films. Incorporation of organic layers may degrade the electrical properties of thin films due to decrease in crystallinity. Therefore, it is necessary to study the thin film structures with optimal mechanical and electrical properties. Although the combination of ALD and MLD is very promising, few studies have been conducted. Especially, there are very few studies on the mechanical properties of organic-inorganic nanolaminate thin films, and studies have been conducted on very limited areas. We deposited zinc oxide (ZnO) – zincone nanolaminate thin films on transparent polyimide (TPI) using ALD and MLD methods and investigated their growth characteristics and mechanical-electrical properties with process conditions. We fabricated thin films with ZnO and zincone ratios of 100:1, 40:1 and 20:1 respectively, in the temperature range of 120 to 240 ℃ and measured the changes in mechanical-electrical properties according to deposition temperature and thin film structures. The mechanical properties of the thin films were measured through nanoindentation and bending tests. The bending test is a method to evaluate the durability of the thin films by measuring the change in electrical resistance of the thin films with bending radius, and it was possible to analyze the effect of zincone layers on the thin film’s durability. In addition, changes in the microstructures of the thin films with process temperature were measured using X-ray diffraction (XRD) and transmission electron microscopy (TEM), and the effect of microstructural changes on mechanical and electrical properties of the thin films were analyzed. From the tests results, as the zincone ratio increased, the crystallinity of the thin films decreased and the electrical conductivity was lowered, but the flexibility was slightly improved.

HM+EM+NS-MoP-9 Understanding of Polymer-Precursor Interactions during Sequential Infiltration Synthesis of Al_2O_3 in Polybutylene Succinate Films*, Alessia Motta*, *G. Seguini, C. Wiemer,* IMM-CNR, Italy*; R. Consonni, A. Boccia,* SCITEC-CNR, Italy*; G. Ambrosio, C. Baratto,* INO-CNR, Italy*; P. Cerruti,* IPCB-CNR, Italy*; S. Tagliabue,* Corapack srl., Italy*; M. Perego,* IMM-CNR, Italy

The amount of plastic has increased exponentially over the years, leading to cumulative environmental damage in terms of microplastics pollution, soil infertility and impact on the wildlife. Therefore, the development of an alternative and sustainable option like bioplastics is highly recommended. In this respect, polybutylene succinate (PBS) is a commercial bio-degradable and bio-based polymer with good mechanical properties, thermal and chemical stability. PBS presents good processability, and is used in different fields such as packaging, agriculture, and biomedical applications. However, PBS has poor gas barrier properties, and it is very stiff, limiting its use as a packaging material. The insertion of inorganic filler or the deposition of inorganic top layer have been proposed to modify its physical characteristics and to overcome these drawbacks. Sequential Infiltration Synthesis (SIS) is a sub-class of ALD and provides an attractive option for the preparation of inorganic-organic composites. SIS is based on the alternating exposure of the polymer to organo-metallic and oxygen precursors, diffusing and reacting into the organic material.

In this work, we investigated the growth of Al_2O_3 in freestanding ~30 um thick PBS films by SIS process at 70°C via trimethylaluminum (TMA) and H_2O precursors. Through a systematic analysis of the composition and morphology of the infiltrated PBS samples at different process conditions, the reaction kinetics was clarified. FTIR and NMR measurements showed that the ester group is involved in polymer-precursors interaction, leading to the formation of a new aliphatic groups with the concomitant rupture of the main polymeric chain. Al_2O_3 incorporation in the infiltrated samples was further confirmed by the XPS analysis. Moreover, SEM-EDX cross sectional images showed a homogeneous Al_2O_3distribution inside the PBS films, depicting a completely different scenario compared to standard ALD that determines Al_2O_3 growth on the more superficial region of the PBS film. Al_2O_3 mass uptake as a function of the number of SIS cycles was studied by infiltration in thin PBS films spin coated on Si substrates ranging from 30 to 70 nm. Mass uptake in the PBS films was found to be much higher than in standard polymethylmethacrylate films, at the same process conditions. Considering that the density of reactive sites in the two polymers is roughly the same, the observed difference in Al_2O_3 mass uptake is explained based on the different free volume of these polymers and the specific reaction mechanism proposed for PBS. These results pave the way towards the application of SIS for the improvement of bio-polymers for food packaging.

HM+EM+NS-MoP-10 On the Development and Atomic Structure of ZnO Nanoparticles Grown within Polymers using Sequential Infiltration Synthesis*, Inbal Weisbord*, *M. Barzilay,* Chemical Engineering Department, Technion, Israel*; A. Kuzmin, A. Anspoks,* Institute of Solid State Physics, University of Latvia*; T. Segal-Peretz,* Chemical Engineering Department, Technion, Israel

Sequential infiltration synthesis (SIS), an ALD-derived method for growth of inorganic materials inside polymeric structures, is an emerging technique for hybrid materials and inorganic nanostructure fabrication which can be utilized in a wide array of applications. In this work, we study the development of ZnO crystalline particles within SU-8, polymethacrolein (PMCHO), and polymethyl methacrylate (PMMA) at the atomic scale. We probe the growth throughout diethyl zinc (DEZ)/H_2O SIS cycles, as well as after polymer removal. The crystalline ZnO structure is deciphered by combining two powerful methods: extended x-ray absorption fine structure (EXAFS) and high-resolution scanning transmission electron microscopy (HR-STEM). Synchrotron-based EXAFS provides large-scale statistical information on the crystals’ long-range order and predicts their Wurtzite structure. HR-STEM of the hybrid polymer-ZnO films corroborates the predicted structure and allows for precise analysis of crystal size, orientation, and existing defects, as well as the dispersion of the particles inside each polymer. Significantly, the polymer matrix allows us to probe the growth, cycle-by-cycle, providing insights to ZnO atomic growth mechanism inside different polymers and extending our understanding of SIS. In addition, the methodology developed for such high-resolution imaging of hybrid films will allow future studies of additional hybrid systems.

HM+EM+NS-MoP-11 Fabrication of Hafnium Oxide Nanostructures Using Block Copolymer Matrices via Sequential Infiltration Synthesis*, Przemyslaw Pula*, University of Warsaw, Poland

Hafnium dioxide (hafnia, HfO_2) is a transition-metal oxide, an electrical insulator with a large energy bandgap ~5.5 eV. Among numerous applications of this material, its thin films have been used as gate insulators in transistors and as optical and corrosion-protective coatings. The scope of applications for porous hafnia nanostructures is even more extensive and includes catalytical and sensing applications.

Atomic Layer Deposition (ALD) is a powerful technique to fabricate thin oxide films with excellent uniformity and conformality on various substrates. While such layers may function as optical or protective coatings, a porous replica with a developed surface is more suitable for catalytic or sensing applications. The latter is readily available to fabricate via a variation of ALD, namely the Sequential Infiltration Synthesis (SIS). Although SIS shares chemical principles with ALD, the main difference is the volume growth of oxide within the polymer or photoresist molecules. Especially, block copolymers (BCPs) are a versatile platform for a synthesis of hybrid organic-inorganic nanostructures with tailored morphology and shape. More inorganic material can be infiltrated in a prolonged exposure step within a selected BCP functional group compared to a self-limited ALD surface growth. Despite the same chemical origin of these two techniques, not all ALD-derived compounds have been already demonstrated in SIS, mainly due to lower reaction temperatures required to sustain the order of a BCP template. Hafnium dioxide is an example of such a compound whose ALD process parameters were quite thoroughly examined while no SIS-derived experiment was successfully performed so far.

Here, we demonstrate the successful SIS block copolymer templated synthesis of a porous hafnium dioxide. The final effect was achieved by merging two factors: generation of more chemically reactive species combined with the increase of reaction temperature without a detrimental effect on the polymeric template order. We have verified the optimal synthesis parameters using an in-situ quartz crystal microbalance setup. The morphology and composition of our replica were investigated in SEM and XPS experiments, respectively.

Results indicated in this experiment show the successful synthesis of hafnia with the use of a large-molecule metal precursor which may catalyze further research in the topic and encourage to test similar compounds for other metals. The method presented here offers an option to modify soft matter samples in order to create hybrid organic-inorganic nanostructures, normally being damaged at standard operational ALD temperature conditions.

HM+EM+NS-MoP-12 ZIF-based Metal-Organic Frameworks for Cantilever Gas Sensors

***Masoud Akbari**, C. Crivello, O. Graniel ,* Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, France*; M. Defort , S. Basrour,* Univ. Grenoble Alpes, CNRS, Grenoble INP, TIMA, France*; K. Musselman,* Department of Mechanical and Mechatronics Engineering, University of Waterloo, Canada*; D. Muñoz-Rojas,* Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, France

Among the different gas sensing platforms, cantilever-based sensors have attracted considerable interest in recent years thanks to their ultra-sensitivity and high-speed response. The gas sensing mechanism in a dynamic cantilever sensor is based on its resonance frequency shift upon adsorption of a gas molecule on the sensor. In order to sensitize the surface of a cantilever, a sensitive receptor material with large surface area is required. Metal-organic frameworks (MOFs) are a class of nanoporous crystalline materials composed of metal ions coordinated to organic linkers. MOFs are promising for gas sensing applications as they have large surface area, rich porosity with adjustable pore size and excellent selective adsorption capability for various gasses.[1] Zeolite imidazole frameworks (ZIFs) are a class of MOFs where metals with tetrahedral coordination (i.e. Zn, Co, Fe, Cu) are the central node and the ligands are imidazolate-based organic molecules.

In this work, we developed a ZIF-based thin film for dynamic cantilever gas-sensing applications. We employed a novel atmospheric pressure spatial atomic layer deposition (AP-SALD)[2][3] technique to deposit a ZnO sacrificial layer on the silicon cantilevers. This technique allows the deposition of high-quality films at atmospheric pressure, faster than conventional ALD. The ZnO layer was then converted to a particular ZIF film with desired porosity and size, through a MOF-CVD process.[4] A gas-sensing bench setup was developed for the cantilever actuation and read-out. We present the chemical and morphological properties of the ZIF, as well as the frequency response of the sensor to various gases. The device showed reliable sensitivity to humidity, CO2 and several VOCs.

References

[1]X. F. Wang, X. Z. Song, K. M. Sun, L. Cheng, and W. Ma, “MOFs-derived porous nanomaterials for gas sensing,” Polyhedron, vol. 152, pp. 155–163, 2018.

[2]D. Muñoz-Rojas, T. Maindron, A. Esteve, F. Piallat, J. C. S. Kools, and J. M. Decams, “Speeding up the unique assets of atomic layer deposition,” Mater. Today Chem., vol. 12, pp. 96–120, 2019.

[3]K. P. Musselman, C. F. Uzoma, and M. S. Miller, “Nanomanufacturing: High-Throughput, Cost-Effective Deposition of Atomic Scale Thin Films via Atmospheric Pressure Spatial Atomic Layer Deposition,” Chem. Mater., vol. 28, no. 23, pp. 8443–8452, 2016.

[4]I. Stassen et al., “Chemical vapour deposition of zeolitic imidazolate framework thin films,” Nat. Mater., vol. 15, no. 3, pp. 304–310, 2016

HM+EM+NS-MoP-13 Tuning the Thermal Properties of Molecular Layer-Deposited Hybrid Metalcone Films via Modulating Metal Mass

M. Hoque, University of Virginia, USA*; R. Nye,* North Carolina State University*; J. Tomko,* University of Virginia, USA*; G. Parsons,* North Carolina State University*; **Patrick Hopkins**,* University of Virginia

Application of polymers as flexible substrates, interfacial binders, and encapsulation layers in electronic devices is often limited by their low thermal conductivities. In this work, we study the thermal properties of two hybrid organic-inorganic metalcone (alucone and tincone) films grown via molecular layer deposition. The thermal conductivity of the alucone and tincone films are measured via steady-state thermoreflectance and found to be 1.14 ± 0.18 and 0.4 ± 0.07 $W\ m^{-1}\ K^{-1}$, respectively. The significantly higher atomic mass of tin compared to aluminum gives rise to this thermal conductivity difference. Furthermore, picosecond acoustics measurements reveal that the longitudinal sound speed, hence the bond strength is nearly the same between the two metalcone films. The thermal conductivity and longitudinal sound speed of the alucone and tincone films fill an important gap between the insulating soft polymers and thermally conductive, high strength polymers. Our study opens up new pathways for tuning the thermal conductivity of hybrid metalcone films without sacrificing the elastic properties.

HM+EM+NS-MoP-14 Analysis of Rearranged Organic/Inorganic Hybrid 2D Tincone Film via Molecular Layer Deposition

***GeonHo Baek**, S. Lee, H. Kim, S. Choi, J. Park,* Hanyang University, Korea

In recent years, research on monolayer and two-dimensional (2D)-based family materials developed, starting with well-known graphene which has emerged an innovative research topic[1]. Through atomic-level thickness control of ultra-thin 2D materials, the design and fusion of electronic devices are possible, enabling applications in various fields as well as in optoelectronics and semiconductors. Organic/inorganic hybrid tincone films were deposited by molecular layer deposition (MLD) using N,N′-tert-butyl-1,1-dimethylethylenediamine stannylene(II) as a precursor and hydroquinone (HQ) as organic reactants. When combined with HQ having a bi-functional hydroxyl group, SnO-based 2D hybrid tincone can be produced. In this study of tincone fabricated with a divalent precursor after a vacuum post-annealing process, the structural rearrangement of the SnO and the benzene ring bonds proceeded to form a SnO-based hybrid 2D structure. The rearrangement of the resulting structure occurred through π-π stacking (without pyrolysis) of the benzene ring. To understand the mechanism of fabrication of 2D hybrid tincone by π-π stacking of the benzene ring, and the strengthening of the crystallinity of SnO after the annealing process, the structural rearrangement was observed using X-ray photoelectron spectroscopy (XPS), grazing incidence X-ray diffraction (GIXRD), grazing-incidence wide-angle X-ray scattering (GIWAXS), and Raman spectra.

As seen in the analyses, the as-deposited tincone originally had weak SnO nano-crystallinity without a specific crystal orientation. One hour after the annealing process at 400 ℃, individual benzene ring bonds were combined with the SnO layer in a repeated arrangement of tincone monomer [-Sn-O-C_6H_4-O-]n. In the visible region (380–750 nm), high transparency (>85%) enabled optical device application through a hybrid layer with the SnO.

Reference

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D.-e. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, science, 2004, 306, 666-669.

HM+EM+NS-MoP-15 Molecuar Layer Depostion (Mld) of Polyamide 6,4

***Marina Borraz Casanova**,* CIC nanoGUNE, Spain

Nowadays innovation in food packaging is considered at the edge of studies to extend the shelf life of food packaging, and prevent microbial spoilage, chemical contaminants, moistures, etc. In order to confer such properties into these materials one of the very promising strategies is to use molecular layer deposition (MLD). In this work, the growth of thin films via MLD are obtained by using malonyl chloride (MC) and 1.6-hexanediamine (HD) as a precursor resulting in the in-situ synthesis of the compound designated as Nylon 6,4.

Herein we conducted detailed studies of different synthetic conditions (i.e., temperature, time, precursors, pulse, substrates). We observed by Fourier transform infrared spectroscopy (FTIR) the presence of characteristic peaks assigned to the final formation of Nylon. In addition, we prove a correlation of the growth of the thin film at increasing the number of cycles by studying the X-Ray reflectivity. These processed of coating suggest that the antimicrobial properties of the synthesized Nylon 6,4 can kill the bacteria’s attached to the surface. Decreasing the amount of gram-positive (Staphylococcus aureus) and gram-negative bacteria (Escherichia coli) on the material surface.

In addition, the relevance of food packaging in the industry is moving towards smart packaging. This involves the ability to sense or measure an attribute of the product, the inner atmosphere of the package, or the shipping environment. Therefore, the ability to induce conductivity into these materials could be a key step for future generations.

This synthesis methodology can introduce new features to the materials, not only limited to food packing but also can be applied in other fields (i.e., textiles).

Nanostructure Synthesis and Fabrication
Room Arteveldeforum & Pedro de Gante - Session NS-MoP

Nanostructures Synthesis and Fabrication Poster Session

NS-MoP-1 Atmospheric Pressure ALD to Increase Organic Solvent Resistance of PDMS*, **Albert Santoso**, A. Damen, S. Khedoe, V. van Steijn, R. van Ommen,* Delft University of Technology, Netherlands

In the field of microfluidics, PDMS (polydimethoxysilane) is one among the most used polymers since it is cheap and allows easy device fabrication. On top of its high transparency, PDMS is also known to be amiable with cells and harsh inorganic solvents, making it good candidates for fluidic researches. However, there is one big downside of PDMS, which is its incompatibility with organic solvents. As a result, swelling of the polymer, and subsequently microchannel collapse, render the use of PDMS microfluidics in oil-water system such as emulsion and liquid-liquid extraction. Furthermore, current researches in increasing the so-called organic solvent "barrier resistance" are limited to finding alternative materials, which ignores the whole benefit of PDMS bulk properties. Therefore, there is a need to increase PDMS' barrier resistance without changing the bulk property. We investigate surface modification using atomic layer deposition (ALD) as an approach to improve the barrier properties of PDMS. Metal oxide such as 'bio-friendly' titanium oxide can be deposited with atomic level precision, leading to formation of barrier layer without compromising other properties of PDMS. This study focuses on the use of atmospheric pressure atomic layer deposition (APALD) on flat thin film PDMS. Compared with the conventional vacuum ALD, the convective transport allows gaseous ALD reactant to flow in high aspect ratio microfluidic channel, which is a big potential in in-situ deposition. The result shows that PDMS film coated with APALD layer has an equilibrium mass swelling ratio of 1.06 after exposure with cyclohexane. This is a large improvement than the non-coated PDMS (1.25) and the ones coated with vacuum ALD (1.22). Further investigation using scanning electron microscopy shows that uniform coating is important to reduce the organic solvent intake. Furthermore, the formation of mixed layer due to ALD reactant infiltration in the PDMS during APALD contributes in the formation of robust and crack-free surfaces, as shown by x-ray photoelectron spectroscopy depth profiling. As an addition, little to no changes are observed in the transparency and mechanical property of PDMS. This study opens up potential of in-situ coating of PDMS microfluidic, that can be used in the field of bio-radio-assays, emulsion, and extraction with organic solvent.

NS-MoP-2 The Fabrication of Heterojunctions by Atomic Layer Deposition for Gas Sensing Application*, **Muhammad Hamid Raza**, N. Pinna,* Humboldt-Universität zu Berlin, Germany

Material and methods for detecting a wide range of harmful species are becoming increasingly necessary as automation and industrial growth increase. Chemoresistive gas sensors using semiconducting metal oxides (SMOX) are fundamental for developing efficient gas sensors. The sensitivity and selectivity of these nanostructured SMOX can be boosted by combining them with other SMOX. Yet control over the thickness of the shell layer is crucial; particularly, a thin shell layer modulates the space charge layer at the interface, thereby influencing effectively the charge conduction channel. The engineering of heterojunctions with well-defined core and shell layers is required to better understand the sensing response of heterostructured nanomaterials. A comprehensive understanding of the role of semiconductor heterojunctions and the sensing response of core-shell heterostructures is achieved by synthesizing a series of well-defined and well-controlled heterostructures with varying core and shell layers. NiO- and SnO_2-based hierarchical coaxial core-shell heterostructures are therefore proposed to achieve this objective. The designed heterostructures exhibit sensing responses related to the NiO or SnO_2-shell layers, or in some cases to the heterojunctions between $_n$SMOX (SnO_2) and $_p$SMOX (NiO). A comparison of the sensing response in order to understand the transduction mechanism across the interfaces in ALD grown heterojunctions will be presented.

NS-MoP-4 Combining Initiated Chemical Vapor Deposition and Plasma-Enhanced Atomic Layer Deposition: A Study of Initial Growth and Interface Formation*, **Lisanne Demelius**, K. Unger, A. Coclite,* Graz University of Technology, Austria

In recent years, atomic layer deposition (ALD) on polymer substrates has attracted increasing interest due to potential applications in organic electronics and photovoltaics, as well as for the surface functionalization of packaging and biomaterials. However, the inherent porous structure of polymeric substrates often leads to non-ideal ALD processes that result in precursor diffusion and subsurface growth of the deposited material. The use of plasma-enhanced ALD (PE-ALD) is known to enhance nucleation due to the surface-activating effect of plasma and can be expected to significantly reduce subsurface diffusion, enabling the surface-limited deposition of thin conformal coatings. However, plasma can also have detrimental effects on polymeric substrates causing polymer degradation or etching.

In our work, we have investigated the initial growth of piezoelectric ZnO during PE-ALD on different polymer thin films deposited by initiated chemical vapor deposition (iCVD). iCVD is a prominent method to deposit highly uniform thin films of a wide range of (functional) polymers while fully retaining their rich chemistry. ZnO growth was monitored via in-situ spectroscopic ellipsometry (SE) and the resulting thin films were further characterized in terms of crystallinity, interface and surface morphology and elemental composition. To gain a better understanding of how the chemical structure of the polymer influences ZnO thin film formation, polymers exhibiting varying degrees of reactivity with the ALD precursor were studied. Furthermore, the influence of plasma power on growth behavior was investigated.

Our results show that film formation on the iCVD polymers is a consequence of two competing processes: ZnO PE-ALD growth and plasma etching of the polymer substrate. During the initial ALD cycles, polymer etching dominates, resulting in an overall decrease in thickness. At a certain point, ZnO growth takes over and the regime of normal ALD growth behaviour is entered. The strength of etching is proportional to the applied plasma power and depends strongly on the type of polymer. Despite the initial etching, the resulting thin films exhibit sharp interfaces and a quality, in terms of surface roughness, crystallinity and ZnO density, comparable to those of ZnO deposited on silicon.

This study sheds light on the mechanisms governing initial growth during PE-ALD of ZnO on different polymers and illustrates the potential of the combined use of iCVD and PE-ALD as means to achieve highly uniform and smooth multilayer structures that could be applied in a wide range of functional devices including sensing or actuation.

NS-MoP-11 Synthesis of Novel Composite Thin Film Systems With Outstanding Mechanical Properties*, L. Pethö,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; C. Guerra,* Swiss Cluster, Switzerland*; T. Xie, T. Edwards, J. Michler, X. Maeder, **Ivo Utke**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Nanoscale multilayered thin films consisting of alternating sublayers of dissimilar materials have attracted extensive attention in recent years due to their electrical, thermal and mechanical properties as compared to their single component counterparts and prove to be very promising for engineering applications. The advantage in mechanical properties are mainly attributed to the dense interfaces and interfacial structure among the different materials that form the multilayers.

We have built a hybrid thin film deposition system by combining physical vapor deposition (PVD) and atomic layer deposition (ALD) into a single machine without breaking vacuum. Multilayer composite systems were synthesized that consist of ALD Al_2O_3 sublayers between pure PVD Al structural layers. By using this system, we obtain precise control of the thickness of each ultrathin alumina layer, well below the native surface oxide thickness of pure aluminum.

We show that the ALD alumina sublayers effectively interrupted the grain growth of the ~250 nm thick Al sublayers by enabling precise grain surface control. Native surface oxide formation on the PVD deposited pure Al sublayers was circumvented by keeping the substrate in high vacuum between processing steps.

The pure Al layers are constituted of equiaxed grains with no epitaxial or texture relationship among the neighboring layers. The Al grain boundaries are parallel to the film growth direction and extend the height of each Al sublayer to form a brick-and-mortar type microstructure.

We have furthermore seen that these multilayer coatings have high yield strength compared to bulk pure aluminum. This is explained by the amorphous alumina layers acting as a dislocation sink, absorbing defects. The high tensile strength and good ductile properties of alumina are shown to restrain the deformation of Al layers and reinforce the structure.

Plenary Session
Room Auditorium - Session PS-TuM1

Plenary Session II

Moderators: Jean-François de Marneffe, IMEC, Erwin Kessels, Eindhoven University of Technology, Netherlands, Harm C.M. Knoops, Oxford Instruments Plasma Technology, Netherlands

8:45am **PS-TuM1-2 Plenary Lecture: Atomic Layer Etching: Real World Utilization and Future Outlook***, **Angélique Raley**,* Tokyo Electron America, Inc.*; H. Masanobu,* Tokyo Electron Miyagi, Ltd., Japan*; M. Hiromasa,* Tokyo Electron Miyagi Ltd., Japan*; T. Nishizuka,* Tokyo Electron Miyagi, Ltd., Japan*; P. Abel, J. Bannister,* Tokyo Electron America, Inc.*; P. Biolsi,* TEL Technology Center, America, LLC*; A. Ranjan, O. Zandi,* Tokyo Electron America, Inc.*; K. Subhadeep,* TEL Technology Center, America, LLC*; T. Hurd, Q. Wang, C. Netzband, S. Voronin, S. Arkalgud,* Tokyo Electron America, Inc. **INVITED**

In recent years, device miniaturization and challenges in integration of semiconductor devices has led to an increased demand for ultra-high selectivity and atomic level control for both etch and deposition techniques. While ALD was first developed and widely adopted in semiconductor manufacturing, its ALE counterpart has made significant strides and has been explored for many critical applications ranging from self-aligned gate contact[1], to advanced patterning[2,3] and back end of line etching [4] . Commercial plasma based ALE systems have been leveraged starting at the 10nm logic node but the low throughput of true ALE processes has limited a broader adoption of the technology.

In this talk we review the historic expansion and implementation of ALE technology in advanced process nodes and contrast it with the latest technological advances in pulsed plasma. We also discuss the benefits and synergy of integrating ALD technologies with plasma etch to improve profile control and enable more degrees of freedom in process optimization. Finally we cover the increased variety of ALE process needs and opportunities for innovations as we continue to move into 3D integration constructs and new technology spaces.

[1] M. Honda and T. Katsunuma, "Etch challenges and evolutions for atomic-order control," 2016 IEEE 16th International Conference on Nanotechnology (IEEE-NANO), 2016, pp. 448-451, doi: 10.1109/NANO.2016.7751325

[2] Masanobu Honda et al. “Novel etch technologies utilizing atomic layer process for advanced patterning,” Proc. SPIE 11329, Advanced Etch Technology for Nanopatterning IX, 1132905 (23 March 2020); https://doi.org/10.1117/12.2555805

[3] Sophie Thibaut et al. "EUV patterning using CAR or MOX photoresist at low dose exposure for sub 36nm pitch", Proc. SPIE 10589, Advanced Etch Technology for Nanopatterning VII, 105890M (17 April 2018); https://doi.org/10.1117/12.2300355

[4] Katie M. Lutker-Lee et al., "Low-k dielectric etch challenges at the 7 nm logic node and beyond: Continuous-wave versus quasiatomic layer plasma etching performance review", Journal of Vacuum Science & Technology A 37, 011001 (2019) https://doi.org/10.1116/1.5079410

9:30am **PS-TuM1-5 ALD 2021 Innovator Awardee Talk: Up, Down and All Around: Controlling Atomic Placement in ALD***, **Stacey Bent**,* Stanford University **INVITED**

With the increased importance of functional nanoscale materials for applications such as electronics, catalysts, and batteries, the interest in atomic layer deposition (ALD) as a method for fabricating structures with atomic-level control is intensifying. Based on sequential, self-limiting gas-surface reactions, ALD provides excellent capabilities for depositing thin solid films, nanoparticles, and other nanoscale materials while offering exceptional conformality, thickness control at the angstrom level, and tunable film composition. Yet despite the powerful film growth capabilities already attained with ALD, there is a compelling need to push the technique even further and control atomic placement not just in the direction of film growth, but also laterally. In this talk, I will describe research into the fundamental processes that drive ALD and ways to manipulate the chemistry to achieve area selective deposition, a bottom-up growth strategy in which deposition is directed only to desired regions of a patterned substrate. Mechanistically, the reaction chemistry of both the ALD precursor and the co-reactant at the growth surface play important roles in the ALD process and can influence both nucleation and growth. Importantly, by modifying the substrate properties, e.g., by the application of molecular monolayers or other surface treatments, the native reactivity of the surface with the ALD precursors can be altered to allow for area selective ALD. I will describe how area selectivity can be achieved across a range of different substrate and film materials, and also highlight challenges and potential solutions to reaching even high selectivities than currently possible.

10:00am **PS-TuM1-7 ALE Student Award Finalist Talk: Direct Integration of HfO_2 ALD and Surface Selective ALE for Controlled HfO_2 Film Growth***, **Landon Keller**, S. Song, G. Parsons,* North Carolina State University

Hafnium oxide (HfO_2) thin films are highly desirable as dielectric materials in transistors and DRAM capacitors in the semiconductor industry due to their high dielectric constant. As device feature size continues to decrease with transition to complex 3D architectures, precise and isotropic methods of depositing and etching materials are needed beyond conventional deposition processes. Despite the growing demand for HfO_2 in nanoscale, complex devices, only few studies report compatible HfO_2 ALD and ALE processes suitable for modern applications.

In this work, we report an integrated HfO_2 ALD/ALE process using a novel etch system for HfO_2. ALD is performed using TDMAH and H_2O, while ALE is performed using WF_6 and BCl_3. The growth and etching rates were determined using an *in-situ* quartz crystal microbalance (QCM). Additionally, the integrated HfO_2 ALD and ALE processes can be supercycled to enhance growth on one surface while suppressing growth on another surface as a means of selective deposition. We evaluated HfO_2 ALD and ALE on various surfaces, including hydroxyl-terminated Si (Si-OH), hydrogen terminated Si (Si-H), thermal silicon dioxide (SiO_2), Ru with native oxide (RuO_x), Co with native oxide (CoO_x), and low-k material (SiCOH). The growth on each surface was studied using *ex-situ* spectroscopic ellipsometry and *ex-situ* x-ray photoelectron spectroscopy.

Previously, our group reported an integrated supercycling ALD/ALE process for controlled TiO_2 film growth on SiO_2 while suppressing growth on Si-H due to an ALD nucleation delay on Si-H.[1] This work focuses on an integrated supercycling ALD/ALE process for HfO_2 at 275°C, but utilizes surface selective ALE. Figure 1 shows QCM mass uptake of integrated HfO_2 ALD and ALE conducted at 275°C, demonstrating 0.11 nm/cycle ALD growth rate and 0.10 nm/cycle ALE etch rate. While the ALD growth rate is consistent on all surfaces studied here, the ALE etch rate is surface dependent. ALD/ALE supercycles were conducted on the aforementioned substrates. Figure 2 shows the HfO_2 film thickness on each starting substrate as a function of the number of supercycles. XPS confirms HfO_2 selective deposition on CoO_x and Si-H vs Si-OH and SiO_2.

These results demonstrate a novel system for HfO_2 ALE as well as HfO_2 selective deposition through integrated ALD/ALE. We believe these findings provide valuable insight into selective deposition processes using surface selective ALE for bottom-up nanofabrication.

26. Song, S. K.; Saare, H.; Parsons, G. N. *Chem. Mater.* **2019**, *31* (13), 4793–4804.

10:15am **PS-TuM1-8 ALE Student Award Finalist Talk: First-principles Insight into Non-equilibrium Chemistry in PEALE of Silicon Nitride with Hydrofluorocarbons***, **Erik Cheng**, G. Hwang,* University of Texas at Austin*; P. Ventzek, Z. Chen, S. Sridhar, A. Ranjan,* Tokyo Electron America

Low energy ion bombardment is a key component of plasma enhanced atomic layer etch (PEALE) which may induce surface reactions unlikely to occur under thermal conditions, moving such systems far from equilibrium. Due to short occurrence times and complexities, such non-equilibrium processes cannot readily be monitored and characterized by experimental techniques alone. They are also difficult to simulate using typical computational methods, as an accurate description of these highly disordered chemical systems requires relatively large system sizes with high chemical accuracy. The inherent randomness of ion bombardment effects at the atomic level further complicates matters, demanding a statistical approach to their study. Thus, a full understanding of the non-equilibrium processes in PEALE has remained elusive.

In this talk, we present a novel molecular dynamics approach based on the self-consistent-charge density-functional tight-binding (SCC-DFTB) method and its use to uncover the underlying mechanisms of PEALE of silicon nitride (SiN) with hydrofluorocarbons (HFCs). While different HFCs have been found to exhibit distinctly different ALE behaviors, a comparison study between two key HFCs, CF_4 and CH_3F, is discussed as an example.

Even on a highly damaged SiN surface, both CF_4 and CH_3F are found to mostly remain physisorbed instead of reacting with the surface, which contradicts popular belief. Under ion bombardment, adsorbed CF_4 and CH_3F are predicted to mainly decompose into $:CF_2 + 2F^-$ and $CH_3^+ + F^-$, respectively. Our simulations clearly show the critical role of F in SiN ALE; this talk will cover detailed reaction pathways and energetics. This also suggests that the relative doubling of F production from CF_4 decomposition can be responsible for the doubling of etch rate, compared to the case of CH_3F, as reported in experimental studies. We also find that CF_2 can be stable enough to be volatile during PEALE, potentially yielding nontrivial precursor loss. However, the presence of a lone pair in CF_2 can also allow for attacks on electron deficient sites on the SiN surface. Products of such reactions can donate more F to the surface with further bombardment. CH_3 fragments, in contrast, tend to be much more reactive with the surface, be less volatile, and can act as H donors upon further bombardment. Our work highlights the importance of accurately describing the formation and reaction dynamics of key intermediates associated with HFC precursor decomposition during the non-equilibrium PEALE process. The improved understanding provides fundamental insights into process optimization and precursor design required for next-generation device fabrication.

ALD Applications
Room Auditorium - Session AA1-TuM2
ALD for Medical Applications

Moderators: Mato Knez, CIC nanoGUNE, Angel Yanguas-Gil, Argonne National Lab

10:45am **AA1-TuM2-1 Plasma-assisted ALD of IrO$_2$ for Neuroelectronic Applications***, **Valerio Di Palma**, A. Pianalto,* University of Milano Bicocca, Department of Materials Science, Italy*; M. Perego, G. Tallarida,* CNR-IMM, Unit of Agrate Brianza, Italy*; M. Fanciulli,* University of Milano Bicocca, Department of Materials Science. CNR-IMM, Unit of Agrate Brianza, Italy

Investigation *in-vitro* of neural networks is fundamental for the development of strategies to study neurological diseases such as Alzheimer's. Large arrays of microelectrodes (MEAs), planar or micro/nanostructured, are commonly used to stimulate neurons and record their response to external stimuli. MEAs materials are selected to perform charge transfer towards the cells medium efficiently and in a reversible way. IrO$_2$ has attracted attention in the field because of its pseudo-capacitive behavior, along with its stability and non-toxicity. In parallel atomic layer deposition (ALD) is confirmed as an efficient tool for the conformal functionalization of micro/nanostructured MEAs, with a good control of the thickness and of the physical properties of the film. In this work we report on the ALD growth of IrO$_2$ thin films and their physical/chemical characterization. The functional properties relevant for neuroelectronic applications, have been addressed with electrochemical measurements. We propose a new plasma-assisted ALD process, using (EtCp)Ir(CHD) as precursor and a mix of Ar/O$_2$ plasma as reactant. The process exhibits a linear growth, with a growth per cycle of about 0.3 Å at 150°C. *In-situ* spectroscopic ellipsometry shows the typical step-like behavior, *i.e.* the thickness increases during precursor absorption and then it decreases, because of the ligands removal, during the O$_2$ plasma step.

XRD analysis exhibits the characteristic peaks reported in the literature for the rutile phase of IrO$_2$. Furthermore, XPS confirms the presence of Ir in the oxidation state of +4, characterized by the chemical shift of the Ir 4f$_{7/2}$ component to 61.7 ± 0.1 eV. AFM characterization shows that ALD prepared IrO$_2$ is smooth and conformal to the substrate. On smooth Al$_2$O$_3$ substrates, IrO$_2$ RMS roughness is 0.7 ± 0.3 nm for a 24 nm thick layer. The chemical characterization via TOF-SIMS indicates that carbon content in the film is below the detection limit, indicating the good quality of the ALD prepared IrO$_2$.

Electrochemical characterization of the IrO$_2$/electrolyte interface was performed by impedance spectroscopy (EIS), cyclic voltammetry (CV) and voltage transient (VT) measurements, using a phosphate buffer solution (PBS) as electrolyte. The EIS results indicate that the interaction IrO$_2$/PBS is purely capacitive, with no faradaic contribution involved in the charge transfer mechanism. In addition, CV measurements confirm that the faradaic contribution is negligible within the range from -0.8 to +0.8 V vs. Ag/AgCl. The charge injection capacity for ALD prepared IrO$_2$ thin films determined by VT measurements is 1.40 mC, in line with the literature.

11:00am **AA1-TuM2-2 Hydrophilic Surface Modification of Microfluidic Channel by Room Temperature PEALD SiO$_2$***, **Chien-Wei Chen,*** Taiwan Instrument Research Institute, NARLabs, Taiwan*; Y. Yu, B. Li,* National Yang Ming Chiao Tung University, Taiwan

Microfluidic devices are often used in biomedical applications for fluidic sample testing and analysis, where multiple tests need to be performed with a small amount of retrieval, and the surface wetness of the flow channel affects the operability and flow rate during sample injection, making it difficult to successfully complete the process with limited retrieval conditions. PMMA is one of the commonly used substrate materials for microfluidic devices, but its surface is relatively hydrophobic (water contact angle >60°), which may be unfavorable when performing aqueous sample analysis.

The most common way to increase hydrophilicity is O$_2$ plasma treatment, but the short duration and limited increase in hydrophilicity are the biggest inconveniences in use. There are other hydrophilic coating methods such as sol-gel, PVD and CVD, but some of the above process may have the limitation that the process temperature is too high for plastic substrates. On the other hand, these methods require the inner side of the channel to be coated with a hydrophilic layer before it can be assembled into a microfluidic device, which not only increases the complexity of the process, but also may reduce the reliability of the device. For the above reasons, we use room temperature PEALD SiO$_2$ process to modify the microfluidic surface. ALD SiO$_2$ thin film not only has better and longer hydrophilic properties than O$_2$ plasma treatment (Figure 1), but also takes advantage of the fact that ALD can be used to deposit a uniform cover film on non-planar or high aspect ratio structures, and can directly deposit SiO$_2$ hydrophilic film on the internal surface of the assembled microfluidic channel. The possibility of contamination of the microfluidic surface during assembly is reduced. Finally, we also designed a simple microfluidic device to verify its autonomous absorption of aqueous solution (Figure 2), which can be used to inject fluidic samples without additional pump system and has high potential for Point-of-care testing.

11:15am **AA1-TuM2-3 Atomic Layer Deposition (Ald) on 5-Aminosalicylic Acid for Delayed and Targeted Drug Release Treatment of Inflammatory Bowel Disease***, **Jaynlynn Sosa**,* University of Central Florida*; P. Banerjee,* University of Central Florida

The incidence of chronic diseases continues to increase worldwide. Exploring new treatment alternatives for chronically ill patients has therefore been an active field of research. To improve patient compliance and reduce harsh side effects, delayed drug release systems have been developed. However, the techniques currently used to coat pharmaceuticals still face limitations in specific site targeting, loading efficiency, and pH tunability when administered orally. To overcome these challenges, we demonstrate the potential of using atomic layer deposition (ALD) as a technique to coat 5-Aminosalicylic acid (5-ASA)—a pharmaceutical drug to treat inflammatory bowel disease—to control the release of 5-ASA throughout the gastrointestinal tract.

5-ASA drug release was investigated by coating 7 mm pellets with 300, 150, and 75 cycles of ALD Al$_2$O$_3$. All pellets were made using a hydraulic pellet press and were then coated using an ALD Fiji Veeco® system at a deposition temperature of 120^{o}C to avoid the decomposition of the organic material. To understand the dissolution rate of the coated pellets, we performed kinetic studies using a UV-1800 Shimadzu spectrometer by monitoring the 5-ASA UV signal at 298 nm. Each pellet was analysed for extended periods of time (< 20,000 seconds) in acidic media with various pH's to track dissolution rates. Successful coating on the 5-ASA powders was further characterized by high resolution transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDX).

Through our investigation, we show ALD's potential in coating 5-ASA as a proof-of concept to achieve delayed and controlled drug release that is tunable based on the ALD coating thickness/chemistry. Our research seeks to promote further research and interdisciplinary collaboration between ALD and pharmaceutical researchers to discover new pathways for personalized treatment for patients who suffer from chronic illnesses.

11:30am **AA1-TuM2-4 Atomic Layer Deposition Enables Dimensionless, Biocompatible Encasings for Medical Implants Pro-Longing Their Lifetime***, **Juhani Taskinen**, R. Ritasalo, M. Pudas, T. Blomberg, M. Matvejeff,* Picosun Oy, Finland **INVITED**

All kinds of medical devices – various types of implants and wearables - must withstand the corrosive environment of salts, temperature variations, electrical stress, and pollutants, inside and outside the human body, for prolonged periods of time. Hermetic sealing of the device to protect it from the outside environment when used in contact with the human body, (and further to protect the body from the device) is a key step to enable a longer service lifetime, better patient safety, and lower number of replacement surgeries.

To make a robust protective sealing for the medical device, the film properties must fulfill many criteria. First and foremost, the film material needs to be non-toxic for human cells, i.e., biocompatible. Secondly, the film needs to function as an extremely good diffusion barrier against the ions and molecules present in body fluids, while also blocking any leaks (ion or molecular) from the device into the body. In addition, the adhesion of the film to the device surface needs to be high enough that delamination of the film will not occur.

Since Intel introduced ALD HfO2-based high-k into their mass production line in mid-2000's[1], ALD has been a gold standard coating method in various electronics industries, and it is now doing the same in the medical field. A key benefit of an ALD coating is that it is one of the very few ways to make a barrier that leaves no surface of the device "visible" to the surroundings, making the device "invisible" to human body fluids and the immune system. Without an immune response, ALD coated device lasts longer than devices that are coated through other methods. At the same time the ALD coatings are virtually dimensionless, e.g., enabling miniaturization of all MEMS devices and improving surface activity on orthopedic implants.

The advantages of ALD over other deposition techniques makes it a powerful method for applications where sensitive substrate materials combined with extreme demands on coating quality and temperature / chemical resistance are needed, such as those often seen in the medical applications.

We will present applications and use cases of ALD in the medical field.

Keywords:

Electronics, encasing, biocompatible, medical devices, electronic implants, implants, immunology

Ref. [1] K. Mistry et al., Electron Devices Meeting 2007, IEDM 2007, IEEE International (2007), pp. 247-250.

ALD Applications
Room Van Rysselberghe - Session AA2-TuM2
ALD for FEOL

Moderators: Cheol Seong Hwang, Seoul National University, Jonas Sundqvist, BALD Engineering AB

10:45am **AA2-TuM2-1 High ALD Equipment and Precursor Demand and 5-Year Forecast Due to Continued Semiconductor Device Scaling and Fab Expansions***, Jonas Sundqvist,* Stockholm, Sweden **INVITED**

The global market for ALD and CVD are experiencing high growth [1]. Total precursor market grew 20% in 2021to approach US$1.4B and will increase by 13% topping US$1.5B in 2022

- Metal & High-k CAGR (2021 to 2026) = 9.3%
- Dielectric CAGR (2021 to 2026 = 6.9%

The growth is driven by advanced logic, DRAM and 3DNAND memory chip fabrication needs. In the short-term forecast, sees the global semiconductor market as very healthy with 15-20% YoY growth in 2021 revenues [2], and overall critical materials market growth >7% YoY. All ALD/CVD metal precursors are in healthy demand, since ALD is critical for fabs running 22-45nm nodes as well as for fabs at the leading edge at 16/14 nm and below. In particular, Co and Hf precursors saw high growth in 2020 and 2021 and are forecasted to see strong demand through 2026. Zr used for DRAM capacitors saw a lower growth but is a big segment on its ow. Ru metal is slowly replacing some of the Co and W interconnects on the most advanced logic chips, with anticipated precursor revenue growth to US$10M in 2025 for this highly strategic material. Metals to observe the next years include Mo, Nb and La. Implementation of ALD in emerging new technologies has high potential since all industries are at Giga scale in HVM: PV, Display, MEMS, Power Electronics, LED/µLED, Optical, Lithium Battery, Solid State Fuel Cells, Parts and powder coating and Medical.

ALD materials and OEM tools are needed for multi-patterning lithography used with DUV Immersion and with EUV in leading logic and memory fabs. Multi-patterning typically uses low-temperature PEALD, either in clusters of 8-16 single-wafer chambers, or in “Spatial” high-throughput tools. It is anticipated that fab investments in Asia will allow South Korean and Chinese OEMs to win near-term ALD orders, and they may soon compete with US, EU, and Japanese OEMs in the global tool market for standard processes that are commoditized. Recent actions taken by the new US administration has boosted logic fab investments in the US and several leading-edge fab investments are on the horizon the next three to five years, which will generate a need for both ALD equipment and a healthy precursor supply chain on all materials above going forward.

[1] TECHCET LLC CA, Critical Materials Reports™ 2021

[2] TECHCET LLC CA, 2021 Critical Materials Council (CMC) Conference, Apr. 14-15, San Diego, USA

11:15am **AA2-TuM2-3 High-k Gate Dielectrics for ScAlN Barrier HEMT Structures***, Neeraj Nepal, V. Wheeler,* U.S. Naval Research Laboratory*; . Downey,* U.S. Army Research Laboratory*; . Hardy, D. Meyer,* U.S. Naval Research Laboratory

There has been increased interest in ScAlN-barrier high electron mobility transistors (HEMTs) as ScAlN has larger spontaneous and piezoelectric polarization fields than those in GaN and AlN, which can lead to larger two dimensional electron gas (2DEG) densities. Also, ScAlN with 18% Sc content is nearly latticed matched with GaN and has bandgap of 5.65 eV. Thus, ScAlN can provide a strain-free barrier for GaN HEMT structures with high carrier concentration. Recently, we have demonstrated ScAlN-barrier GaN HEMT structures with electron mobility of 910 cm^2/V-s and 2DEG density >3x10^{13} cm^{-2} [1]. However, these ScAlN/GaN HEMT devices still suffer from high leakage current [2]. Integrating gate dielectrics into these novel ScAlN-barrier HEMTs is necessary to decrease the leakage current, maintain high electric field breakdown and mitigate dc-RF dispersion in order to realize the full potential of these devices.

In this talk we report growth optimization and electrical properties of atomic layer deposition (ALD) grown TiO_2 gate dielectric on ScAlN-barrier HEMTs using Ultratech Fiji Gen2 ALD reactor. ALD process windows were initially monitored and optimized on Si substrates using *in-situ* ellipsometry. Films were deposited using tetrakis(dimethylamino)titanium (TDMAT) and an Ar/O_2 plasma at 300W. The TDMAT precursor temperature was maintained at 75 ^{o}C, while the pulse duration was varied from 0.25 to 0.35 sec. The plasma gas chemistry was also optimized. Optimal deposition parameters were used as initial condition to further optimize ALD conditions on ScAlN surface. On ScAlN barrier HEMT structures, deposition temperature was varied from 150 to 350 ^{o}C.

Atomic force microscopy was measured before and after ALD deposition showing minimal change in roughness as a result of the TiO_2 deposition.Contactless resistivity measurements performed before and after ALD and were also consistent, indicating that no plasma induced damage was occurring during ALD gate deposition. Vertical current-voltage and capacitance-voltage measurements were made on a Schottky-contacted HEMT structure and compared to devices with TiO_2 gate dielectrics deposited at different temperatures to discern the full electrical impact. As an example, an extracted dielectric constant of TiO_2 layer deposited at 200°C with O_2 flow of 20 sccm was 50 with no significant change in 2DEG density (changed from 2.7x10^{13} cm^{-2} to 2.6x10^{13} cm^{-2}after TiO_2 layer). Finally, we will present the band alignment of an optimum ALD TiO_2 on ScAlN structure using x-ray photoelectron spectroscopy.

References:

27. Hardy et al., *Appl. Phys. Lett.***110**, 162104 (2017).
28. Green *et al.*, *IEEE Electron Device Letters***40**, 1056 (2019).

11:30am **AA2-TuM2-4 Ultra-thin High-κ Dielectrics Growth by ALD on MoS$_2$***, Emanuela Schilirò, R. Lo Nigro,* CNR-IMM, Italy*; S. Panasci,* CNR-IMM, Department of Physics-University of Catania, Italy*; A. Mio,* CNR-IMM, Italy*; S. Agnello, F. Gelardi,* Department of Physics and Chemistry, University of Palermo, Italy*; F. Roccaforte, F. Giannazzo,* CNR-IMM, Italy

MoS_2 is one of the most investigated 2D-materials belonging to the wide class of transition metal dichalcogenides (TMDs). The great interest in MoS_2 is mainly attributable to the existence of a bandgap that, differently from graphene, makes it suitable also for logic and switching devices. In particular, monolayer-MoS_2 presents a direct-gap semiconducting behavior with a bandgap of 1.8 eV. However, to guarantee high-performance in terms of field-effect mobility (100-500 cm^2/V s), sub-threshold swing (~ 70 mV/dec) and on/off ratio (~ 10^8) the MoS_2-devices requires high-κ dielectrics (Al_2O_3, HfO_2) as top-gate layers. Atomic layer deposition (ALD) is the most appropriate technique to grow uniform high-κ layers with accurate control of thickness. Nevertheless, the uniformity of ALD-nucleation on 2D surfaces can be poor due to lacking out-of-plane bonds, which should act as nucleation sites. Seed-layers and/or pre-functionalization are, hence, necessary to activate ALD-growth on 2D-materials. Their undesired effects on the interfacial quality with 2D-materials encourage the research of new solutions. The substrate, as the driving force of nucleation, is one of the more promising. In fact, similarly to graphene [1,2], also for MoS_2 [3], a metal substrate (gold), has been demonstrated to be a key factor to obtain uniform ultra-thin layers of Al_2O_3. In this work, a large area of monolayer-MoS_2 was exfoliated from bulk molybdenite to a gold substrate. Direct ALD processes of Al_2O_3 and HfO_2 were carried-out on MoS_2/Au substrate, and the structural and insulating properties of high-k were investigated. In particular, ALD coverage degree was evaluated, using standard and conductive-AFM, since the early stage of nucleation. Lower coverage was found for HfO_2, during the early cycles of deposition (40 cycles), than Al_2O_3. However, for longer processes (80 cycles), both high-k show similar ad optimal coverage (higher 95%) but also propitious structural and insulating properties already from very ultra-thin thickness (~ 3.5 nm). Uniform, adherent and compact layers were observed by HR-TEM characterization. Homogeneous insulating behavior and congruent breakdown electric field values were demonstrated, for both high-k, by conductive-AFM measurements.

These results can have an important impact on the realization of devices based on large-area MoS_2 membranes.

This work has been supported by the FLAG-ERA JTC2019 project “ETMOS”

[1] B. Dlubak et al Appl. Phys. Lett., 100, p. 173113 (2012).

[2] E. Schilirò et al Adv. Mater. Interfaces 1900097 (2019).

[3] E. Schilirò et al Adv. Mater. Interfaces., 2101117 (2021).

11:45am **AA2-TuM2-5 Fabrication of a MOSFET Based on ZnO Using an Atomic Layer 3D-printer***, **Sonja Stefanovic**, N. Gheshlaghi,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; I. Kundrata,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Dominica*; D. Zanders,* Ruhr Universität Bochum, Germany*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

Area-selective atomic layer deposition (as-ALD) is bottom-up nanofabrication by using atoms as building blocks. As-ALD has the potential to overcome many of the challenges the semiconductor industry is facing by enabling self-aligned fabrication, instead of lithography’s cost, complexity. However, the main challenges in as-ALD are the need for pre-patterned substrates, defects outside of the desired growing area resulting from insufficient selectivity, and a limited selection of substrate materials that allow deposition.

We have devised and manufactured a direct patterning atomic layer 3D-printer (AL 3D-printer) equipment with a special nozzle design that enables producing direct patterning of various materials with atomic precision. Our invented device is a flexible and efficient tool for reducing the cost and time spent for designing and manufacturing. AL 3D-printer in principle functions similar to conventional g-ALD and all the commercially available precursors which have been used in g-ALD are compatible with our invented equipment. i.e. we have already deposited different materials such as TiO_2, Pt, SiO_2, Al_2O_3 successfully. In addition, the special design of the device allows us to explore new reactions with precursors which are not preferred because of their low vapour pressure or less reactivity.

In this work, we focused on the development of ZnO films with water and a new precursor named $Zn(DMP)_2$(DMP = dimethylaminopropyl) which has a very low vapour pressure compared to a well-studied diethylzinc ($ZnEt_2$) precursor which has a very high vapour pressure and reactivity. Using the proposed direct patterning technique, high-aspect-ratio patterns of ZnO films with our new precursor were fabricated. The patterned films are closed-packed with sharp edges and residual-free surfaces. Our characterization results on the deposited ZnO films with our new precursor shows they have the same structure and composition as with $ZnEt_2$. The produced films are crystalline and the crystals are oriented in a roughly isotropic manner. The growth rate is 1.0 Å per cycle at 200°C. Finally, to assess the reliability and feasibility of the proposed direct patterning method in microelectronic applications, we fabricate a metal oxide transistor MOSFET to demonstrate the practical applications of the device.

ALD Fundamentals
Room Van Eyck - Session AF-TuM2

Simulation, Modeling, and Theory of ALD II

Moderators: Simon Elliot, Schrödinger, Inc., Michael Nolan, University College Cork

10:45am **AF-TuM2-1 Theoretical Understanding on the Chemical Principles of Atomic Layer Deposition***, **Bonggeun Shong**,* Hongik University, Korea (Republic of) **INVITED**

Atomic layer deposition (ALD) is a vapor phase thin film deposition technique based on sequential, self-limiting surface reactions. Through ALD, exceptional conformality on high-aspect ratio structures, thickness control at the Angstrom level, and tunable film composition are achievable. Furthermore, area-selective ALD (AS-ALD) has recently emerged as a possible alternative bottom-up approach for nano-patterning. With these advantages, ALD is gaining interest as a powerful tool for many industrial and research applications, especially in microelectronic fabrication. Since the entire ALD process should be based only on the surfaces of the substrates, it is important to understand the surface chemical reaction mechanisms during ALD, in order to improve the process conditions and material quality of ALD. With development of modern simulation tools, utilization of quantum mechanical calculation is becoming increasingly useful toward deeper understanding and design of such chemical reactions. In this talk, fundamental principles governing the surface chemistry of ALD processes will be discussed. Especially, the talk will focus on the recent examples that theoretical analysis of various surface reactions together with experimental approaches could be synergistically enhance the research and development of ALD.

11:15am **AF-TuM2-3 A Study of Area-Selective TiO_2 Deposition Using First Principles Based Thermodynamic Simulations***, **Yukio Kaneda**,* Sony Semiconductor Solutions Corporation, Belgium*; E. Marques,* Katholieke Universiteit Leuven, Belgium*; S. Armini, A. Delabie, M. Setten, G. Pourtois,* IMEC, Belgium

Recent transistor developments consider not only dimensional scaling but also design device structures in the vertical direction to reduce the active footprint. Consequently, the structures and process steps are becoming increasingly complex. In that context, area-selective deposition (ASD), which enables film formation from the bottom-up in a specific area, has been attracting attention. In this field, a lot of work aims to improve selectivity and to increase the material variations that make ASD possible to suit the different target applications [1]. Understanding the atomic-scale physics and chemistry during ASD processes is essential for interpreting the results, as well as for enabling further developments and new applications.

Here, we propose a simulation technique to analyze chemical reactivities based on first-principles calculations and statistical thermodynamics as a method to gain insight into atomic-scale physics. In this framework, we will show how we can investigate the effects of chemical reactivity, and hence selectivity, on many chemical species and process conditions.

In this presentation, we report the results of the analysis performed on the ASD of TiO_2 on substrates patterned with end groups including OH and alkyl-silyl groups. First, we evaluated our method by comparing with experimental results of TiO_2 ALD using $TiCl_4$ and $Ti(OMe)_4$ as precursors, whose selectivity was already confirmed [2]. The theoretical results demonstrate better selectivity with $TiCl_4$ as precursor, consistent with experiment. The impact of the process temperature and purge times during ALD was also qualitatively consistent with the experimental results. Moreover, the theoretical results also indicated that the mechanism of selectivity degradation may be due to the desorption of inhibitors during ALD at the higher process temperature. Therefore, we used this technique to investigate whether the precursors and coreagents referred in [3] and inhibitors with altered ligand size, which are the end groups of the non-growing surface, are effective in improving the selectivity. In conclusion, we confirmed that the best performance had been obtained by combining $TiCl_4$ as a precursor and trimethylsilyl termination as an inhibitor.

[1] Gregory N. Parsons and Robert D. Clark, Chem. Mater. 2020, 32, 12, 4920–4953

[2] Job Soethoudt, et al., The Journal of Physical Chemistry C 2020 124 (13), 7163-7173

[3] Janne-Petteri Niemelä et al., Semicond. Sci. Technol. 2017 9 (32),

093005

11:30am **AF-TuM2-4 Chemistry of Plasma Enhanced Atomic Layer Deposition of Co using CoCp2 and Nitrogen/Hydrogen Plasma*, Ji Liu,* *M. Nolan,* Tyndall National Institute, University College Cork, Ireland

The copper interconnect issue that has arisen with the downscaling of semiconductor devices is a major challenge in the nanoelectronics industry. One solution is to find alternate materials that do not suffer these issues to replace Cu. Transition metal cobalt has attracted much attention due to low resistivity, particularly at small dimensions, and good physical and chemical stability. The deposition of metals onto the typical high aspect ratio structures in nanoelectronics devices is difficult and the atomic layer deposition (ALD) is applied due to the resulting conformality and precise thickness control at the atomic scale. Plasma-enhanced ALD (PE-ALD) is used for low-temperature thin film growth by alternating exposures of metal precursors and plasma reactants. The PE-ALD of Co has been experimentally investigated using Cp-based precursors. However, the reaction mechanism is not clear and theoretical studies on the reaction mechanism is entirely lacking.

In this presentation, we study the PE-ALD growth of Co by first principle calculations. The following central questions will be addressed: (Q1) what is the coverage and stability of the NH_x-terminated Co surfaces? The (001) surface, with a hexagonal structure, is the most stable and the (100) surface with a zigzag structure is less stable but has high reactivity. These two surfaces allow the study of the influence of the surface facet. The surface NH_x saturation coverage is studied by considering co-adsorption of NH and NH_2 terminations on both surfaces. (Q2) What is the reaction mechanism for the elimination of Cp ligands in $CoCp_2$ on these NH_x-terminated Co surfaces? A plausible reaction pathway includes: precursor adsorption, hydrogen transfer, CpH formation and desorption. The barrier for hydrogen transfer is calculated and the results show that (100) surface has higher activity than (001) surface. The final terminations after metal precursor pulse are determined. (Q3) What is the role of plasma radicals in the plasma cycle? Here, we focus on two parts: (1) how the remaining Cp ligands and surface NH_x terminations are eliminated with plasma generated radicals N_xH_y; and (2) how the metal surface is recovered with NH_x terminations at the post-plasm stage. Our DFT results highlight the importance of NH_x species to deposit high-quality and low-impurity Co thin films.

11:45am **AF-TuM2-5 Adsorption Mechanics of Trimethyl Metal Precursors on AlN, GaN and InN*, Karl Rönnby,*** *H. Pedersen, L. Ojamäe,* Linköping University, Sweden

Aluminum nitride (AlN), gallium nitride (GaN) and indium nitride (InN), collectively known as the group 13 nitrides (13Ns), are important materials in many semiconducting applications, for example in optoelectronics as the range of band gaps, 6.3 eV for AlN to 0.7 eV for InN, ranges from UV to IR.

The standard ALD approach for growth of 13Ns is to use a trimethyl metal (TMMe, Me=Al, Ga or In) precursor together with ammonia as co-reactant. Although similar to the typical ALD process of Al_2O_3 from TMA and water, the growth of the 13Ns is much more challenging. This can be attributed to a much lower reactivity of nitrogen compared to oxygen. The badly tuned chemistry is evident by the non-stoichiometric ratios between the precursors in continuous CVD and the need to utilize plasma-enhanced processes, especially for InN, to achieve good growth rates. Theoretical investigations into the growth mechanism would yield a possibility to understand the limitations and apply targeted improvements to the process.

In this work, we modeled the adsorption mechanisms of the TMMe precursor by density functional theory (DFT) on a periodic surface slab. TMMe molecules were placed in proximity to possible adsorption sites and their structures were optimized. Further surface decomposition mechanisms were then explored. Transition states along the reaction paths were investigated by the nudge elastic band method (NEB). Investigations of the lateral interactions between adsorbed precursor molecules were performed by introducing multiple molecules into the simulation cell. A kinetic model was then derived, showing how the surface evolve over time during the metal pulse.

When introduced to a NH_2-terminated surface, the first TMMe precursor adsorbs by forming a Lewis adduct to a surface NH_2 group by donating its empty p-orbital to the electron pair on the surface nitrogen. From this position, the adsorbed precursor could decompose, reaching an end state with all methyl ligands removed. A second TMMe shows preferred adsorption close to an already adsorbed metal atom, indicating a nucleation effect. As not enough hydrogen atoms are cleared by the absorbing molecules, the surface will reach a saturation at a much lower coverage than 1 ML.

We also investigate how the different rates of adsorption, diffusion, and decomposition affect the separation of initial nucleation points and the rate of cluster growth during the ALD half-cycle.

Atomic Layer Etching
Room Baekeland - Session ALE-TuM2

Atomic Layer Cleaning (ALC), ALE Integrated with ALD, and Alternative ALE Approaches

Moderators: Jessica Murdzek, University of Colorado Boulder, Fred Roozeboom, University of Twente & LionVolt B.V., Netherlands

10:45am **ALE-TuM2-1 ALE from Selective Etching to Selective Deposition*, Christophe Vallee,*** SUNY POLY, Albany*; M. Bonvalot, M. Jaffal,* LTM-CNRS, University Grenoble Alpes, France*; C. Mannequin,* Tsukuba University, Japan*; R. Gassilloud, N. Posseme, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France **INVITED**

Atomic layer etching (ALE) is a powerful process to perform either isotropic or anisotropic etching at the atomic scale with a quasi-infinite selectivity. In this presentation, we will address an emerging technological concept based on the selective etch characteristics of ALE to selectively deposit a material on a patterned substrate on a given surface or space direction. This concept relies on a standard atomic scale deposition process (ALD) sequentially combined with ALE to advantageously lead to a selective deposition process [1-2]. We will show, by discussing examples from the literature, that combining atomic-scale deposition and etching processes offers new perspectives in materials thin film elaboration with accurate control of their physical properties, such as roughness, density and microstructure. We will also discuss various strategies for the optimization of this sequential selective deposition process to overcome its inherent weaknesses in terms of contamination and throughput, in view of its potential implementation in high volume manufacturing lines.

[1] M. Bonvalot C. Vallée, M. Jaffal, C. Mannequin, R. Gassilloud, N. Posséme and T. Chevolleau, *Dalton Trans.***51** (2022) 442-450

[2] M. F. J. Vos, S. N. Chopra, J. G. Ekerdt, S. Agarwal, W. M. M. Kessels and A. J. M. Mackus, *J. Vac. Sci. Technol. A***39 (**2021) 032412.f

11:15am **ALE-TuM2-3 Surface Modification for Atomic Layer Etching of TiAlC Using Floating Wire-Assisted Liquid Vapor Plasma at Medium Pressure*, Thi-Thuy-Nga Nguyen,*** Nagoya University, Japan*; K. Shinoda, H. Hamamura,* Hitachi, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech, Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Isotropic and selective etching of metal gate materials such as TiC, TiAlC, and TiN is required in the fabrication of fin-type or nanosheet field effect transistor (FET) of logic semiconductor devices. Ternary material TiAlC belongs to high-melting point, high-hardness, and high-wear resistance materials, and there are only few reports for wet etching this material by H_2O_2 mixtures with poor etching performance and device damages. No dry etching of TiAlC has been reported yet. Therefore, development of a high-performance etching method with highly selective and isotropic removal of TiAlC over TiN at an atomic layer level is strongly demanded.

In this study, an atomic layer etching of the ternary material TiAlC has been first developed by a transferring approach from wet etching to dry etching using a floating wire (FW)-assisted liquid vapor plasma of Ar gas mixed with NH_4OH-based liquid vapors. The FW-assisted non-halogen liquid vapor plasma generated at medium pressure can produce a large amount of etchant or co-reactant species to enhance the reaction rate with sample surface. This radical-rich environment (electron density of 10^{14} cm^{-3}) plays a key role in controlling isotropic etching of 3D multilayer semiconductor devices. Surface modifications, such as oxygenation, hydroxylation, hydrogenation, and nitridation of the TiAlC film were obtained by controlling the active radicals, such as O, OH, H, and NH. This leads to form volatile products having chemical bonds including methyl ($Al–CH_3$), methylamine ($Ti–(NH_n(CH_3)_{2-n})$), and alkoxy ($Ti–(OC_nH_{2n+1})$) groups. Thus, the treated TiAlC surface can be removed via the formation of modified layers. A mechanism for selective etching of TiAlC over TiN is proposed here. This FW-assisted plasma technique is expected to be available for highly selective and isotropic atomic layer etching of metal and metal compounds in semiconductor device fabrication.

11:30am **ALE-TuM2-4 Atomic Layer Processing Approach for Achieving Abrupt Epitaxial Interfaces on AlN**, ***Virginia Wheeler***, *D. Boris, A. Lang, G. Jernigan, N. Nepal, S. Walton,* Naval Research Laboratory

Next generation devices will require novel heterojunctions with abrupt, pristine, defect-free interfaces. Naturally occurring surface oxides on semiconductor materials represent a significant impediment to achieving such interfaces. AlN is one of several ultra-wide bandgap semiconductor of interest for future high power, high frequency devices. Since Al has a high affinity for oxygen, it is hard to completely remove oxygen from AlN surfaces by traditional wet or dry etching methods. Even if successful, AlN immediately reoxidizes during transfer to deposition chambers. This amorphous native oxide layer (typically 3-10nm thick) consists of species with high bond energies requiring temperatures in excess of 900°C to remove, which can alter the characteristics and prevent the formation of an intimate, crystalline optical or electrical interface. Thus, for promoting atomic layer epitaxy at ≤ 500°C a new approach is necessary to attain pristine AlN surfaces.

Here, we merge a low temperature fluorine-based plasma etch process [1] with a etch/passivation technique previously applied to Al mirrors [2], to simultaneously remove the AlN native oxide and passivate the surface with a stable oxi-fluorine film. The process employs a pulsed, electron beam driven plasma produced in an Ar/SF_6 background with an RF substrate bias of -40V. XPS and TEM results show this produced a 1nm $Al_xO_yF_z$ layer that was stable even after 3 days in atmospheric conditions. Temperature dependent XPS revealed that the majority of this layer was removed at 500°C in ultra-high vacuum conditions. AFM and TEM measurements also revealed that the plasma-processed surfaces were slightly smoother than as-received AlN substrates.

To demonstrate the feasibility of this approach as an ex situ process, plasma treated AlN substrates were transferred to a Veeco Fiji G2 ALD system. Samples were exposed to an in-situ anneal at 400°C in 10^{-7} Torr, after which they were cooled under vacuum to 295°C and a 20nm optimum TiN film was deposited. TEM analysis shows a defective, abrupt, interface between the polycrystalline TiN and AlN substrate. EELS was used to show that the majority of the interface has a N-K edge that shifts from AlN to TiN in only 1-2 pixels without any evidence of residual fluorine or oxygen. Occasionally, pyramidal defects containing fluorine and oxygen were observed and resulted in localized crystallinity loss within the TiN film. This demonstrates the importance of clean, abrupt interfaces for promoting epitaxial films by ALD.

[1] S.G. Walton, et al. *J.Vac. Sci. Technol. A***39**, 033002 (2021)

[2] L.V. Rodriguez de Marcos, et al. *Opt. Mat. Expr.***11(3)**, 740-756 (2021).

ALD Applications
Room Van Rysselberghe - Session AA1-TuA
ALD for Display Applications

Moderators: Jin-Seong Park, Hanyang University, Ganesh Sundaram, Veeco-CNT

1:30pm **AA1-TuA-1 Atomic Layer Deposition for Display from Photoluminescent Materials to Devices and Encapsulation***, **Rong Chen,*** State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, China **INVITED**

As display plays an increasingly important role, from mobile phones, display screens, to AR/VR and metaverse glasses. There are increasing demands for pursuing more vivid displays, requiring higher resolution, wider color gamut with high stability. Atomic layer deposition (ALD) has been developed as an attractive method to modify and stabilize the photoluminescence materials and devices.[1] In this presentation, several applications through ALD are introduced. For photoluminescence (PL) applications, ALD is performed to coat dense layer on fluoresce materials and passivate defects. For example, Al_2O_3 coating on RLSO:Eu^{2+} phosphor demonstrates outstanding moisture resistance and PL stability.[2] For quantum dots, low-temperature plasma enhanced ALD is developed to enhance the stability of $CsPbBr_3$ QDs films in light, water and heat, which originated from the crystal stabilization after coating.[3-5] Ultra-stable luminescent microspheres structures are fabricated to confine QDs with SiO_2 sphere to improve stability for backlight display.[6] In terms of light-emitting diode (LED), ALD is exploited to infill oxides between QDs, improving the carrier mobility.[7,8] The ultrathin functional layers prepared with ALD could effectively balance the carrier and block the migration of metal ions from the electrode to the functional layers to avoid device damage.[9] For flexible encapsulation, ALD plays an important role for OLED, QLED and micro-LED etc.,[9] inorganic-organic composite layers, nanolaminated packaging structures with total thickness of 100 nm are fabricated as encapsulation layer and significantly improve mechanical stability under bending and stretching tests.[10] The atomic layer infiltration (ALI) has been developed to prepare hybrid organic-inorganic layers with better flexibility.[11,12] Our works provide a versatile method for LED illumination and flexible displays, it is also beneficial to fabricate oxides with high mobility (ZnO, IGZO etc.) for TFT, in the future, the manufacturing equipments (spatial ALD, particle ALD) with mass production capability are also urgent needed for commercial applications.

References

[1]*Opto-Electronic Advances***2020**, *3*.

[2]*Angewandte Chemie International Edition***2020**, *59*, 12938.

[3]*Chemistry of Materials***2018**, *30*, 8486.

[4]*ACS Appl Mater Interfaces***2020**, *12*, 53519.

[5]*Chemistry of Materials***2020**, *32*, 10653.

[6]*Advanced Optical Materials***2020**, *8*, 1902118.

[7]*physica status solidi (RRL)* **2020**, *14*, 2000083.

[8]*ACS Applied Electronic Materials***2021**, *3*, 2398.

[9]*Advanced Materials Interfaces***2020**, *7*, 2000237.

[10]*Advanced Materials Interfaces***2021**, *8*, 2100872.

[11]*Dalton Trans***2021**, *50*, 16166.

[12]*Advanced Materials Interfaces***2022**, 2101857.

2:00pm **AA1-TuA-3 High-Stability and High-Performance PEALD-IZO/IGZO Top-Gate Thin-Film Transistor via Nano-Scale Thickness Control***, J. Park, **Yoon-Seo Kim**, W. Lee, H. Oh, T. Hong,* Hanyang University, Korea

Oxide semiconductors have already been adopted for mass-production of display backpanes because of their advantages of high field effect mobility (10~30 cm^2/Vs), large-area uniformity, low-cost manufacturing and low-temperature process. The next generation of display technology such as super high vision and memory/logic technology requires the semiconductor which has electron mobility higher than 30 cm^2/Vs with high stability. In addition, for application in 3D structures such as 3D NAND, uniform thickness and composition control in 3D structures are required. Therefore, further than the conventional PVD method, it is necessary to study ALD-based oxide semiconductors that can control the thickness of an atomic level and form a film with low defects based on self-limit reaction. Furthermore, the ALD method facilitates the development of high-performance oxide semiconductors by controlling the homogeneous/heterogeneous vertical structure and composition. Therefore, ALD is suitable as a powerful deposition method candidate for oxide semiconductor development. However, since most research of stacking oxide semiconductor which is the methods to overcome the mobility and reliability trade-off is based on sputter or solution deposition, the ALD-based oxide semiconductor stack studies have rarely been reported. In this study, PEALD-based IZO (back-channel)/IGZO top gate thin film transistor investigated relation between the thickness of the IZO layer and electrical/reliability properties of devices. The mobility increases proportionally according to the IZO thickness. In addition, the PBTS reliability is excellent with an absolute value ΔV_{th} of less than 0.4 V in all of PEALD based TG-TFTs. In particular, the reliability of PBTS is improved proportionally according to the IZO thickness in IZO/IGZO TFT compared to IGZO TFT. Finally, we fabricated PEALD IZO/IGZO TG-TFTs with high mobility (~40 cm^2/Vs) and high stability of PBTS under 10800 s (ΔV_{th} = -0.07 V) through nano scale thickness control.

2:15pm **AA1-TuA-4 Atomic Layer Infiltration Enabled Flexible Encapsulations***, **Fan Yang**, Y. Zhang, D. Wen, K. Cao,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China*; R. Chen,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology , China

Due to the, low-cost, large area, light weight, high transparency and high flexibility, polymer based thin-film encapsulation (TFE) and substrates have emerged as one of the most attractive methods for flexible electronics hermetic sealings. However, the intrinsic barrier performances of various polymeric substrates are still too low to prevent moisture and oxygen in an ambient atmosphere to permeate into and degrade the protected devices at its static state, not even mention when at bending or stretching. Different novel configurations, such as wrinkled structures, island-bridge, serpentine structure, origami structure, and helical coil, have been developed to improve the flexibility of polymer FTEs, while at the cost of either low device-coverage density or low transparency. Therefore, effective method and the underlying modification mechanism are in desperate desire for polymer TFEs with high stretchability, excellent transparency, and good barrier property.

In our work, different polymer substrates including polydimethylsiloxane (PDMS) and commercial polyethylene naphthalate (PEN), are modified with atomic layer infiltration (ALI) method. A clear "nucleation-filling-coating" modification mechanism is proposed and elaborated in detail by in-situ quartz crystal microbalance (QCM). The optimized PDMS and PEN hybrid films both exhibit relatively low water vapor transmission rate (WVTR) values and excellent mechanical reliability under bending or stretching conditions. Moreover, patterned sensitive quantum dots (QDs) and based devices encapsulated with the modified hybrid polymer films retain outstanding performances and lifetimes, comparing with ones protected with unmodified polymers. We believe the proposed ALI modification and mechanism will have great and practical implications for encapsulations for future flexible electronics.

References:

1, Highly-stable PEN as a gas-barrier substrate for flexible displays via atomic layer infiltration. Yun Li, Di Wen, Yinghao Zhang, Yuan Lin, Kun Cao, Fan Yang and Rong Chen,*Dalton Trans.,* ***2021****, 50, 16166.*

2, Stretchable PDMS Encapsulation via SiO2 Doping and Atomic Layer Infiltration for Flexible Displays. Yinghao Zhang, Di Wen, Mengjia Liu, Yun Li, Yuan Lin, Kun Cao, Fan Yang, and Rong Chen, *Adv. Mater. Interfaces* ***2021****, 2101857*

2:30pm **AA1-TuA-5 Impacts of Deposition Temperatures on Insulation Properties of Atmospheric Pressure Spatial ALD Al_2O_3 Thin Films for Flexible PEALD IGZO TFT***, **Dong-Gyu Kim**, K. Yoo, S. Lee, W. Lee, J. Park,* Hanyang University, Korea

In the past decades, aluminum oxide (Al_2O_3) has attracted attention because its unique properties such as a wide band gap (~9 eV), a reasonable breakdown electric field (5-10 MV/cm), excellent dielectric properties (6–9), strong adhesion to various materials, and high thermal/chemical stability. There are various Al_2O_3 deposition methods. Among them, atomic layer deposition (ALD) is regarded as a promising conformal film deposition tool. Although ALD-derived Al_2O_3 films have abundant advantages, the ALD method is not always compatible with industrial needs because of its extremely low growth rate (0.1 nm/s). Therefore, many groups have suggested spatially separated ALD (S-ALD) concept to increase growth rate for mass production. In the S-ALD operation, both precursor and reactant are continuously injected and purged from different zones. A moving substrate crosses each zone for chemical reactions between the adsorbed precursor and reactant, and the time-consuming purge steps are no longer needed. Meanwhile, as market demand increases for flexible display, several researchers developed the S-ALD method that works at atmospheric pressure (AP S-ALD). These include roll-to-roll/sheet-to-sheet processes and low investment costs. Although the AP S-ALD have gained increasing interest, the AP S-ALD-derived Al_2O_3 film properties have not clearly observed as a function of deposition temperatures to date. Furthermore, the possible applications of the oxide-based thin film transistors (TFTs) as an insulator should be evaluated.

In this work, we report AP S-ALD-derived Al_2O_3 growth behaviors with different process parameters. For more in-depth growth temperature studies, we conducted X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) analyses. We fabricated metal-insulator-metal (MIM) devices to evaluate the dielectric constant and breakdown electric field. Based upon results, we used the optimal Al_2O_3 as a B.L and G.I to investigate the application in PEALD IGZO TFT. We evaluated instability of the IGZO TFT as a function of gate field stress time and mechanical bending cycle number to understand the Al_2O_3-adopted PEALD-IGZO TFT flexible display.

2:45pm **AA1-TuA-6 Enhanced Crystallinity Using in-Situ Atomic Layer Deposition Process of Al_2O_3 on P-Type SnO Thin Film and the Associated Device Applications***, **Hye-Mi Kim**, S. Choi, J. Park,* Hanyang University, Korea

Tin monoxide (SnO) is promising p-type material which have low formation energy of tin vacancy (V_{Sn}) and high hole mobility arise from the delocalization of hole conduction path. However, low thermal stability of p-type SnO and facile phase transition to n-type tin dioxide (SnO_2) is major hardship to achieve superior electrical properties and stability[1,2]. In this study, we focused on the effect of Al_2O_3 on SnO film properties especially on the crystal structure and electrical performance. Al_2O_3 is already known for effective materials for the passivation layer of SnO TFT in many reports. However, we figured out that Al_2O-$_3$ not only passivate the surface defect of SnO but also highly influence on the crystallinity and following electrical properties. Also, this effect is enhanced when Al_2O_3 is deposited as in-situ ALD process. To identify the mechanism of the improvement of crystallinity, the nucleation energy and the chemical potential difference of SnO and Al_2O_3 stacked SnO crystallites is calculated. SnO TFT with in-situ processed Al_2O_3 exhibits 1.14 cm^2/Vs of field-effect mobility, 4.4E+05 of on/off ratio and low subthreshold swing as 0.15 V/decade. Our study confirms that the mechanism of the improvement in electrical performance of SnO TFT when Al_2O_3 passivation layer is adopted, and in-situ process is far more effective to achieve high performance.

References

(1) Fortunato, E.; Barquinha, P.; Martins, R. Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances. Adv. Mater. 2012, 24 (22), 2945−2986.

(2) Luo, H.; Liang, L. Y.; Cao, H. T.; Liu, Z. M.; Zhuge, F.Structural, Chemical, Optical, and Electrical Evolution of SnO x Films Deposited by Reactive Rf Magnetron Sputtering. ACS Appl. Mater. Interfaces 2012, 4 (10), 5673−5677

3:00pm **AA1-TuA-7 Oxidant- and Temperature-Dependent Growth Behavior of ALD-Processed ZnO Thin Films and their Applications inTransistors***, J. Yang, A. Bahrami, **Sebastian Lehmann**, S. He, N. Kornelius,* Leibniz Institute for Solid State and Materials Research, Germany

ZnO thin films were deposited by atomic layer deposition (ALD) using diethylzinc (DEZ) as the Zn source and H_2O and H_2O_2 as oxygen sources. The oxidant- and temperature-dependent electrical properties and growth characteristicsare systematically investigated. Materials analysis results suggest that H_2O_2 provides an oxygen-rich environment so that the oxygen vacancies (V_O) is suppressed, implying a lower carrier concentration and a higher resistivity. The lower growth rate makes it possible for the ZnO thin films to grow along the lower surface energy direction of <002>, leading to a lower Hall mobility. Furthermore, the ZnO semiconductor was integrated into thin film transistor (TFT) devices, and the electrical properties are analyzed. The TFT with H_2O_2-ZnO grown at 150 °C shows good electrical properties, such as a high field-effect mobility of 10.7 cm^2 V^{-1} s^{-1}, a high ratio I_{on}/I_{off} of 2×10^7, a sharp subthreshold swing (*SS*) of 0.25 V dec.$^{-1}$, and a low trapping state (N_{trap}) of 2.77×10^{12} eV^{-1} cm^{-2}, which provides a new pathway to optimize the performance of metal-oxide electronics.

3:15pm **AA1-TuA-8 Origins of High Off-current of P-type SnO TFTs and Reduction by Source/drain Modulation***, **Su-Hwan Choi**, H. Kim, J. Park,* Hanyang University, Korea (Republic of)

Tin monoxide (SnO) is a promising material for p-type thin-film transistors (TFTs) due to its high hole mobility because SnO forms a delocalized and isotropic hole conduction path with hybridized spherical Sn 5s orbitals and O 2p orbital. However, SnO TFTs have a high off-current because of their ambipolar characteristics, which operate n-type mode at back-channel. The high off-current is undesirable for low power consumption and high CMOS gain. High off current originates from a redox reaction [1], oxygen vacancy generation of SnO [2], and electron injection through source/drain [3] In this study, the origin of the high off-current for P-type SnO thin-film transistor (TFT) is examined by source/drain (S/D) electrode materials. The electrical properties of Ni electrode TFT are superior to the ITO electrode TFT in terms of mobility. However, Ni electrode TFT has a high off-current originating from redox reaction and electron injection through Ni electrode. The ITO interfacial layers (ILs) are adopted to reduce the off-current by restraining the redox reaction and electron injection. For 10nm ITO ILs TFT, optimum electrical properties are achieved, such as field-effect mobility of 2.5 cm2/Vs, a threshold voltage of -1.9 V, a subthreshold swing of 0.43 V/decade, and especially high Ion/Ioff of 1.7×103. Reference : [1] H. Luo, L. Y. Liang, H. T. Cao, Z. M. Liu, and F. Zhuge, “Structural, Chemical, Optical, and Electrical Evolution of SnO,” 2012. [2] J. M. Chem, J. P. Allen, D. O. Scanlon, F. J. Piper, and G. W. Watson, “Journal of Materials Chemistry C,” pp. 8194–8208, 2013, doi: 10.1039/c3tc31863j. [3] L. Y. Liang, H. T. Cao, B. Chen, Z. M. Liu, F. Zhuge, and H. Luo, “Ambipolar inverters using SnO thin-film transistors with balanced electron and hole mobilities,” vol. 263502, pp. 1–5, 2012.

ALD Applications
Room Van Rysselberghe - Session AA2-TuA
ALD for BEOL

Moderators: Scott Clendenning, Intel Corporation, John Conley, Oregon State University

4:00pm **AA2-TuA-11 Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Titanium Nitride Using Ammonia Reactive Background Gas***, **Zachary Sobell**, S. George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiN_x films. In addition, a new method of EE-ALD was employed with a reactive background gas (RBG) concurrently present during the EE-ALD process (shown in Figure 1). Using the RBG is possible because the hollow cathode plasma electron source (HC-PES) employed for this EE-ALD can operate with reactor pressures in the mTorr range. EE-ALD with a RBG displayed rapid film nucleation and produced continuous, low resistivity ultrathin films. The use of the RBG opens many potential routes for novel EE-ALD film deposition. For example, these ultrathin EE-ALD films should be useful for barriers in backend interconnects.

The TiN_x EE-ALD was performed using tetrakis(dimethylamido) titanium (TDMAT) as the Ti precursor. The EE-ALD was performed using sequential exposures of TDMAT and electrons. During these sequential exposures, ammonia (NH_3) was present continuously in the reactor as the RBG at ~1 mTorr. NH_3 is believed to interact with the electron beam and liberate H and N radicals. The N radicals may facilitate Ti nitridation and the H radicals may remove C as CH_4. Using a RBG was not possible during earlier EE-ALD work with an electron gun because the electron gun has a hot filament that would react with the RBG.

The TiN_x EE-ALD films were grown with the RBG at low temperatures of T<70 °C. In situ ellipsometry demonstrated that the TiN_x EE-ALD films nucleated rapidly on both Si native oxide films (shown in Figure 2) and Si_3N_4 films. The TiN_x EE-ALD films produced using the NH_3 RBG also displayed excellent properties. The composition of the TiN_x EE-ALD films using the NH_3 RBG was close to 1:1 Ti:N as measured by XPS. The carbon content in the TiN_x EE-ALD films was ~2 at.% by ex situ XPS. In contrast, the carbon content was ~60 at.% without the NH_3 RBG. The as-deposited TiN_x EE-ALD films also displayed ultralow resistivities. In situ ellipsometry measured resistivities as low as 105 μΩ-cm (shown in Figure 2). Ex situ spectroscopic ellipsometry obtained resistivities as low as 115 μΩ-cm using a model that agrees well with literature values for the optical properties of TiN. Ex situ four-point probe also measured resistivities as low as 123 μΩ-cm. The TiN_x EE-ALD films were crystalline as determined by GI-XRD. XRR modeling also revealed that the films were dense at approximately 98% of the theoretical bulk density of 5.24 g/cm^3 for TiN.

4:15pm **AA2-TuA-12 Atomic Layer Deposition of MoNx Thin Film Using New Synthesized Liquid Mo Precursor***, **Byunguk Kim**, T. Kang, S. Kim, H. Jeon,* Hanyang University, Korea

Recently, as the resistivity of the metal thin film is increased due to the scaling down of the memory device,interest in Mo metal, which is a metal with low resistivity, is increasing. However, nucleation delay occurs during the deposition process due to the nature of the metal film such as Mo film.To prevent this, the need for a low-resistivity seed layer is emerging. Among them, MoNx film is spotlighted as a seed layer. Because MoNx thin film has excellent thermal stability, low resistivity, and excellent process efficiency because it uses the same precursor as Mo film.

3D-NAND, which is spotlighted as a next-generation memory device, is a high aspect-ratio device, and since a thin film must be deposited with high uniformity on the upper and lower layers, the need for the ALD process is emerging. This is because the ALD process is easy to control thickness and has excellent step characteristics. Therefore, an experiment was performed to deposit a low-resistivity MoNx film using the ALD process. Also, recently, a halide solid precursor such as MoO2Cl2 is used to deposit Mo/MoNx film. However, in the case of a solid precursor, it is difficult to maintain process conditions. Therefore, in this study, a self-synthesized liquid Mo precursor was used to deposit the MoNx film. As reactants, NH3 gas and H2 gas were used. The reason that H2 gas as well as NH3 gas is used as a reactant is that a MoNx film with less impurities can be deposited by reacting with NH3 gas after removing the ligand using H2 gas. XRR, AES, XRD and 4-point probe were used to evaluate the physical and electrical properties of the deposited MoNx film.

As a result of AES analysis of the MoNx film deposited using the ALD process, Mo and N were 62-64% and 29-32%, respectively, and the impurity, C, was detected to be less than 2% and O was detected to be about 5-6%. Additionally, the sheet resistance of the deposited MoNx film was confirmed to be 400ohm/□ confirming that it was a low-resistivity film.

Through the results of this study, it is possible to establish the MoNx film deposition process, which is considered as a next-generation metal seed layer, and we think that the results of this study will be widely used in the next-generation memory device industry.

4:30pm **AA2-TuA-13 Atomic Layer Deposition of Tungsten Nitride Thin Film using WCl_5 as a Fluorine-free W Precursor and its Application into the Diffusion Barrier for Cu and Ru Interconnects***, **Kang-Min Seo**, G. Bea, S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Tungsten(W) is applied to the current semiconductor devices such as W-plug process, metal gate of 3D NAND flash, or bit line of DRAM, due to its extremely low bulk resistivity. Additionally, some thin films of other tungsten compounds like WN_x, WC_x, and WN_xC_y also have an important role in the current semiconductor devices applications as a diffusion barrier. On the other hand, as the size of semiconductor devices has become extremely narrow (in few nm), it has become difficult to deposit a thin film with a precise thickness in a complex structure. In this regard, atomic layer deposition (ALD) seems to be the best option to prepare any thin film which would find its suitability in future technology. So far, the ALD of W or W-based thin films are deposited using WF_6 as a precursor. However, due to the highly corrosive and toxic properties of the F and by-products such as HF, WF_6 thin film process has obvious limitations. In this study, ALD processes using tungsten pentachloride (WCl_5) as an F-free W precursor and various reactants such as NH_3, TBH (tert-butyl hydrazine) molecules, and its plasma as reactants were reported. Preliminary results indicated that, among these reactants, the best quality ALD-WN_x film can be obtained using N_2 + H_2 mixture plasma as a reactant, and further experiments were done mainly using N_2 + H_2 mixture plasma. The deposition was done with a temperature ranging from 200 to 300 ℃at the chamber pressure of ~ 1 Torr. Self-limited growth behavior, the key characteristic of the ALD process was first investigated at the deposition temperature of 250 ℃.At the optimized pulsing condition, the saturated growth per cycle (GPC) was ~1.1 Å. The properties of ALD-WN_x with deposition conditions were analyzed using various tools such as XRD, XPS, 4-point probe, SEM, SIMS, RBS, TOF-ERD, and TEM. The XRD analysis showed that the WN_x thin films have a mix-phase of WN and W_2N. And XRD on WN_x films annealing at high temperature showed a high thermal stability and phase transition (WN to W_2N) at high temperature. Furthermore, the RBS and TOF-ERD analysis showed that the composition of which WN_x thin films has a phase of WN rather than W_2N and reveals relatively low impurities(oxygen, chlorine). Finally, we applied the deposited ALD-WN_x as a diffusion barrier/glue layer for Cu and Ru metallization and the results will be reported in the conference.

4:45pm **AA2-TuA-14 Thermal Atomic Layer Deposition of Ru With H_2 Molecules for Emerging Ru Interconnects***, **Yohei Kotsugi,*** Chemical Materials Development Department, TANAKA Precious Metals, Japan*; Y. Kim, T. Cheon, S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Ru has been in the limelight as one of the alternatives for Cu interconnects due to its shorter electron mean free path than that of Cu. Therefore, in this regard, a lot of Ru-ALD processes have been investigated. However, most of them has been deposited with O_2 as a reactant gas, and there is an inevitable concern that the oxidation of the metallic underlayer may occur even if the Ru film itself is not oxidized. For these reasons, plasma-enhanced ALD technologies have often been proposed, but they also have a problem of the limited conformality on a high AR 3D structure. Here, we introduce plasma-free atomic layered deposition of Ru using H_2 molecule as a non-oxidative reactant and a Ru metal-organic precursor. The film properties, such as the crystallinity, resistivity, impurities contents, and grain size, were compared with those of the film deposited using the same Ru precursor and O_2. The deposition conditions were optimized with regard to the already reported O_2 process. A thin Ru film of ~4 nm was deposited with∼100% step coverage on a narrow dual-trench substrate. The low film resistivity of as grown film of ∼23.0 μΩ·cm was further reduced to low resistivity of ∼10.7 μΩ·cm by the post-annealing (700 °C) treatment. These results suggested that H_2–based thermal ALD process without using plasma-enhanced techniques can also produce high-quality Ru films. However, the resistivity and impurity concentration were slightly higher than those of the O_2 process. Moreover, this H_2-based ALD process has the disadvantage that it takes longer time to complete one cycle than the O_2-based one. In order to overcome the above issues, we designed a new method to minimize the oxidation of under substrates, whereas the film quality was as high as or better than that of the films deposited using O_2 as a reactant. The low resistivity comparable to that of the O_2-based process was obtained in the 40 nm-thick ALD Ru films and it should be noted that, for ultrathin films of 10 nm or less, its resistivity value was even lower than that of O_2–based one. Additionally, the formation of highly pure Ru film with negligible carbon and oxygen impurities were confirmed by secondary ion mass spectroscopy and excellent step coverage on a narrow dual-trench substrate was demonstrated using transmission electron microscopy analysis. The obtained high-quality Ru film can have the potential to be adopted as a Cu substitute material.

5:00pm **AA2-TuA-15 The Oxygen-Free Thermal ALD and Area Selective ALD of Ruthenium Film***, I. Liu,* SAFC HITECH TAIWAN CO., LTD., Taiwan*; **Bhushan Zope**, G. Liu,* EMD Performance Materials Corp.*; J. Woodruff,* EMD Electronics*; J. Chiu,* SAFC HITECH TAIWAN CO., LTD., Taiwan

Ru thin films have been extensively studied for various applications in semiconductor devices such as electrodes for DRAM and MOSFET due to the good stability, low resistivity (7.1 μΩ·cm in the bulk), and high work function (4.7eV). Conventional methods to prepare Ru film are to use plasma-enhanced atomic layer deposition (PEALD) and thermal ALD with oxygen coreactant. As technology nodes continue to shrink, the plasma process may cause poor uniformity and conformality of deposited Ru film. Oxygen coreactant may also result in the oxidation of Ru film or underlying materials. Therefore, oxygen-free thermal Ru processes attract the attention of semiconductor industry to fabricate future devices.

In this study, the newly developed oxygen-free thermal Ru ALD process is reported. Highly uniform, smooth and conformal Ru films were deposited by thermal atomic layer deposition from Ru precursor, RuEM8, and H2 at low deposition temperature (235 ~ 275 ℃). The GPC of RuEM8/H2 process is 0.6Å/cycle. The Ru films grown on SiO2 were smooth (Rq = ~0.22nm) with low resistivity (20 uohm-cm for 8nm film), which indicates good continuity. XPS analysis shows that the Ru films are pure, and the concentration of impurity is under the detection limit. Conformality of Ru growth were studied on via with aspect ratio 20:1. The preliminary results suggest that the conformality can be optimized to 85 ~ 90% (Figure 1).

In addition to basic Ru film growth, area selective ALD (ASALD) applications of RuEM8/H2 process were also studied. For patterning of microelectronics, metal on metal ASALD is becoming an important need to grow metal capping layer or seed layer for gapfill. By incorporating the inhibitor in the process, the RuEM8/H2 can selectively grow Ru film on Ru surface, but not on SiO2 surface. The selectivity of 7.6 (thickness of Ru on Ru / thickness of Ru on SiO2) for RuEM8/H2 ASALD process was achieved (Figure 2)

5:15pm **AA2-TuA-16 ALD-Prepared 2D Transition Metal Dichalcogenides as Diffusion Barriers in Interconnects***, **Sanne Deijkers**, A. de Jong,* Eindhoven University of Technology, The Netherlands*; H. Sprey, J. Maes,* ASM Belgium*; E. Kessels, A. Bol, A. Mackus,* Eindhoven University of Technology, The Netherlands

For sub-5 nm technology nodes scaling of interconnects is becoming a real challenge. This holds particularly for Cu diffusion barriers, as the typically used TaN/Ta layers fail at thicknesses below 3 nm [1]. The impossibility to scale the diffusion barrier limits the dimensions of the Cu in the interconnect and thus increases the resistivity drastically. To reduce the thickness of the barrier, the TaN/Ta layers could be replaced by atomically-thin 2D transition metal dichalcogenides (TMDs). In this work we report on the diffusion barrier performance of 2D-TMDs prepared by atomic layer deposition (ALD). Up to this point, literature reports concerning 2D-TMDs as barrier layers are limited to chemical vapor deposition (CVD) processes [2]. The advantages of using ALD are the BEOL-compatible temperatures, the excellent control of both film thickness and morphology, and the high conformality that can be obtained for continuous ultra-thin films on demanding nanostructures.

Various 2D-TMDs have been deposited by ALD at BEOL-compatible temperatures on 90 nm thermal SiO_2. MoS_2 has been deposited using $Mo(NMe_2)_2(N^tBu)_2$ as precursor and H_2S containing plasma as co-reactant [3]. Variations in the process conditions, such as the deposition temperature and the implementation of additional plasma steps, result in different morphologies including amorphous, crystalline and out-of-plane-oriented (OoPO) nanolayers [3]. The barrier performance of the barrier layers against Cu diffusion has been characterized by time-dependent dielectric breakdown (TDDB) tests. Additional insight into the Cu diffusion mechanism through the barrier layer has been obtained from scanning electron microscopy inspection. The results show that polycrystalline MoS_2 displays good barrier performance with a median time-to-failure ($TTF_{50\%}$) of $(8 \pm 1)\cdot 10^3$ s at an electric field of 6 MV/cm. This is a substantial improvement compared to barrierless samples, where $TTF_{50\%} = (1.9 \pm 0.3)\cdot 10^2$ s.

[1] Lo *et al., npj 2D Mater Appl* **1**, 42, (2017)

[2] Lo *et al., J.Appl.Phys.* **128**, (2020)

[3] Sharma *et al.,Nanoscale*, **10**, 8615, (2018)

5:30pm **AA2-TuA-17 Evolution of Structural and Electrical Properties of Molecular Layer Deposited Hafnicone Films after Thermal Processing for Applications in Low-*K* Etch Stops***, **Vamseedhara Vemuri**,* Lehigh University*;* *S. King,* Intel, USA*; N. Strandwitz,* Lehigh University

Molecular layer deposition (MLD) yields in conformal hybrid organic-inorganic thin films with precise control over the thickness and conformality similar to atomic layer deposition (ALD). The MLD films have in-organic constituents bonded to organic moieties. This work examines the effect of temperature on the electrical, chemical and structural properties of as-deposited MLD thin films.

The hafnicone films were grown using tetrakis(dimethylamido)hafnium (TDMAH), and ethylene glycol (EG) at 120 ºC. The as-deposited hafnicone films were annealed from 150-350 ºC in an inert atmosphere under a vacuum.

The incorporation of organics and the difference in the chemistry of hafnicone from hafnia films is observed using the ex-situ fourier transform infrared spectroscopy (FTIR). Hafnicone films show a decrease in the intensity of hydrocarbon peaks, whereas the intensity of hydroxyl peaks decreases with annealing in the case of hafnia films. The crystallization behaviour of the hafnia and hafnicone films is probed using the in-situ x-ray diffraction. The ethylene glycol moieties present inside the hafnicone delay the crystallization during annealing when compared to hafnia films. The removal of organics in the hafnicone films may be causing structural collapse and decrease in thickness leading to densification which can be observed by ex-situ X-ray reflectivity data. The dielectric constant of the as-deposited and annealed hafnicone films is lower than as-deposited and annealed hafnia. The dielectric constant of the hafnicone films increases with annealing and can be attributed to removal of organics and densification as observed by FTIR and x-ray reflectivity whereas the dielectric constant of the hafnia films decreases with annealing. This decrease can be attributed to the removal of hydroxyl species after annealing as observed by FTIR. The etch rate of as-deposited hafnicone films is measured in CF_4/O_2 plasma which decreases with increasing annealing temperature to 350 ºC, whereas the etch rate of the hafnia films stays constant even after annealing. The dielectric constant of hafnicone is much lower than hafnia, and the etch rate of the 350 ºC annealed hafnicone film is similar to the etch rate of hafnia. Our study thus proves that the MLD films offer a high degree of tunability and can be used as potential low-*k* etch stops.

ALD Fundamentals
Room Van Eyck - Session AF1-TuA

Characterization I

Moderators: Jan-Willem Clerix, Imec , Aile Tamm, University of Tartu

1:30pm **AF1-TuA-1 Reaction Mechanisms of ALD of Transition Metal Oxides from Metal Amido Complexes and Water***, **Giulio D'Acunto**, R. Timm, J. Schnadt,* Lund University, Sweden

Atomic layer deposition (ALD) is an outstanding deposition technique to deposit highly uniform thin films with atomic precision. In particular, ALD of transition metal oxide layers from metal amido complexes and water finds its way in several technological fields, including green energy devices and the semiconductor industry. These ALD reactions are believed to follow a reaction scheme based on the ligand exchange mechanism. The first half cycle of ALD of HfO_2, via tetrakis-dimethylamido hafnium and water, is expressed, according to the ligand exchange scheme, by the following equation: $HfL_4 + n$S-(OH) -> S-O_n-HfL_{4-n} + nLH, where S stands for surface and L for the amido ligand of the metal precursor.

Here, the surface S is supposed to play a largely passive role, and it is that it is hydroxylated. L remains chemically unchanged during the reaction. To address whether the model is correct or not, we employed time-resolved *in situ* and *operando* ambient pressure X-ray photoelectron spectroscopy (APXPS) during the ALD of HfO_2 on InAs covered by a thermal or native oxide, TiO_2, and SiO_2.

We find that the classic ligand exchange reaction mechanism does not describe the reaction path in any of the investigated sample systems. In particular, we find that ALD of HfO_2 on SiO_2 follows a bimolecular reaction mechanism based on the insertion of a β-hydride of one of the ligands in an amido complex dimer into the bond between another ligand and of the Hf ions in the dimer. As a result of its bimolecular nature, this reaction can take place only at sufficiently high coverage of physisorbed complexes on the SIO_2 surface. On TiO_2 we find that the early stage of the reaction is based on dissociative adsorption, followed by mono- or bi-molecular reaction paths, leading to the formation of new sets of surface species never identified in ALD reactions.

Moreover, for an easily reducible surface we find evidence of HfO_x formation already during the first ALD half-cycle due to the transfer of O atoms from the surface to the metal complex. Clearly, this contradicts the passive role of the surface in standard ALD models. Interesting, in the case of InAs covered by a thermal or native oxide, this phenomenon, which lies behind the so-called self-cleaning effect, guarantees a sharp interface between the III-V material and HfO_2, a prerequisite for next-generation MOSFETs.

Our results open new doors for improving devices based on ALD. Time-resolved *in situ* and *operando* APXPS allows us to follow the kinetics and mechanisms involved in ALD, in real time at second time resolution with significant benefit for the further improvement of our general understanding of ALD reactions.

1:45pm **AF1-TuA-2 An *in-Vacuo* X-Ray Photoelectron Spectroscopy Study of the Reaction of Trimethylaluminum With Water, Oxygen and Argon Plasma for Low Temperature Atomic Layer Deposition***, L. Cao, **Jin Li**, M. Minjauw, J. Dendooven, C. Detavernier,* Department of Solid State Sciences, Ghent University, Belgium

Low temperature atomic layer deposition (ALD) has been drawing great research interest because of its capability to coat on heat-sensitive substrates, such as flexible devices, polymers and biological materials. As a process with widespread applications, the surface chemistry of Al_2O_3 ALD at low temperature is still under extensive investigation.[1,2] In this work, the growth of Al_2O_3 using trimethylaluminum (TMA)/water and TMA/O_2 plasma have been investigated with *in vacuo* X-ray photoelectron spectroscopy (XPS) in the temperature range from 60 to 300 °C. Samples are transferred back and forth between the ALD chamber and the XPS analytical chamber without vacuum break to analyze the surface chemical state after each reactant exposure, providing insight into the evolution of surface species.

Our results confirm that the low temperature TMA/water process undergoes an incomplete surface reaction during the water exposure

(Figure S1), resulting in a low growth per cycle of 0.66 Å/cycle at 60 °C. Persistent -CH_3 groups are present on the growth surface after the water exposure and its concentration increases with reducing temperature, in accordance with previous reports.[1,2] In spite of the continuous presence of surface -CH_3 groups during the whole process, the C impurity concentration in the film is found to be surprisingly low. XPS depth profiling showed that C only exists at the very surface region, and is not incorporated into the film (Figure S2). According to *in situ*spectroscopic ellipsometry data, the growth at low temperature still displays a linear growth behavior (Figure S3). Our results indicate that, although the reaction during one water half cycle is incomplete at lower temperature, the next few water half cycles tend to finish the job and no carbon is built into the film. In contrast, oxygen plasma can combust all carbon ligands regardless of the surface temperature (Figure S1), boosting the growth rate to 2 Å/cycle at 60°C. To further explore the power of plasma for low temperature ALD, a three-step TMA/Ar plasma/H_2O process is also investigated. The Ar plasma is found to change the Al–CH_3 surface groups into an intermediate product that can react more easily with H_2O to allow a more complete reaction, increasing the growth rate from 0.66 Å/cycle to 1.1 Å/cycle at 60°C while avoiding potentially damaging effects on sensitive substrates caused by the chemically active O_2 plasma.

[1] V. Vandalon and W.M.M. Kessels, Appl. Phys. Lett. **108**, 1 (2016).

[2] Z. Jin, S. Lee, S. Shin, D.S. Shin, H. Choi, and Y.S. Min, J. Phys. Chem. C **125**, 21434 (2021).

2:00pm **AF1-TuA-3 *In Vacuo* Cluster Tool for Studying Reaction Mechanisms in ALD and ALE Processes*, Heta-Elisa Nieminen*,** *M. Chundak, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Film growth during an ALD process is solely dependent on the chemical reactions on the substrate surface. Well-behaving surface chemistry enables the key qualities which make ALD a superior thin film deposition method. In addition, surface reactions define the outcome of each process and can set critical challenges on the process development and integration. For these reasons, studying the chemical reactions in the film growth is of utmost importance to fully understand the growth process and exploit the advantages ALD has to offer. Exactly the same applies to atomic layer etching (ALE) processes.

A new cluster tool in HelsinkiALD laboratory allows reaction mechanism studies on a wide variety of process chemistries without exposing the sample to ambient atmosphere. In this tool a commercial flow-type ALD reactor is connected directly to a set of ultra-high vacuum analysis techniques so that after interrupting the process at a selected point the substrate can be transferred *in vacuo* straight from the ALD reactor to surface analysis. The chemical composition of the surface including reaction intermediates can be precisely investigated after each precursor pulse individually. The resulting information will be beneficial for resolving the overall ALD and ALE mechanisms.

The cluster tool contains currently x-ray photoelectron spectroscopy (XPS), hard x-ray photoelectron spectroscopy (HAXPES), ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS), and temperature programmed desorption (TPD). The film growth can also be monitored *in situ* by a quartz crystal microbalance (QCM) and ellipsometer which are connected directly to the ALD chamber. As the system contains a flow-type ALD reactor, the mechanisms can be solved without compromising true ALD conditions. The system has been tested and the operation procedures optimized with TMA and H_2O for depositing Al_2O_3 at temperatures of 150 – 300 ˚C. The state of the surface was investigated by TPD and XPS after each precursor pulse. After the initial testing with this well-known process, new ALD and ALE chemistries will be studied in detail.

Funding from the Academy of Finland by the profiling action on Matter and Materials, grant no. 318913, the Doctoral Programme in Materials Research and Nanoscience (MATRENA) and the use of ALD Center Finland research infrastructure are acknowledged.

2:15pm **AF1-TuA-4 Watching the ALD of Pt Films in Real-Time*, Esko Kokkonen,*** Max IV Laboratory, Sweden*; M. Kaipio, H. Nieminen,* University of Helsinki, Finland*; F. Rehman,* Lund University, Sweden*; V. Miikkulainen,* Aalto University, Finland*; M. Putkonen, M. Ritala, S. Huotari,* University of Helsinki, Finland*; J. Schnadt,* Lund University, Sweden*; S. Urpelainen,* University of Oulu, Finland

We have used in situ and operando techniques to study the growth of Pt films on different substrates in real-time. In this study, we have focused on investigating the growth of metallic Pt on Si, Ir, and Ir oxide substrates. The precursors for this reaction were chosen as trimethyl(methylcyclopentadienyl)platinum(IV), or $MeCpPtMe_3$ and O_2 gas.

The experiments were done using the so-called ALD cell, which is an synchrotron-based ambient pressure X-ray photoelectron spectroscopy (APXPS) sample environment specifically dedicated for studies of ALD processes. The system is located on the SPECIES beamline [1] at the MAX IV Laboratory in Lund, Sweden. With a wide energy range of 30-1500 eV, the beamline offers wide measurement capabilities for both core-level XPS as well as valence band (ultraviolet photoelectron spectroscopy) UPS using surface sensitive photon energies. This setup has been recently used in several studies to gain deeper insight into different ALD processes [2, 3].

We have followed various core-levels on the surface using XPS as it was exposed to the first half-cycle with the $MeCpPtMe_3$ precursor. Interesting effects are seen on the three different substrates. Firstly, the Pt 4f core-level shows a clear intensity increase, naturally following from the addition of Pt containing precursor onto the surface. However, an interesting finding is that for all substrates, the Pt 4f binding energy shifts during the deposition. Moreover, the shifting of the Pt 4f peaks occur at a different timescale than the saturation of the surface based on the XPS intensity. A tentative explanation could be that the Pt precursor initially attaches to the surface with a higher oxidation state, perhaps still partially attached to some of the methyl groups, which rather quickly dissociate (or combust) and are released into the gas phase. This mechanism then could be on-going while the surface is only partly covered by the Pt since saturation is not yet reached.

[1] E. Kokkonen, et al. "Upgrade of the SPECIES beamline at the MAX IV Laboratory." *Journal of Synchrotron Radiation***28**, 2, 588-601 **(2021)**, DOI: 10.1107/S1600577521000564
[2] G. D'Acunto, et al. "Oxygen relocation during HfO_2 ALD on InAs." *Faraday Discussions* Accepted Manuscript (2022). DOI: 10.1039/D1FD00116G
[3] E. Kokkonen, et al. "Ambient pressure x-ray photoelectron spectroscopy setup for synchrotron-based in situ and operando atomic layer deposition research." *Review of Scientific Instruments* 93.1, 013905 (2022). DOI: 10.1063/5.0076993

2:30pm **AF1-TuA-5 In Situ X-Ray Studies of Lamellar Dichalcogenides Prepared by Molecular Layer Deposition and Thermal Annealing*, Petros Abi Younes,*** CEA/LETI-University Grenoble Alpes, France*; E. Skopin,* LTM - MINATEC - CEA/LETI, France*; M. Zhukush, C. Camp,* Univ. Lyon, CNRS-UCB Lyon 1, France*; N. Aubert , G. Ciatto,* Synchrotron SOLEIL Beamline SIRIUS, France*; N. Schneider,* UMR-IPVF, CNRS, France*; M. Richard,* ESRF, France*; N. Gauthier,* CEA/LETI-University Grenoble Alpes, France*; E. Quadrelli,* Univ. Lyon, CNRS, France*; D. Rouchon,* CEA/LETI-University Grenoble Alpes, France*; H. Renevier,* Laboratoire des Matériaux et du Génie Physique, France

Metal Dichalcogenides **(MDs)** have recently emerged as a class of exceptional materials with many potential applications and are receiving great attention. Among them, lamellar Titanium disulfide (**TiS_2**) is the lightest and cheapest member of the Transition MDs(**TMDs)** family,[1]with a 1T-TiS_2 crystallographic structure. Its electrical properties allow it to use in many fields of applications (optics, thermoelectric, and batteries).[2–5]

However, the lack of scalable fabrication methods of continuous ultra-thin films on developed surfaces, at moderate temperature, stems a sizeable bottleneck for the full deployment of these materials. Besides the conventional Atomic Layer Deposition (ALD) process, which suffers from limitations, an innovative **2-step process** comprising Molecular Layer Deposition (**MLD**) and **thermal annealing** has been developed to achieve an atomically-thin synthesis of 2D TMDs MoS_2 and WS_2.[6,7] Interestingly, the process does not use the highly toxic H_2S molecule. By using this approach we have succeeded to synthesize continuous and textured TiS_2 thin films on thermal SiO_2[8]. An intermediate amorphous polymer (Ti-thiolate) is deposited by MLD at low temperature (T_{sub} = 50°C) upon a reaction between the metal precursor (TDMAT = $Ti(NMe_2)_4$) and organic sulfide molecule (1,2-ethanedithiol). Then, the amorphous thin film undergoes a thermal annealing under hydrogenated argon flow.

Both the MLD and thermal annealing were monitored by *in situ* synchrotron radiation techniques, including x-ray fluorescence (XRF), x-ray reflectivity (XRR), and x-ray absorption fine structure (XAFS), at SIRIUS beamline (SOLEIL, St Aubin), and *in situ* ellipsometry. The main results will be presented. Importantly, both the sulfur K and Ti K fluorescence line intensities could be recorded simultaneously, allowing us to monitor simultaneously the S and Ti contents throughout the whole process and from the very early stage of the Ti-thiolate deposition. The repetitive self-limiting growth behavior during the MLD step could be demonstrated. Upon thermal annealing, the Ti-thiolate thin film transforms into lamellar TiS_2 monolayers parallel to the substrate surfaces observed by Raman spectroscopy, transmission electron microscopy (TEM) and x-ray linear dichroism at the Ti K-edge. Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS) and lab-scale Hard XPS (HAXPES) show stoichiometric TiS_2 in the presence of carbon.

References

[1]*Nano Today***2014**,*9*,604; [2]*Nano Lett.***2018**,*18*,4506; [3]*Phys. Rev. B***2019**,*99*,165122; [4]*Photonics Res.***2018***6*,C44; [5]*Phys.Chem.Chem.Phys.* **2012**,*14*,15641; [6]*Nanoscale***2017**,*9*,538; [7]*JVST A.***2017**,*35*,061502. **[8]Chem Mater 2022 (submitted)**

2:45pm **AF1-TuA-6 *In Situ* Spectroscopic Ellipsometry of 3D Patterned Nanostructures for Real Time Profile Evolution During ALD***, **S. Novia Berriel,*** University of Central Florida*; N. Keller,* Onto Innovation*; P. Banerjee,* University of Central Florida

In situ techniques are used to gain understanding of ALD processes in real time. In nearly all cases, planar substrates are used to monitor surface reactions and film growth. However, since ALD is used for conformal deposition in high-aspect ratio structures, the use of in situ techniques on planar substrates present a challenge in interpreting deposition characteristics on non-planar substrates and optimizing processes which can lead to conformal growth of ALD films inside high-aspect ratio structures.

In this talk, we will describe an optical-based metrology technique to monitor real time growth of ALD ZnO on patterned SiO_2 nano trenches. The primary advantage of this technique is that our hardware remains a spectroscopic ellipsometer (SE), whereas back-end data analysis and modeling is conducted using a rigorous coupled-wave analysis (RCWA) technique.

Patterned SiO_2 trenches with a width of 80 nm and a depth of 325 nm were used as substrates. Real-time polarization data (Ψ and Δ) were obtained across two runs – one, in which the trenches were parallel; and two, in which the trenches were perpendicular to the beam path. The profile evolution of ALD ZnO was monitored for 300 cycles, corresponding to a thickness of 55 nm on planar substrates. RCWA of the polarization data was used to generate 3D cross-section profiles of the SiO_2 trenches filling with ZnO from the beginning to the end of deposition.

The film thicknesses at various points along the trench and the resulting conformality were confirmed using cross-section SEM analyses. We find that RCWA is successfully able to predict thickness to within 7.8% and conformality to within 8.1% of true experimental data. Furthermore, the RCWA predicts the merging of growth fronts at the bottom of the trench in accordance with geometrical modeling and experimental observations. These promising results highlight the potential for real-time monitoring of in-trench conformality via a combination of SE and RWCA techniques

3:00pm **AF1-TuA-7 Pyroelectric Calorimetry: Measuring the Time-Resolved Heat of ALD Half Reactions***, **Ashley R. Bielinski,** A. Martinson,* Argonne National Laboratory **INVITED**

In Situ characterization methods provide insight into ALD reactions as they occur.We've implemented pyroelectric calorimetry as an *in situ* technique to measure the heat evolved in ALD half reactions with unrivaled thermal and temporal resolution.On high surface area substrates like nanoparticles or metal organic frameworks, ALD has been observed to cause temperature increases greater than 10°C.The small temperature changes (<0.1 °C) predicted for planar substrates are more challenging to accurately measure.We designed custom pyroelectric calorimeters for implementation in an ALD tool with thermal and temporal resolution down to 0.1 μJ/cm^2 and 50 ns.To put this in perspective, this corresponds to a temperature increase of about 10^{-5}°C, which is less than 0.1% of the heat evolved in the reaction between trimethylaluminum (TMA) and water.The calorimeter response time is more than 10^4 times faster than our measurement of the reaction time of TMA on a hydroxylated alumina surface.

Analysis of time resolved heat generation in ALD reactions provides information on thermodynamics and kinetics as well as how real reactions deviate from simplified textbook examples.Experimental reaction heats can be compared with theoretical and computational predictions of the interaction between specific precursors and surface sites, showing which of the hypothetical pathways best represent reality.Additionally, pyroelectric calorimetry is orders of magnitude faster than many complementary *in situ* analysis techniques, providing more granular insight and subdivision of individual half reactions.

We've combined pyroelectric heat generation analysis with *in situ* spectroscopic ellipsometry in a saturation study of the prototypical reaction between TMA and water.This represents the most accurate measurement to-date of ALD reaction heats.Comparison between these parallel *in situ* measurements provides insight into the reaction energy as the surface saturates within a single half reaction and the time-resolved data highlights the limitations of slow water reaction kinetics.In addition to fundamental studies of ALD surface reactions, careful analysis of heat transfer due to precursor flow can provide information on precursor delivery and flow dynamics within the ALD reactor.

The development of pyroelectric calorimetry for ALD provides many opportunities for future investigations.Of particular interest are applications requiring sub monolayer detection such as precursor reactions with specific surfaces sites in area or defect selective ALD as well as time-resolved kinetics studies.

ALD Fundamentals
Room Van Eyck - Session AF2-TuA

Characterization II

Moderators: Bart Macco, Eindhoven University of Technology, Juan Santo-Domingo Peñaranda, Ghent University, Belgium

4:00pm **AF2-TuA-11 Get the Full Picture: Full-Range Time-Resolved In Situ Mass Spectrometry During ALD***, **Andreas Werbrouck,** J. Dendooven, C. Detavernier,* Ghent University, Belgium **INVITED**

In situ measurements are indispensable for developing, characterizing, and understanding ALD processes. Quadrupole mass spectrometry (QMS) is one technique available to monitor the gas mix in the reactor (or at the exhaust) while surface reactions are ongoing. In QMS, gas from the reactor is sampled, ionized, and fragmented. These fragments have specific mass-to-charge ratios, and their relative intensities provide a way to fingerprint the chemical species present. However, typical tools can only detect a single mass at a time, leading to poor time resolution. Additionally, the generated reaction products may be complex, unexpected, and as they are generated by a self-limiting surface reaction, they are only present in the reactor for a limited amount of time.

Here, we propose a way to exploit the cyclic nature of ALD, collecting QMS data over multiple cycles in order to collect a full-range, time-resolved picture of the gas mix in the reactor during an ALD process. This allows to effectively bypass the limitations of traditional QMS during ALD with only minimal hardware changes to the reactor. Over the past years, we have used this technique to investigate the archetypal TMA-water process and detected a secondary reaction product for water, to study the deposition of lithium-containing films, and to study the deposition of ruthenium dioxide.

In the first part of the presentation, the data collection and post-processing routines will be clarified. The second part of this talk will handle specific use cases, and the tools that can be used to make sense of the large amount of collected data will be discussed. Time-resolved, full-range quadrupole mass spectrometry measurements may be indispensable to get the full picture of your atomic layer process.

4:30pm **AF2-TuA-13 Strategies to Produce Boron-Containing ALD Thin Films Using Trimethyl Borate Precursor: From Thermal to Plasma to Combined-Plasma Approach***, **Arpan Dhara,** A. Werbrouck, J. Li, J. Dendooven, C. Detavernier,* Ghent University, Belgium

Recent research takes interest in boron-comprising thin layers that are useful in many applications such as dopant for semiconductors, neutron detection and absorption layer in nuclear reactors, ceramic reinforcements, and lithium ion batteries. The most fundamental boron-containing layer, B_2O_3, is highly hygroscopic, and therefore ternary oxides (like $Al_xB_yO_z$) or B-doped oxide (like ZnO:B) are more commonly prepared, using a so-called

ALD supercycle approach. Generally, the boron concentration in these films is unequivocally poor (~1-10%) when the metal oxide to boron oxide cycle ratio is 1:1. Stoichiometric films are obtained only from a particular (pyrazolyl) type of precursor, however the high vaporization temperature (~200°C) hampers their practical use. Therefore, there is a need of finding a suitable precursor and convenient process to produce boron-containing thin films.

In this work, we demonstrate different strategies (figure 1) to produce aluminium borate thin films by ALD using trimethyl borate (TMB) as the boron source. Films obtained from *thermal* processes (***TMA-H_2O-TMB*** *or* ***TMA-H_2O-TMB-H_2O***) show a moderate growth per cycle (GPC, 0.85 & 1.5 Å respectively), and contain considerable carbon impurities. Also, a constant increase in growth rate is observed with temperature which suggests a low reactivity of the TMB molecule. The reactivity can be improved by using oxygen plasma (***TMA-O_2^*-TMB-O_2^****) instead of H_2O as O source. The GPC certainly improves a bit (~1.8 Å) along with a reduction in carbon contamination. However, the boron concentration in the films remains very low for the investigated processes (~5-10%).

To improve the growth rate and boron concentration further, we introduce a novel approach where a combination of H_2O and TMB is used in plasma form (**TMA-[TMB+H_2O]***). It is proposed that the TMB molecules ***polymerize in-situ*** in the plasma, as reported before for trimethyl phosphate plasma.[1] However, using TMB alone in plasma form does not yield self-limiting ALD growth, as polymerized species continuously accumulate on the substrate. Interestingly, by adding H_2O to the TMB plasma, saturated growth of aluminium borate films is achieved with a high GPC of ~3.5 Å/cycle. Moreover, the films contain a considerably larger amount of boron (~15-20%). We hypothesize that H_2O in the TMB plasma helps to hydrolyse surface groups, which in turn aids in preventing continuous polymerization. We also performed ***time resolved transient in-situ mass spectroscopy*** (figure 2) and ***in-vacuo XPS*** studies to reveal the mechanism of all three different approaches explained above.

29. T. Dobbelaere et. al., *Chem. Mater.***26**, 6863–6871 (2014)

4:45pm **AF2-TuA-14 Examining Large Grain Growth and Low Temperature Crystallization Kinetics for TiO_2 Thin Films Prepared by Atomic Layer Deposition (ALD)**, ***Jamie Wooding***, *K. Kalaitzidou, M. Losego,* Georgia Institute of Technology

This presentation will describe an atomic layer deposition (ALD) process to prepare large crystal anatase TiO_2 thin films (>1 micron at <100 nm thickness) and provide a roadmap to determine fundamental crystallization kinetics quantities for thin film systems. Films are deposited using tetrakis(dimethylamino)titanium(IV) (TDMAT) and water at 140 °C and 160 °C, followed by an *ex situ* low-temperature post-deposition anneal (PDA) from 140–200 °C. All as-deposited thin films are amorphous by X-ray diffraction (XRD) and Raman spectroscopy. During the post-deposition anneal, the crystallization process is tracked via scanning electron microscopy (SEM). As depicted in Figure 1, these low anneal temperatures achieve large grain growth resulting in crystal sizes of 0.8–1.2 µm in lateral dimension for a film thickness of 50 nm. The time-dependent transformation fraction is fit to the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model (Figure 2a), which reveals a continuous nucleation process and a two-dimensional growth mechanism, consistent with the observed large grains.Crystal nucleation rate is observed for short annealing times to determine the critical free energy for anatase nucleation and then combined with the transformation reaction rate from the JMAK equation to determine the activation energy for grain growth (Figure 2b). The energy required for nucleation of 1.32–1.35 eV K^{-1} $atom^{-1}$ is an order of magnitude greater than the activation energy for grain growth of 0.12–0.24 eV K^{-1} $atom^{-1}$; as such, nucleation has the more significant energy barrier at these lower temperatures. Films deposited at 160 °C have higher nucleation rates than those deposited at 140 °C despite both films having comparable critical free energies for nucleation. These greater nucleation rates originate from an increased nucleation frequency factor (Figure 2b), indicating improved mobility or a higher degree of proto-nuclei. Using this TiO_2 large grain crystal growth study as a prototype, this work demonstrates a method to predict post-deposition crystallization behavior in ALD thin films.

5:00pm **AF2-TuA-15 Deposition and Characterization of Hafnium Dioxide Films Embedding Nickel Nanoparticles**, ***Markus Otsus,*** *J. Merisalu, T. Viskus, T. Kahro, A. Tarre, K. Kalam, A. Kasikov, P. Ritslaid, J. Kozlova, K. Kukli, A. Tamm,* University of Tartu, Estonia

Controlled defects introduced in nanolaminates designed for use in resistive switching devices can improve the overall performance of memristors. Nanoparticles (NP) can guide the process of conductive filament formation thus lowering voltage and enhancing stability of resistive switching [1]. As overall the density of conductive filaments is low, observations of conductive filaments in or around a NP with scanning transmission electron microscopy (STEM) imaging could be possible. Studying the filaments shape and composition with STEM imaging and energy dispersive X-ray spectroscopy (EDS) analysis may allow us to better understand the process and mechanism of their formation [2].

Resistive switching properties of four different structures were examined. The aim was to produce otherwise similar structures (Figure 1) with and without Ni-NPs, using two different precursor systems at the same substrate temperature (220 °C), $HfCl_4$ +O_3, and tetrakis(ethylmethylamino)hafnium (TEMAH) + O_2 plasma, and two different atomic layer deposition (ALD) reactors – a flow-type in-house built hot-wall reactor and a Picosun R200 Advanced System, respectively. Starting with a Si(100) planar wafer substrate covered with a conductive TiN film, a two-step ALD process was used to embed the nickel NPs in-between a HfO_2 layer. Following the deposition of the dielectric layer, titanium top electrodes were produced using maskless photolithography and electron beam evaporation.

Scanning electron microscopy (SEM) showed the NPs uniformly dispersed across the sample area, apart from a few clusters observed. Current-voltage measurements were carried out, and in the samples with NPs, lower voltages were needed to switch between high-resistive state (HRS) and low-resistive state (LRS) (Figure 1), compared to the particle-free samples. SEM-focused ion beam was used to produce lamellas from films with and without Ni-NPs, which were then analyzed with STEM and EDS to evaluate the composition and uniformity of the layers (Figures 2 and 3). Nanocrystals were monitored in HfO_2 grown from TEMAH, while the $HfCl_4$ based oxide layer appeared structurally homogenous. Conclusively, electrical and microscopy findings were compared and a possible cause for the results observed was proposed.

[1] W. Banerjee, Q. Liu, and H. Hwang, "Engineering of defects in resistive random access memory devices," *J. Appl. Phys.*, 127 (2020) 051101, doi: 10.1063/1.5136264.

[2] D.-H. Kwon *et al.*, "Atomic structure of conducting nanofilaments in TiO_2 resistive switching memory," *Nat. Nanotechnol.*, 5 (2010) 148-153 doi: 10.1038/NNANO.2009.456.

5:15pm **AF2-TuA-16 Biased QCM for Studies of Reductive Surface Chemistry Induced by Plasma Electrons**, ***Pentti Niiranen***, *H. Nadhom, D. Lundin, H. Pedersen,* Linköping University, IFM, Sweden

Metallic films are an immensely important part of the modern world e.g., in a variety of applications such as sensors, catalysts, optoelectronics and nanoelectronics. For any ALD, or CVD, approach to metal films using a metal precursor with a positive valence, the fundamental surface chemistry is a reduction reaction. However, reduction of electropositive metals in ALD and CVD is especially difficult due to the shortage of precursors with the appropriate reduction power to overcome the thermodynamical disadvantage and complete the reduction. In a recent study, the electrons from a plasma discharge was used for the reduction of first-row transition metals (Co, Fe and Ni) in a CVD process, instead of using a co-reactant as a reduction agent.[1] By applying a positive bias to the surface, the plasma electrons were drawn to the substrate surface and facilitated metal growth. The process is also demonstrated to be inherently area-selective from the electrical resistivity of the substrate, depositing metal only on low-resistivity surfaces, leaving high-resistivity surfaces uncoated.[2] The surface chemical model for this process must be developed to understand and develop the method. As a first step to develop the surface chemical model, we here present a biased QCM system, capable of attracting plasma electrons to the QCM-head. Initial result shows the great potential of the modified QCM for the process where plasma electrons are used as reducing agents.[1] By using the biased QCM in combination with residual gas analysis and quantum chemical modelling we are building a surface chemical model of the process. The biased QCM-method can also aid us in our efforts to develop the method into a time-resolved method. We note from the QCM-curves that they suggest that self-limiting surface chemistry is possible using the new plasma electron based CVD method.

[1] Nadhom, et al. *J. Vac. Sci. Technol. A*, 2020, 38, 033402, 2020.

[2] Nadhom, et al. *J. Phys. Chem. Lett.*, 2021, 12, 4130.

5:30pm **AF2-TuA-17 NHC Monolayer Growth Behaviour and Film Durability Measured by QCM***, **Eden Goodwin,*** Carleton University, Canada*; A. Veinot, I. Singh,* Queens University, Canada*; P. Ragogna,* Western University, Canada*; C. Crudden,* Queens University, Canada*; S. Barry,* Carleton University, Canada

We have previously seen N-heterocyclic carbene (NHCs) containing gold precursors etch gold surfaces during quartz crystal microbalance (QCM) studies (Goodwin, AVS ALD 2021). Although we have proposed an etch mechanism, the role of the surface NHC remains unclear.

NHCs have been shown to reconstruct gold surfaces by dislocation and displacement of individual atoms on the surface and to bind to gold surfaces in several different conformations (upright, flat, in clusters) dependant upon their functionalization (Smith et al., 2019). The di-isopropyl NHC that was previously reported is expected to bind in an upright manner, a binding behaviour that can not be predicted and needs to be determined through scanning tunneling microscopy (STM) imaging on single crystal gold surface. Analyzing NHC binding behaviour this way has several downsides: cost of single crystal gold surfaces, availability of STM imaging facilities, and lengthy processing time. To alleviate these issues, we propose to quantify coverage and corroborate binding geometry by QCM studies. Additionally, we are investigating the effect of gold species ($AlCl_3$, (Me)AuNHC, $(Me)_3AuPMe_3$) on both the carbene monolayer and gold surface.

In this work we deposit a series of simple NHCs in a home-made tube furnace reactor using a 100-cycle pulse sequence (60s pulse, 20s N_2 purge) and subsequently expose these to gold-containing species. Real time high resolution (10 counts per second) surface analysis is done using a 6 MHz in-situ polished gold coated QCM crystal. Time resolved mass gain analysis is used to confirm saturative growth behaviour, determine the number of occupied gold sites, and to test film stability when exposed to a variety of Au species. A low resolution (<300 AMU) in-situ quadrupole mass spectrometer (QMS) is used to confirm the presence of free NHC and determine volatile products formed during surface decomposition or etch processes.

Atomic Layer Etching
Room Baekeland - Session ALE1-TuA
In situ Studies, Mechanisms and Modeling of ALE

Moderators: Sumit Agarwal, Colorado School of Mines, Dmitry Suyatin, Lund University

1:30pm **ALE1-TuA-1 Surface Reaction Mechanisms by Metal-Organic Compound Formations in Atomic Layer Etching Processes***, **Tomoko Ito,*** Osaka University, Japan*; A. Basher,* King Abdullah University of Science and Technology, Saudi Arabia*; K. Karahashi, S. Hamaguchi,* Osaka University, Japan **INVITED**

Transition metals are known as hard-to-etch materials for reactive ion etching (RIE). In recent years, atomic layer etching (ALE) based on the formation of highly volatile metal compounds from surface metals and organic gases has been proposed as atomically controlled and damage-less etching for transition metals [1]. In chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes, various volatile metal-organic compounds such as β-diketonates (such as nickel(II) acetylacetonate: $Ni(acac)_2$ and Nickel(II) hexafluoroacetylacetonate: $Ni(hfac)_2$) and metallocenes (such as nickelocene) are known as metal precursors. The metal ALE process mentioned above, where volatile metal β-ketone enolates or metallocenes are formed on a metal surface, may be considered as a reverse process of such ALD. The development of new ALE processes for various transition metals requires a better understanding of surface reactions of metals with gas-phase organic molecules. Therefore, the goals of this study are to understand how organic compounds absorb on transition metal surfaces and react with transition metal surfaces. Moreover, we want to clarify the mechanisms of the formation of volatile metal compounds and their desorption processes. In this study, we focused on the surface reactions of Ni and Co with hexafluoroacetylacetone (hfacH) and acetylacetone (acacH) gases, which were analyzed experimentally with the Atomic Layer Process (ALP) Analysis System and theoretically with density functional theory (DFT) calculations [2,3]. The ALP Analysis System, which consists of an *in situ* high-resolution X-ray Photoelectron Spectroscopy (XPS) system and an ALP reaction chamber, allowed us to examine the chemical compositions and bond formation of the metal and metal oxide surfaces on which hfacH or acacH molecules adsorbed. ALE processes of Ni and Co films were also confirmed experimentally with oxidation and hfacH exposure at elevated temperatures. DFT calculationsalso clarified the mechanisms of self-limiting reactions in thermal ALE of Ni with hfacH and acacH exposure, which were found to be consistent with experimental observations.

[1] J. Zhao, et. al., Appl. Surf. Sci. 455, 438 (2018).

[2] A. H. Basher, *et al.*, J. Vac. Sci. Technol. A 38, 052602 (2020).

[3] A. H. Basher, *et al.*, Jpn. J. Appl. Phys. 59, 090905 (2020).

2:00pm **ALE1-TuA-3 Atomic Layer Etching of Al_2O_3 on Metallic Substrates Using *in situ* Auger Electron Spectroscopy***, **Andrew Cavanagh**, S. George,* University of Colorado at Boulder

Ultra-sensitive techniques are required to observe the final cycles of atomic layer etching (ALE) as the etch process becomes a surface cleaning procedure at the interface of the film and the substrate/etch stop. With a sensitivity of ~1% of a monolayer, Auger electron spectroscopy (AES) is well suited for measuring the removal of a film with ALE. AES peak height ratios of the film and the underlying substrate provide a quantitative measurement of the film thickness during ALE. The peak height ratios were evaluated using a model developed by Holloway.

ALE of Al_2O_3 was performed using hydrofluoric acid (HF, 10% solution in pyridine) and trimethylaluminum (TMA). The sample stack was $Al_2O_3/Au/Y_2O_3$ (adhesion layer) /SiO_2 (native oxide)/Si. The gold underlayer provided a chemically inert, highly conductive interface ideal for AES studies. AES measurements were conducted periodically throughout the etch process and used to determine the thickness of the Al_2O_3 film. The instrument used for these measurements allowed for the transfer of the sample from an ALE process chamber (~1 Torr) to the ultra-high vacuum analysis chamber used for AES (10^{-10} Torr) without exposure to atmosphere.

The reduction in the aluminum and oxygen AES peak intensities from the Al_2O_3 film and the increase in the gold substrate peak intensity was observed as a function of the number of ALE cycles at 250°C (Figure 1). As monitored by AES, the etch per cycle of Al_2O_3 with HF and TMA at 250 °C was determined to be 0.3 $Å \cdot cycle^{-1}$. At the Al_2O_3 – Au interface, once the Al_2O_3 film had been nominally removed, Al and O atoms remained on the surface. Additional cycles of HF and TMA continued to remove this material, effectively cleaning the substrate surface (Figure 2). AES observations for the Al_2O_3 ALE process on Au substrates will be presented for different reaction conditions.

2:15pm **ALE1-TuA-4 In-situ Optical Emission Spectroscopy as a Tool to Characterize Cyclic Quasi-Atomic Layer Etching***, **Yoana Ilarionova,*** Lund University, Sweden*; M. Karimi,* AlixLabs, Sweden*; D. Lishan, D. Geerpuram,* Plasma-Therm LLC*; R. Jafari Jam, D. Suyatin, J. Sundqvist,* AlixLabs, Sweden*; I. Maximov,* Lund University, Sweden

Atomic layer etching (ALE) is one of the most advanced etching processes today, which enables atomic precision in a cyclic etching, where the material is removed layer-by-layer. In an implementation of ALE, a monolayer of reactive gas is chemisorbed on the surface of the etched material providing surface activation. The activated surface is then removed by plasma - usually by low-energy ions extracted from the discharge. They provide sufficient energy to remove only the reaction products leaving inactivated material.

In practice the ions may contribute to the physical sputtering of the etched material, thus increasing the total etch rate above the values of pure ALE. The residual reactive gas in the reaction chamber can dissociate in the plasma and also increase the etch rate. This etching mode can be defined as a “quasi-ALE” with contributions from the sputtering and reactive ion etching (RIE). To realize a “real or pure” ALE regime with negligibly small unwanted effects, careful optimization of process conditions is necessary. In the current work, we apply optical emission spectroscopy (OES) in a quasi-ALE cyclic process to monitor the relative concentration of active Cl_2 species in the chamber and relate it to the observed etch rate of Si.

In our experiments, we used a commercially available Inductively Coupled Plasma RIE Takachi™ tool (Plasma-Therm LLC, USA) with Cl_2 and Ar as process gases. Silicon samples were patterned with Talbot displacement lithography to produce specimens with resist masks. The etch rates were measured after the samples were cleaved and inspected with a scanning electron microscope. The OES measurements were performed in the wavelength range 191 - 887 nm using an in-situ spectrometer. The etch cycle included the following steps: injection of molecular Cl_2, purging with Ar to remove the excess chlorine, Ar-plasma etching and purging again.

Here we present a correlation between the average Si etch rate per cycle (EPC, determined by the etch depth divided by the number of cycles) and the intensity of the 257 nm Cl-peak as measured by the OES. The peak is generated during the Ar plasma step due to the presence of excess Cl_2. The experiments show that both the EPC and the Cl-peak increase with the increase of injection time and follow the same trend. A dependence between the EPC and the OES intensity is also observed. The measured EPC of 6.3-8.2 Å exceeds the expected EPC for pure ALE, indicating an excess of Cl_2. This indicates that the purging time affects the amount of residual Cl_2. Finally, we also discuss other applications of OES in the optimization of a quasi-ALE process.

2:30pm **ALE1-TuA-5 Atomic Layer Etching of CAR/SOG in EUV Patterning of 300 Mm Wafers - Selectivity and Roughness Mechanisms***, **Francois Loyer**, P. Bezard, R. Blanc, F. Lazzarino, S. De Gendt,* IMEC, Belgium

Future technological nodes (N3 and below) will see further shrinking of not only the pattern dimensions, but of photoresist film-thickness as well. The etching of Spin-On-Glass (SOG) using a Chemically-amplified-resist (CAR) mask following lithography is strongly affected by this trend as the selectivity of the conventional etch processes will soon no longer be sufficient. Furthermore, roughness reduction techniques as we know them will also be challenged as they typically consume some of the already-meagre CAR budget. Therefore, the reactive-ion-etching – based atomic layer etching (RIE-ALE) of SOG with a CAR mask is investigated as a softer and more selective alternative to conventional RIE. The RIE-ALE of SOG and the transfer into underlying hard mask have been demonstrated on coupons as well as on 300 mm full wafers, highlighting a strong increase of selectivity compared to RIE in coupons. However, the ALE process also yielded a higher roughness than RIE which doesn't meet the requirements for EUV patterning.

An investigation of the mechanisms leading to this improvement of selectivity together with the deterioration of the roughness is provided, highlighting the lack of chemical contrast due to the reactivity of the fluorocarbons, the role of redeposition mechanisms and the importance of interfacial interactions. Indeed, the mechanisms of fluorination during the patterning process become essential to understand and optimize the processes, as the very thin layers become deeply modified within their bulk.

The selectivity observed on patterned wafers can be explained by redeposition mechanisms, as the fluorocarbon-mixed layers formed in ALE are sputtered and redeposit on the CAR mask. Redeposition mechanisms are not suitable for an optimal roughness control as their statistical distribution leads to an increase of the LER and LWR. Moreover, the surface properties of both the CAR photoresist and SOG underlayer being deeply altered during the fluorination, the formation of complex interfaces as the ALE process occurs are expected to occur which induce further stress – hence roughness – within the layers. Surface free energy (SFE) measurements highlight the evolution of the dispersive (*i.e.*, London force) and polar (*i.e.*, Coulomb force) components of the layers during the patterning. Those interactions driving the gas to solid interactions before the formation of the mixed layer and the interface with the bulk, they provide valuable information on the potential stress within the stack.

2:45pm **ALE1-TuA-6 Ab Initio Calculations on the Thermal Atomic Layer Etching of Copper***, **Xiao Hu**, J. Schuster,* Chemnitz University of Technology, Fraunhofer Institute for Electronic Nano Systems, Center for Materials, Architectures and Integration of Nanomembranes (MAIN), Research Fab Microelectronics Germany., Germany

Copper interconnects are widely used in ULSI circuits due to their low resistivity and superior resistance to electromigration. Traditionally, the patterning of copper and barrier metals in the damascene process relies on chemical mechanical planarization (CMP), which may cause damages to fragile low-k interlayer dielectrics. Thermal atomic layer etching (ALE) is an emerging technique that uses sequential, self-limiting reactions to remove materials with high selectivity [1]. Thermal ALE is being considered an alternative to CMP as a final material removal step in the copper damascene process [2]. Recently, the thermal ALE of copper was demonstrated using O_2 or O_3 and H(hfac) (hexafluoroacetylacetonate) as the reactants [3]. Besides the oxidation mechanism, metal ALE can also be achieved through halogenation and ligand volatilization. For example, Co ALE has been demonstrated using Cl_2 and H(hfac) as the reactants [4]. In this work, theoretical calculations based on density functional theory (DFT) were performed to explore the possibility of Cu ALE through halogenation and ligand volatilization.

Using ab initio thermodynamic calculations, we have compared the Gibbs free energies of the reactions between H(hfac) and CuO, Cu_2O, and $CuCl_2$, as shown in Figure 1. It is found that the CuO + H(hfac) and Cu_2O + H(hfac) reactions are exothermic and have negative ΔG values between 300 K and 700 K. In contrast, the $CuCl_2$ + H(hfac) reactions are only favorable at temperatures higher than 425 K. Thermodynamic calculations suggest that a higher reaction temperature is required for Cu ALE using Cl_2 and H(hfac) as the reactants. In the next, we performed DFT calculations to investigate the elementary reaction steps of Cu ALE. During the Cl_2 exposure, the Cu surface is chlorinated to $CuCl_2$. During the H(hfac) exposure, the surface $CuCl_2$ is converted to gaseous HCl and $Cu(hfac)_2$. The surface reaction between $CuCl_2$ and H(hfac) consists of several elementary steps including H(acac) dissociation, hydrogen diffusion, $Cu(hfac)_2$ formation, and HCl and $Cu(hfac)_2$ desorption. The rate-limiting step is found to be the desorption of HCl and $Cu(hfac)_2$, with an activation energy of about 1.7 eV. Lastly, we focused on the computational evaluation of ligands for $CuCl_2$ volatilization. Various candidate ligands including acac, NacNac, dki, pyrim, dmap, and amd have been considered in this work.

[1] George, S.M. et al., ACS Nano, 2016, 10, 4889-4894. [2] Carver, C.T. et al., ECS J. Solid State Sci. Technol., 2015, 4, N5005-N5009. [3] Mohimi, E. et al., ECS J. Solid State Sci. Technol., 2018, 7, P491-P495. [4] Konh, M. et al., J. Vac. Sci. Technol. A, 2019, 37, 021004.

3:00pm **ALE1-TuA-7 Transport and Reaction Kinetics Modelling of Thermal ALE in High Aspect Ratio Hafnium Oxide Structures***, **Andreas Fischer**, D. Mui, A. Routzahn, R. Gasvoda, J. Sims, T. Lill,* Lam Research Corporation

Thermal atomic layer etching is rapidly becoming an important complementary processing technology in manufacturing 5 and 3 nm devices in the semiconductor industry.Critically, stacked chip architectures such as 3D NAND and 3D DRAM require conformal isotropic etching to remove material such as HfO_2 in hard-to-reach locations with aspect ratios that can be >50.To achieve repeatable device performance throughout a 3D stack, the removal rate (etch per cycle) of the etched material during an etch process need to be controlled such that the overall etch is the same from top to bottom of the device stack.In this work, we have modelled the reaction kinetics and transport processes of reactants and by-products during a cyclical ligand exchange-based ALE process. This ALE process consists of two steps: a fluorination step, followed by a fluorine-to-chlorine ligand exchange-based removal step.Experimental data revealed that the fluorine dosing during the fluorination step was predominantly responsible for controlling the etch rate of the ALE process but had only a minimal impact on the etch profile inside these holes.The ligand exchange dosing, on the other hand, predominantly controlled the etch profile (depth loading) with equal etch rates top-to-bottom obtained when the step was operated close to saturation.Our model predicts, in agreement with the experiment, that adsorption and reaction rates during fluorination on HfO_2 surfaces are significantly slower than transport times inside these deep holes leading to essentially flat fluorination profiles even if the fluorination step is not operated in saturation mode.In contrast, transport rates with the ligand exchange molecule are slow in comparison but adsorption and ligand exchange rates with the fluorinated hafnium appear to be significantly higher than for fluorine during the fluorination step.Slow transport in combination with high surface reaction rates for the ligand exchange step led to an etch rate that was dependent on aspect ratio (feature depth) in processes that used sub–saturation exposures.

3:15pm **ALE1-TuA-8 Damage Formation in the Underlying Silicon after the Removal of Silicon Nitride by Atomic Layer Etching: A Molecular Dynamics Study***, **Jomar Tercero**,* Osaka University, Japan*; A. Hirata,* Sony Semiconductor Solutions Corporation, Japan*; M. Isobe, K. Karahashi,* Osaka University, Japan*; M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; S. Hamaguchi,* Osaka University, Japan

Molecular dynamics simulations were performed for a better understanding of the formation mechanisms and extent of damage in the underlying silicon (Si) material when a silicon nitride (Si_3N_4) layer above it was removed by atomic layer etching (ALE). ALE is an etching technique known to remove a surface layer of a material with atomic-level control and precision. On account of this, extensive research was focused on devising ways to obtain a uniform and stable etching performance with good selectivity to other materials, to cope with high demand from the semiconductor industry. However, though ALE is known to etch a very thin layer at a time, problems such as over-etching or damage on the underlying material layer might still occur during the fabrication [1]. Therefore, in this study, ALE of Si_3N_4 formed on a Si surface was examined, with the use of molecular dynamics simulation. As in experiments, the surface modification step was performed with the adsorption of CH_2F radicals, and the removal step was performed with the irradiation of the modified layer with Ar ions. To assist the removal of the remaining HFC species, O ions were introduced after the removal step. Recent experimental observations showed that the HFC species penetrated deeply into the underlying Si during the first ALE cycle [2]. Our simulation showed that the HFC and Si_3N_4 species penetrated the underlying Si material to a depth of around 4 nm, in the removal step with 300 eV of Ar ion incident energy. The higher the Ar ion incident energy was, the deeper penetration depths of the HFC were observed. Moreover, the bond distributions showed that those penetrated species formed chemical bonding with surrounding Si atoms. As a consequence, the extent of damage or the thickness of the amorphized Si layer was also found to be around 4 nm. The results also showed that physical sputtering tended to dominate the ALE process as the Ar ion incident energy increased, where a large number of monoatomic species left the surface during the removal step. The results suggest that the Ar ion incident energy has a significant contribution to the damage generation in the underlying Si material.

References

1.Tinacba, E., Isobe, M., and Hamaguchi, S., *JVST A***39**, 042603 (2021).

2.Hirata, A., Fukasawa, M., Kugimiya, K., Karahashi, K., Hamaguchi, S., Hagimoto, S., and Iwamoto, H., DPS 2021 (2021).

Atomic Layer Etching
Room Baekeland - Session ALE2-TuA
Plasma and/or Anisotropic ALE II

Moderators: Ankur Agarwal, KLA-Tencor, Christophe Vallee, SUNY POLY, Albany

4:00pm **ALE2-TuA-11 Plasma Processes for Isotropic and Anisotropic Atomic Layer Etching***, **Adrie Mackus,*** Eindhoven University of Technology, Netherlands **INVITED**

While plasma etching has been the cornerstone technology in semiconductor fabrication in the past decades, future technology nodes require material removal with atomic-level accuracy as provided by atomic layer etching (ALE). Plasmas conventionally allow for anisotropic etching with high etch rates because synergistic effects between ions and radicals accelerate the surface reactions. In anisotropic ALE, more accurate control is obtained by decoupling the ion and radical contributions. Radical-dominated plasmas can also be employed for isotropic ALE, an option that is largely unexplored compared to the recent focus on thermal chemistries. In this contribution, plasma processes for both isotropic and anisotropic ALE are discussed, focusing on the unique merits provided by plasmas when accurately tuning the exposure to specific plasma species.

For isotropic ALE, two different types of chemistries were explored: (1) surface fluorination by SF_6 plasma exposure, followed by ligand-exchange reactions,[1] (2) diketone etchant (e.g. Hhfac, Hacac) exposure, followed by a plasma clean step.[2] The main merits of using plasmas for isotropic etching as compared to thermal chemistries were demonstrated for the fluorination / ligand-exchange process, namely the ability to etch at lower temperatures and with a higher etch per cycle. For the second process, in-situ Fourier transform infrared spectroscopy studies reveal that the self-limitation of the diketone etching reaction relies on the adsorption of diketone species in bonding configurations that do not contribute to etching. The ability of plasmas to effectively remove deactivating species and restore the original surface enables new ALE chemistries.

Although the ion energy is the most important parameter in anisotropic ALE, conventional radio-frequency biasing typically provides a broad distribution of ion energies. Ions with a well-defined energy are obtained in our work by employing tailored waveform biasing.[3] This precise control of the ion energy allows for sputtering in between the thresholds of chemically-modified and bulk materials, thereby opening up ion energy windows for highly-synergetic or -selective etching.

1. Chittock et al., *Appl. Phys. Lett.* 117, 162107 (2020).

2. Mameli et al., *ACS Applied Materials & Interfaces* 10, 38588 (2018).

3. Faraz et al., *J. Appl. Phys.* 128, 213301 (2020).

4:30pm **ALE2-TuA-13 SF_6 and Ar Plasma Based Atomic Layer Etching of Gallium Nitride (GaN)***, **Lamiae Hamraoui**, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*; M. Boufnichel,* STMicroelectronics Tours, France*; R. Dussart,* gremi CNRS/Université d'Orléans, France

Gallium nitride (GaN) is a powerful and promising semiconductor that perfectly fills and enhances the function obtained with silicon in technology development and in the fabrication of next generation of high-power devices as for example, the normally-off High Electron Mobility Transistors (HEMTs). The development and optimization of a damage-free etching process is still a research topic. Therefore, the Atomic Layer Etching (ALE) process has become predominant for the development of GaN-based HEMT and the conservation of its electric characteristics since it provides more precise etching depth and is less damaging compared to continuous plasma etching.

Up to today, the largest part of the research on the GaN ALE process has been carried outusing chlorine-based chemistries for the modification step, considering that the $GaCl_3$ etch by-product is volatile under ion bombardment [1,2]. However, the fluorinated chemistry is less investigated as compared to the chlorinated chemistry for the ALE of GaN [3,4]. This is primarily due to the non-volatility of GaF_x etch by-products as the GaF_3, which has a boiling temperature of 1000°C at atmospheric pressure [5]. Among the few fluorine based GaN ALE research reports, K. Nakazawa et al [3] have performed a two-step ALE process that involves a $CF_4/O_2/Ar$ plasma adsorption step and an Ar plasma with ion bombardment activation step. A separate study of thermal ALE of GaN using fluorine chemistry was carried out by another group where each cycle is initiated by an exposure to XeF_2 gas, followed by an Ar purge step, and lastly an exposure to BCl_3 gas [4].

In our work, the ALE of GaN process consists of a cyclic modification (fluorination) step using SF_6 plasma and an Ar plasma removal step performed in an Inductively Coupled Plasma (ICP) reactor. In this paper we report on the results of energy scan, the synergy and the self-limiting regime of ALE process using fluorinated chemistry. The influence of different plasma parameters such as the ICP power and the pressure on the Etch Per Cycle (EPC) and the RMS surface roughness was also investigated using Atomic Force Microscopy.

The authors would like to thank the European Union (IPCEI standing for Important Project of Commun European Interest) and Région Centre Val de Loire for their support through the Nano2022 project. We also acknowledge CERTeM 2020 platform, which has provided the majority of the equipment.

30. Ohba, T et al, Jpn. J. Appl. Phys. 56, 06HB06, 2017
31. Le Roux, F et al, Microelectron. Eng. 8, 2020
32. Nakazawa, K et al, DPS, 2019
33. Johnson, N. R et al, Appl. Phys. Lett. 114, 243103, 2019
34. Pearton, S. J et al, J. Appl. Phys. 86, 1–78, 1999

4:45pm **ALE2-TuA-14 SF_6 Physisorption based Cryo-ALE of Silicon***, **Jack Nos**, G. Antoun, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*; A. Girard, C. Cardinaud,* IMN CNRS/Université de Nantes, France*; R. Dussart,* GREMI CNRS/Université d'Orléans, France

Cryogenic Atomic Layer Etching (Cryo-ALE) using C_4F_8 as a precursor gas has been previously presented as an alternative method to achieve ALE of SiO_2. In this process, C_4F_8 is injected in gas phase during the "chemical modification" step, in order to physisorb on a cooled SiO_2 surface. The etching step is then achieved using an Ar plasma with a low energy ion bombardment. The temperature window of this process was between -120°C and -90°C [1,2]. A self-limiting etching regime was obtained with a regular etch per cycle (EPC) through several tens of nanometers which demonstrates the process stability without any contamination of the reactor walls.

In this paper, we show the results using SF_6 molecules as precursors for cryo-ALE of silicon.

In 1996, Royer *et al.* studied the chemisorption of sulfur and fluorine on Si during a simultaneous exposure to SF_6 gas and Ne^+ ion beam. In this work, they showed by XPS measurements that the fluorine quantity on the Si surface tends to increase as the temperature decreases, for a process window between 20°C and 130°C [3]. Therefore, a cryo-ALE study based on SF_6 physisorption was carried out to extend the use of this alternative approach to other materials.

The work presented in this paper was carried out using a cryogenic ICP reactor equipped with in-situ diagnostics. Mass spectrometry measurements enabled to characterize the SF_6 physisorption and its surface residence time at different temperatures. Spectroscopic ellipsometry was used to monitor the etching rate and to characterize the sample surface at the nanoscale during the three process steps: SF_6 physisorption, pumping and Ar plasma etching. Tests were performed on SiO_2, Si_3N_4 and p-Si coupons glued on SiO_2 6" carrier wafers.

SF_6 physisorption experiments will first be presented notably to determine the optimal temperature and purging time for the process. Subsequently, cryo-ALE test results on Si, SiO_2 and Si_3N_4 will be shown. These results will finally be compared to the ones obtained previously using C_4F_8 physisorption.

This research project is supported by the CERTeM 2020 platform, which provides most of the equipment and funded by the European Union (FEDER fund) as well as the French National Research Agency (ANR PSICRYO fund).

1. Antoun *et al., Appl. Phys. Lett.***115**, 153109, 2019

2. Antoun *et al., Sci. Rep.* 10, 2021

3. Royer *et al., J. Vac. Sci. Technol. A***14**, 234–239, 1996

5:00pm **ALE2-TuA-15 Precision and Repeatability of ALE Process in AlGaN/GaN Layer by in-Situ Etch Depth Monitoring**, ***Sungjin Cho,*** Oxford Instruments Plasma Technology, UK*; M. Loveday,* 1Oxford Instruments Plasma Technology, UK*; A. Newton,* Oxford Instruments Plasma Technology, UK*; D. Cornwell, M. Binetti, T. Zettler,* Laytec AG, Germany

GaN-based hetero structured high-electron-mobility transistors (HEMTs) are key components for the next generation of RF (radio frequency) and high power applications due to their high breakdown field, high-temperature operation, and their strong spontaneous and piezoelectric polarization-induced 2D electron gas (2DEG) of high carrier density and mobility. For safety considerations, normally-off operation HEMTs are vital for power applications. Due to their high gate voltage sweep and low leakage current, gate recessed metal insulator semiconductor (MIS)-HEMTs have been intensively investigated for normally-off operation. But their manufacturing has proven so far too challenging. Among the most significant challenges is sub-nanometer etch monitoring and controlling, to leave a thin (typically under 5 nm) layer of AlGaN, obtaining repeatable device performance.

In this work, we have realized of precision and repeatability of 5nm and 2nm AlGaN left on GaN by in-situ etch depth monitoring. we demonstrate how complementing a relatively slow, low damage atomic layer etch process with monitoring of the remaining AlGaN thickness allows excellent etch depth control of the AlGaN. The AlGaN layer thickness is determined by an AlGaN/GaN-optimized LayTec TRIton™ in-situ UV reflectance metrology tool with ±0.5nm. The accuracy and repeatability of the 2 and 5 nm target depths of AlGaN have been qualified by TEM. All ALE processes were controlled by monitoring the AlGaN depth through the UV reflectance interferometry traces. Furthermore, the UV reflectance results imply that GaN cap and neighbouring AlGaN etch at a varying rate, lower than the reproducible etch rate of bulk AlGaN. The UV reflectance traces clearly resolve the etch steps, which depends on the details of the cyclic ALE process. We have verified the good correlation between AlGaN thicknesses determined by TEM, and in-situ by real-time UV reflectance.

5:15pm **ALE2-TuA-16 Investigation of Self-Limiting Sputtering of Fluorinated Al_2O_3 and HfO_2: Where's the Limit?**, ***Nicholas Chittock,*** *W. Hoek, S. Balasubramanyam,* Eindhoven University of Technology, The Netherlands*; J. Escandon Lopez, K. Buskes,* ProDrive Technologies, Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, UK*; E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

ALE is becoming increasingly popular due to the high level of etch control and low damage etching it can provide. The use of self-limiting half-cycles for ALE is well-documented, however why and how half-reactions self-limit is less well understood. Such fundamental insight into sputter thresholds and yields is vital information that is missing from the literature for many ALE chemistries. In this work we examine (i) the self-limiting nature of the removal step of anisotropic ALE, (ii) the required energy window and (iii) how the etch rate changes as the material is sputtered.

The sputtering of fluorinated Al_2O_3 and HfO_2 is investigated, where the fluorination is performed by a SF_6 plasma and removal by directional Ar ions. Exploration of surface fluorination goes beyond the widely investigated case of Si ALE by chlorination,[1] providing insight into possible alternative ALE chemistries. To accurately evaluate the minimum energies required for material removal, we utilize tailored waveform (TW) biasing,[2] which allows for improved ion energy control over conventional radio-frequency biasing. The sputter thresholds for Al_2O_3 and HfO_2 were determined to be 59 ± 5 eV and 81 ± 5 eV, respectively. Following modification with an F-based plasma both films were shown to have a decreased sputter threshold, 23 ± 4 eV for Al_2O_3 and 37 ± 4 eV for HfO_2, which opens an ALE window. Additionally, the sputter yield of the modified films is increased as compared to bulk material aiding in removal of the modified layer.

Another important consideration for ALE processing is ensuring that the modified layer can be fully removed. By performing a SF_6 plasma exposure followed by multiple Ar plasma removal steps, we investigated how the layer is removed as a function of Ar plasma exposure time. Initially the etch rate of the modified layer is high, but as the modified layer is removed, the etch rate reduces back to that of bulk material. In our case this suggests the presence of an intermixed AlF_xO_y layer between the surface AlF_3 and bulk Al_2O_3.

Improved understanding of material removal, both in terms of ion energy windows and rate, will facilitate future development of anisotropic ALE processes, and thereby the integration into advanced IC fabrication.

Berry, I.L., et al. J. Vac. Sci. Technol. A 36, 01B105 (2018)

Faraz, T., et al. J. Appl. Phys. 128, 213301 (2020)

5:30pm **ALE2-TuA-17 Isotropic Plasma ALE of Al_2O_3 using F-based Plasma and $AlMe_3$: Key Parameters, Upscaling and Applications**, ***Yi Shu,*** Oxford Instruments Plasma Technology, UK*; N. Chittock, E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands*; A. O'Mahony,* Oxford Instruments Plasma Technology, UK*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands

Isotropic ALE processes are being considered for a range of applications such as controlled thinning of material, smoothing of surfaces, and removal of contaminated or damage surface layers. Although most reported isotropic ALE processes use thermal processes, also plasma-based ones are of recent interest, due to a promise of easier to handle precursors and expanded process parameter space. In our recent work, isotropic plasma ALE of Al_2O_3 was performed using SF_6 plasma and $AlMe_3$, which was demonstrated on a small-scale homebuilt reactor.[1] The $AlMe_3$ dose in the process needs to be sufficient to cause net etching since otherwise AlF_3 deposition is observed.[2] The required $AlMe_3$ dose for net etching will furthermore depend on the degree of fluorination of the various surfaces in the reactor. Therefore, a long and extensive fluorination by the SF_6 plasma could cause challenges in achieving uniform etching with a given $AlMe_3$ dose.

In this contribution we will discuss the transfer of this ALE process to a commercial ALD tool (Oxford Instruments FlexAL) which would also allow process sequences combining ALD and ALE. Depending on the used substrate temperature, plasma dose and precursor dose, either deposition or etching was found to occurred. After obtaining understanding of these parameters, a decent ALE uniformity was achieved (~2% 1-sigma thickness non-uniformity over 150 mm wafer area). Possible applications (e.g., in quantum and power electronics) and parameters to keep in mind for process transfer will be discussed in this contribution.

35. Chittock et al.,Appl. Phys. Lett. 117, 162107 (2020)
36. Vos et al., Appl. Phys. Lett. 111, 113105 (2017)

ALD for Manufacturing
Room Auditorium - Session AM1-TuA

ALD for Manufacturing I

Moderators: Hardik Jain, TNO/Holst Center, Maksym Plakhotnyuk, ATLANT 3D Nanosystems

1:30pm **AM1-TuA-1 Atomic Layer Deposition Equipment Used in Industrial Production of More Than Moore Devices*, Taguhi Yeghoyan,*** Yole Développement, France

In semiconductor community, Atomic Layer Deposition (ALD) is often associated with upmost advanced nodes, used for manufacturing of logic and memory devices, so called More Moore (MM) applications. For MM, ALD is used in High Volume Production (HVM) already for 20 years, starting with DRAM capacitor coating and logic transistor node shift from 65 nm to 45 nm. From that time on, ALD played a vital role to enable subsequent nodes and transistor architecture evolution, first to FinFet and currently to Gate-All-Around (GAA).HVM of MM devices is done with 300 mm Si wafers, with ALD equipment tailored to a specific process and high throughput. Thus, only few ALD equipment makers are present in MM HVM, generating highest equipment sales revenue.

On the other side of semiconductor industry, More-than-Moore (MtM) device production flourishes with diversified substrates in terms of material, size and sometimes shape. MtM devices encompass MEMS and sensors, Radiofrequency (RF) devices, power devices, CMOS Image Sensors (CIS), photonic devices and various packaging approaches. Among all MtM devices, CIS are manufactured mostly on 300 mm Si wafers on MM-like production lines and require similar ALD equipment. Other MtM devices are manufactured mostly on up to 200 mm production lines at lower volumes and with varied process flow. This MtM devices need flexible ALD equipment able to deposit often thicker films thermally or with plasma assistance, on various substrate sizes and substrate material, i.e. compound, Si, piezoelectric, dies on frame tape among others. Currently, more MtM ALD equipment providers qualify their equipment for Fab production, driven by several applications, where ALD is indispensable. These are for example: GaN HEMT transistors, mini-LEDs and microLEDs as well as wafer level encapsulation.

This presentation aims to give a market research overview on ALD equipment used in industrial production of MtM devices, with market size estimated to $345M in 2020, which is expected to increase to $680.5M in 2026. Moreover, ALD supply chain is outlined: ALD equipment subparts and inspection, process developers and materials suppliers. Finally, commercial MtM devices with identified ALD use are showed.

1:45pm **AM1-TuA-2 Spatial ALD on Large-Area Porous Substrates: How to Avoid Supply Limitation and Maximize Precursor Efficiency?*, Paul Poodt,*** SALDtech B.V., Netherlands

One of our greatest challenges for the coming decade is the transition to a sustainable way of generating, storing, and converting energy. High performance batteries, fuel cells, electrolyzers and solar cells are part of the solution, but still face many challenges that need to be solved. Efficiencies and capacities need to increase, the use of scarce and expensive materials needs to reduce and the life-time needs to improve. There are many examples where ALD has been used to improve on these aspects. For example, by applying thin and highly conformal films on porous substrates using ALD, the lifetime of Li-ion batteries can be improved, the loading of expensive catalyst materials in fuel cells and electrolyzers can be reduced and new devices such as 3D solid state batteries are enabled.

In order to enable large-scale mass production of these applications, Spatial ALD can be used for high deposition rates on both large substrates (square meters) and roll-to-roll. Scaling-up Spatial ALD processes on large area porous substrates, however, can lead to problems with supply limitation; i.e. when the required precursor flow to cover a high surface area substrate exceeds the amount of precursor that can actually be supplied, e.g. due to a low vapor pressure. Furthermore, in case of very expensive precursors, it is required to maximize the precursor efficiency to minimize costs.

The dependency of the precursor dose on aspect ratio, sticking coefficient and reactor pressure has been studied in great detail. However, for supply limitation, the effective surface area of porous substrates is the most important parameter. Furthermore, transport of precursor from the inlet towards the substrate and exhausts has to be taken into account. We have developed a numerical model to solve the diffusion-convection-reaction equation for porous substrates in a spatial ALD reactor, named 3D-DCR. The model combines parameters such as the porosity and effective area of the substrate with reactor dimensions, gas flow rates and deposition rate requirements to calculate and optimize the required precursor dose, precursor mass flow and utilization efficiency.

We will discuss several important results from this model, such as: 1) increasing the efficiency means decreasing the deposition rate and vice versa, 2) the required precursor dose does not only depend on pore aspect ratio but also on the reactor dimensions and used flows and 3) precursor efficiencies exceeding 80% are possible for porous substrates. Furthermore we will show how the these results can be used to optimize Spatial ALD processes and equipment for large scale manufacturing of high performance energy devices.

2:00pm **AM1-TuA-3 Atmospheric-Pressure Plasma-Assisted Spatial Atomic Layer Deposition of Silicon Nitride*, Jie Shen,*** TNO-Holst Centre, Netherlands*; F. Roozeboom,* University of Twente, Netherlands*; A. Mameli,* TNO-Holst Centre, Netherlands

Silicon nitride is a ubiquitous material in device fabrication, largely employed as an insulating dielectric layer or a gas permeation barrier layer, for example. Despite the effort that has been devoted to the development of effective SiN$_x$ atomic layer deposition (ALD) processes, reports on novel precursors and processes for SiN$_x$ continue to be regularly published. This highlights that some of the challenges such as low deposition rate and poor conformality, to cite the most common ones, are yet to be completely solved, especially at low deposition temperature.[1]

In this work we investigate the feasibility of SiN$_x$ spatial ALD at atmospheric pressure as a possible method for reaching high-quality and high-throughput SiN$_x$. Deposition temperatures between 150 ^{o}C and 250 ^{o}C were explored, resulting in growth per cycle (GPC) values between 0.3 Å/cycle and 0.2 Å/cycle, respectively and in a total ALD cycle time of ~2.4 s. The SiN$_x$ films were grown in a dedicated rotary lab-scale spatial ALD reactor,[2] using either a two-step process, employing bisdimethylaminosilane (BDEAS) and N_2 plasma from a direct dielectric barrier discharge (DBD);[3] or a three-step process, consisting ofBDEAS, followed by a first plasma exposure to N_2/H_2 DBD and a second N_2-only DBD plasma step. The influence of H_2 and N_2 plasma settings, and deposition temperature will be discussed in detail on the basis of the results from X-ray photoelectron spectroscopy (XPS) and Fourier transformed infrared spectroscopy (FTIR).[4] The best results in terms of layer composition and wet etch rate (WER), in 1:100 diluted HF were obtained at a deposition temperature of 250 ^{o}C. Here, 10% O_2 and 7.4% C contamination levels were detected, for layers with an N/Si ratio of ~ 1.29and a WER of 18 nm/min.

In conclusion we have demonstrated the first atmospheric-pressure spatial ALD process for SiN$_x$. The results presented herein are therefore very encouraging for low-temperature and high-throughput SiN$_x$ spatial ALD in large-area as well as in roll-to-roll mode. Based on the relevant process details explored in this work, we suggest possible next steps for further improving the quality of the spatial ALD deposited SiN$_x$ layers.

This work was supported in part by Semiconductor Research Corporation (SRC).

References

[1] X. Meng, *et al.*, *Materials*,**9**, 1007 (2016).

[2] P. Poodt, *et al.*, *Adv. Mater.*, **22**, 3564 - 3567 (2010).

[3] Y. Creyghton, *et al.*, Proc. Int. Conf. on Coatings on Glass and Plastics (ICCG 2016), Braunschweig, Germany, June 12-16, 93-97 (2016).

[4] R. Bosch, *et al.*, *Chemistry of Materials*, **28**, 5864–5871 (2016).

2:15pm **AM1-TuA-4 Recent Development of Large Scale ALD for Non-IC industrial Applications*, Wei-Min Li,*** Jiangsu Leadmicro Nano Technology Co. Ltd., China **INVITED**

Recent advance in ALD technology has shown prospect of HVM applications in several non-IC industry areas. For instance a breakthrough has been achieved during past few years for high efficiency solar cell HVM thanks to the rapid increase of global clean energy demand. ALD offers not only excellent material properties and functions, but also meets the manufacturing throughput and up-time requirements with significantly reduced manufacturing cost. Growing interests is seen for energy storage and flexible electronics applications as well. The great differences in material chemistry and various substrates to be handled however, calls for continuous innovation for different industrial applications. Author highlights current large scale ALD that are used or with high potential in some of the non-IC industry applications.

In PV industry, both ALD and PEALD have become the enabling technology not only for current mainstream PERC/PERL/PERT, but also finds applications for next generation TOPCon, IBC, HJT, as well as tandem solar cell technology. Batch type ALD and PEALD reactors are exclusively used for wafer based *c*-Si solar cell applications. A record throughput at over 15000 wafers/hour has been achieved with excellent film properties. A typical p-PERC cell efficiency has reached above 23.5%, and novel n-TOPCon solar cell has reached a cell efficiency of above 24.5% in pilot production. While an increase of conversion efficiency can be achieved for ALD enabled high efficiency solar cell manufacturing, the cost-of-ownership is also significantly reduced. With continuous improvement of materials and process integration, further enhancement for high efficiency solar cells are expected.

Significant progress has been achieved as well for ALD industry applications with flexible substrates that requires high permeation barriers properties. A commercial “roll-to-roll” ALD can now handle an effective web width of 1500 mm of PET substrate and achieve WVTR of 10^{-4} mg/day/m^2 at a maximum coating speed of >5 m/min. Large volume powder coating for lithium ion battery and catalyst applications at hundreds kilogram scale is seen approaching commercialization. Nevertheless, novel material and precursor chemistry and innovative reactor design combined with “intelligent manufacturing” to further improve the performance, enhance the productivity as well as reduce the production cost are highly desired.

Recent advances of ALD technology and contribution to some of the key industry areas shows that with continuous innovation and efforts, large scale ALD is becoming a generic and prospective technology for novel non-IC industrial applications.

2:45pm **AM1-TuA-6 An Innovative Method for in Situ Calorimetry of ALD/ALE Surface Reactions***, **Anil Mane**, J. Elam,* Argonne National Laboratory

Calorimetry is an essential analytical technique for determining the thermodynamics of chemical reactions. In situ calorimetry during atomic layer deposition and etching (ALD/ALE) would be a valuable tool to probe the surface chemical reactions that yield self-terminating growth and removal of material at the atomic scale. Additionally, in situ calorimetry would reveal the partitioning of chemical energy between the individual half-reactions that constitute the ALD or ALE cycle. In this study we present an alternative strategy that exploits temperature-induced resistance changes in ALD thin films. Our approach utilizes a thin film ALD nanocomposite resistive layer deposited conformally on the inner surfaces of a borosilicate capillary glass array (CGA) [1]. The ALD nanocomposite has a high resistivity and a well-defined thermal coefficient of resistance (TCR), both of which can be tuned by adjusting the resistive layer composition. In practice, the resistive CGA (RCGA) calorimeter is installed in the ALD system and electrically biased to produce a current in the microamp range that is recorded in real time. During the ALD/ALE surface reactions, heat exchanged with the coating produces transient current features due to the non-zero TCR of the nanocomposite film. These transient features are highly reproducible and can be used to calculate the reaction enthalpies of the individual surface reactions based on the TCR value and the thermos-physical properties of the CGA. Moreover, the RCGA can be calibrated by subjecting the device to well-defined voltage pulses and measuring the resistance changes induced by Joule heating. The RCGA is highly sensitive due to the high surface area of the CGA, the rapid response of the nm-scale resistive coating, and the tunable TCR value. In addition, the device is relatively low cost and easily integrated into ALD/ALE systems. To demonstrate the RCGA calorimetry method, we performed in-situ calorimetry measurements for a range of ALD processes including Al_2O_3, AlF_3, $Al_xO_yF_z$, ZnO, MgO, TiO_2, and ZrO_2. We also studied the nucleation behavior when transitioning between ALD materials and the use of alternative precursors for ALD Al_2O_3, TiO_2, and AlF_3 ALD. We find good agreement between reported enthalpy changes for ALD reactions and the values measured by in situ RCGA calorimetry. We believe that RCGA calorimetry is a versatile in situ method to study the thermodynamics of ALD/ALE surface reactions and a convenient diagnostic for real-time ALD/ALE process monitoring in a manufacturing environment.

1) A. U. Mane et. al., Chem. Vap. Deposition, **19**, 186–193, (2013).

3:00pm **AM1-TuA-7 Production-Suitable 200 Mm Batch ALD/MLD Thin Film Encapsulation Toward Flexible OLED Manufacturing***, **Jesse Kalliomäki**, E. Rimpilä, R. Ritasalo, T. Sarnet,* Picosun Oy, Finland

Organic electronics (OE) have rapidly become a mainstream technology due to their desired properties like low weight, high energy efficiency, flexibility and low manufacturing costs [1]. These advantages can be traced back to the fact that components can be routinely printed on plastics in huge roll-to-roll manufacturing lines. What has changed in the last decade or so is the introduction of thin film encapsulation solutions (TFEs) as a key enabling technology. TFEs can mitigate one of the biggest downsides of OEs - their susceptibility to oxidation by moisture [2]. TFEs allow the devices to stay light, transparent and flexible and help them to achieve their full potential.

TFEs rely heavily on vacuum-based thin film deposition techniques like ALD and MLD, which are not as straightforward to scale to roll-to-roll. Indeed, most of the research on TFEs are carried out on chip-scale and focuses on improving already excellent barrier properties [3]. To avoid bottlenecks in manufacturing, scaling up these TFE processes must be realized. Previously we have reported an industrially viable ALD/MLD process [4], which we have continued to scale with serious production in mind.

We present characterization and scale up results of single-chamber TFEs (Fig 1.). The moisture barrier properties were analysed with tuneable diode laser absorption spectroscopy (Sempa HiBarSense 2.0), delivering excellent results from a very large area (3320 mm^2). Bending properties were analysed by applying tensile stress by bending films deposited on polycarbonate and determining the crack-onset-strain with an optical microscope. Confirming TFEs can resist defects up to 2% tensile stress. All films were deposited using a Picosun P-300B batch ALD tool with batch sizes up to 27 pcs of 200 mm wafers. The process scales to larger chambers and achieves several Å/min growth rates and 2% chip-2-chip uniformities over full wafer batches.

In this work, we have demonstrated that ultra-barrier level TFEs can be coated on surfaces areas meaningfully measured in m^2. The barrier properties are also confirmed from a large enough area, to reflect the performance of the final product.

[1] Chang et al. (2017), doi:10.1109/JETCAS.2017.2673863
[2] Steinmann et al. (2018), doi:10.1557/jmr.2018.194
[3] Li et al. (2019),doi:10.1557/jmr.2019.331
[4] Kalliomäki et al. (2021), ALD2021, conference presentation

3:15pm **AM1-TuA-8 Roll-to-Roll ALD Coatings for Battery Cell Interfaces at Production Scale***, **Andrew Cook**,* Beneq, Finland

ALD is an enabling technology, which has been shown to improve battery performance, through the introduction of thin film coatings to modify interface surfaces on cathodes, anodes and separators. ALD can help to improve thermal stability, stabilise SEI layer, suppress dendrite, inhibit transition metal dissolution, and increase interfacial contact between layers, all of which are current issues facing lithium ion battery technology. This presentation will demonstrate how Beneq use ALD technology to solve these issues and show how this can be scaled to production levels within a Gigafactory environment.

Atomic Layer Deposition (ALD) is an advanced coating technique, which has been extensively studied for more than 10 years for uses in battery applications on small scale batch systems. ALD coatings have been applied to cathode, anode, and separator materials to modify the surface interfaces, and improve battery performance. This presentation will describe the current R2R ALD system, Beneq has developed for high throughput production.

ALD for Manufacturing
Room Auditorium - Session AM2-TuA

ALD for Manufacturing II

Moderators: Rong Chen, Huazhong University of Science and Technology, Ruud van Ommen, Delft University of Technology

4:00pm **AM2-TuA-11 High-Throughput Nanocoating Technology for Energy Applications*, Dmitrii Osadchii,*** Delft IMP B.V., Netherlands

In order to decarbonize the automotive sector, increased adoption of electric vehicles (EVs) is necessary. Two technologies are seen as a major driver for this development: Li-ion batteries (LIBs) and fuel cells (FCs). Many challenges still exist to enhance the performance of these power sources, such as the stability, cost, and environmental impact.

At the heart of these challenges are the active materials. For example with LIBs, much research is focused on the substitution of cobalt with nickel in the cathode. Not only does this enable a reduction of the battery cost, but it also enhances the capacity. Unfortunately, these benefits come at a cost, and significant stability issues still remain. A solution to enhance the stability can be found by protecting the surface of cathode powders. As such, there is a large body of literature showing that Atomic Layer Deposition (ALD) is well-suited to enhance the stability of low-cobalt cathode materials.

To capitalize on the benefits that ALD can bring, there is a growing need to bring powder ALD from lab to fab. For that, several challenges need to be overcome. Delft IMP tackles these challenges by developing high-throughput technology based on powder ALD. By combining pneumatic transport with ALD a continuous stream of nanocoated powder can be produced. In this talk we will showhow Delft IMP's unique technology allows to increase the cycle life of cathode materials up to 100% at up to 40% lower costs compared to traditional wet coating technologies.

4:15pm **AM2-TuA-12 Optimizing Vapor Delivery of Transition-Metal Diazadienyl Complexes for ALD Processes*, James Maslar,*** *B. Kalanyan,* NIST-Gaithersburg*; V. Dwivedi,* NASA Goddard Space Flight Center*; D. Moser,* EMD Electronics

Metal ALD processes have potential applications in many areas, including microelectronics and heterogeneous catalysis. However, such processes have not been widely demonstrated for many of the transition metals. Transition-metal diazadienyl complexes represent a class of precursors that has been used for metal ALD, including deposition of cobalt and nickel films. Furthermore, these precursors have been shown to deposit metal films at low temperatures and with substrate selectivity, making them suitable for many microelectronics applications. In this investigation, the delivery of bis(1,4-di-*tert*-butyl-1,3-diazadienyl)nickel [$Ni(DAD)_2$] was studied for ALD of nickel metal. $Ni(DAD)_2$ is a solid at typical delivery temperatures and, in general, delivering a constant flux of a solid precursor can be difficult. However, this may not be an issue for an ideal ALD process unless the total precursor dose is insufficient to saturate all surface reactive sites. Unfortunately, under some conditions the dose of $Ni(DAD)_2$ has been observed to decrease significantly after storage for nominally identical delivery conditions, complicating subsequent ALD. The primary goal of this investigation is to elucidate the factors impacting $Ni(DAD)_2$ delivery, including any conditions resulting in irreproducible delivery. To achieve this goal, both $Ni(DAD)_2$ and the DAD ligand (the primary decomposition product under the conditions of this study) were monitored as a function of delivery conditions using direct absorbance measurements. Measurements were performed with an ultraviolet-visible spectrometer and a two-channel gas analyzer. The gas analyzer employed broadband ultraviolet-visible sources, a beam splitter, bandpass filters for wavelength isolation, and avalanche photodiode detectors. The results from this investigation should provide more insight into conditions to optimize the delivery of transition-metal diazadienyl complexes.

4:30pm **AM2-TuA-13 Inherently Selective Atomic Layer Process Based on Spatial Micronozzles: Microreactor Selective Area Direct Atomic Processing (µSADALP)*, Maksym Plakhotnyuk,*** ATLANT 3D Nanosystems, Denmark*; I. Kundrata,* ATLANT 3D Nanosystems, Germany*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), ATLANT 3D Nanosystems, Germany **INVITED**

In parallel to additive manufacturing leading the revolution in traditional manufacturing, by supplementing the weaknesses of substractive machining, so can additive manufacturing supplement the weaknesses of traditional thin film deposition techniques. Where lithography struggles, for example with rapid iterations for prototyping or incompatibility with the used chemistry, additive manufacturing can shine. Indeed, several approaches are in development for 3D nanopriting[1,2,3].

Atomic Layer Deposition, and in more general Atomic Layer Processing, offers a unique opportunity for 3D printing due to its two-step chemical reaction. While simple in theory, due to well-developed examples of Spatial Atomic Layer Deposition (SALD), in practice minimization of SALD requires substantial effort into the creation of suitable micro-nozzles. Uniquely, ATLANT 3D Nanosystem has developed proprietary Spatial ALD micronozzles, naming the process microreactor Selective Area Direct Atomic Processing - µSADALP™.

In general fields such as advanced materials innovation, MEMS & sensors, RF devices (transparent antennas), Optics & Photonics (Optical coatings, surface modifications) and many other can benefit from µSADALP™.

As for now, µSADALP™ is in its development stage, with several standard ALD processes explored, but further research is being done in using it for Atomic Layer Etching and Molecular Layer Deposition, or even Atomic Layer Surface Doping (ALSD) which further opens the door for more processes and thus more applicability for this technology in advanced materials, functional surfaces and electronics design, development and manufacturing.

5:00pm **AM2-TuA-15 Atomic Layer Rastering*, Ivan Kundrata,*** ATLANT 3D Nanosystems ApS, Slovakia

Atomic layer deposition is, due to its inherent separation of reactions, uniquely suitable for adaptation into a 3D printer. In fact, the concept of spatial atomic layer deposition, which can be considered as a precursor for 3D atomic layer printing, goes all the way back to 1974.[1] Despite the many challenges of creation and miniaturization of spatial ALD reactors, atomic layer 3D printing was successfully proved as a concept recently.[2,3]

The Atomic Layer 3D printer, by its nature of exploiting a physical precursor/reactant separation, is in sharp contrast to Area Selective ALD[4,5] which exploits a chemical reaction to achieve localization. Therefore, no pre-patterning or tricks are needed for spatial Atomic Layer 3D printing to produce localized deposition. However, the cost of achieving localization via spatial separation is the difficulty in design and manufacture of micronozzles, which the Area Selective ALD does not need to struggle with. This inherent spatial separation, agnostic of the ALD chemistry used, or the substrate, allows to explore and use techniques normally associated with fused filament printing or plotting, such as sacrificial layer deposition or rastering.

Rasterization is a traditional technique from printing and engraving, where the picture is broken down into line and then “rastered”. Its use so far for nanostructuring has been limited, however using Atomic Layer 3D printing allows us to explore the creation if nanostructures by rastering. Furthermore, there are unique effects created by the nozzle geometry of Atomic Layer 3D printing, that can be exploited in rastering, which for example results in the ability to controllably print gradients.

In this study, we use the Atomic Layer 3D printer to manufacture rastered structures, from simple structure of 2 lines overlapping with various overlaps, to rastered squares in of various complexity, to a set of concentric circles with a 600 nm line overlaps. To show that the technique is not materially dependent rasters were performed both in TiO_2 and Pt. We demonstrate that we can control both the pattern, to the resolution of the kinematic apparatus, and the aspect ratio with ALD resolution.

5:15pm **AM2-TuA-16 Maskless Localized Atomic Layer Deposition: Surface Structuration and Functionalization***, L. Midani, W. Ben-Yahia, V. Salles,* Université Lyon 1, France*; **Catherine Marichy,*** CNRS-LMI, France

Nowadays, interest in nanotechnologies is strongly expanded in many domains like nanoelectronics, energy, transportation, medicine, and the environment. Precise designs of micro- and nanostructures are sought after for many devices and applications such as thin films transistors, diodes, electrocatalysts, solar cells, sensors, or membranes. Additive and subtractive technologies are thus areas of extensive research. In particular, additive approaches permit the controlled stacking of layers made of different materials. However, they display limitations either in thickness of the deposited material, in lateral resolution, or structuring scale. Combining control of at least one dimension at the nanometer level with large-scale patterning is still challenging in the direct write approach. Atomic Layer Deposition (ALD) is a technique of choice for depositing thin films with a thickness control at the atomic scale. In particular, direct patterning can be realized using spatial ALD (SALD).(*1–3*)

Herein, maskless deposition of uniform and homogenous oxide thin films is successfully demonstrated with a lateral resolution tuned from millimeters to hundred micrometers range while keeping a film thickness in the range of a few to hundreds of nanometers with a control at the nanoscale. A modified open-air SALD head is employed to fabricate complex oxide patterns on various substrates.(*4*) The co-reactant being kept in the surrounding atmosphere *i.e.* water from relative humidity in the present case, a simple injection head that consists of three concentric nozzles with only one precursor outlet has been designed. An easy and reversible modification in the diameter of the metal precursor outlet that permits direct patterning with different lateral sizes is demonstrated. Typical SALD characteristics are observed. Deposition on various planar and structured substrates is also investigated as well as complex and multilayer oxide patterns. This maskless SALD approach also enables controlled surface functionalization. In particular, local tuning of the wetting properties is successfully realized that permits controlling the water dropwise condensation.

37. C. A. Masse de la Huerta *et al.*, *Advanced Materials Technologies*. **5**, 2000657 (2020).
38. P. Poodt, B. Kniknie, A. Branca, H. Winands, F. Roozeboom, *physica status solidi (RRL) – Rapid Research Letters*. **5**, 165–167 (2011).
39. M. Aghaee, J. Verheyen, A. A. E. Stevens, W. M. M. Kessels, M. Creatore, *Plasma Processes and Polymers*. **16**, 1900127 (2019).
40. L. Midani, W. Ben-Yahia, V. Salles, C. Marichy, *ACS Appl. Nano Mater.***4**, 11980–11988 (2021).

5:30pm **AM2-TuA-17 New Spatial ALD/CVD Approaches for Area-Selective Deposition***, **David Muñoz-Rojas**,* CNRS-LMGP, Université Grenoble Alpes, France*; C. Masse de la Huerta,* LMGP, France*; V. Nguyen,* phenikaa University, Viet Nam*; A. Sekkat, C. Crivello, F. Toldrá-Reig, C. Jimenez, O. Graniel, M. Dibenedetto,* LMGP, France

Within the materials deposition techniques, Spatial Atomic Layer Deposition (SALD) is gaining momentum since it is a high throughput and low-cost alternative to conventional ALD. SALD relies on a physical separation (rather than temporal separation, as is the case in conventional ALD) of gas-diluted reactants over the surface of the substrate by a region containing an inert gas.[1] Thus, fluid dynamics play a role in SALD since precursor intermixing must be avoided in order to have surface-limited reactions leading to ALD growth, as opposed to CVD growth. Fluid dynamics in SALD mainly depend on the geometry of the reactor and its components. While care is normally taken to prevent precursor crosstalk when using SALD, we have shown that the spatial separation principle can also be applied to perform CVD reactions (SCVD), i.e. growth not limited to the surface, yielding yet faster deposition rates while maintain the film quality and conformality typical of ALD and SALD. [2,3] We have also shown that selective deposition can be achieved by working in SCVD mode. In this new approach to area-selective deposition (ASD), the depositions are performed in static mode (i.e. no relative movement between the reactor and the substrate), and Computational Fluid Dynamics (CFD) simulations are used to control de effect of the different deposition parameters on the SCVD mode. [4] In this presentation we will show how close-proximity SALD based on a manifold injection head working in the open air can be tuned to deposit custom patterns without the need of pre-patterning steps. This is achieved by using the system in static SCVD mode and by a proper design of the injection head using 3D printing.[5] We will also show other new approaches to ASD developed with our SALD system.

1. Muñoz-Rojas, D., et al. Spatial Atomic Layer Deposition. inIntech open1 (2019). doi:10.5772/32009

2. Musselman KP, et al. Rapid open-air deposition of uniform, nanoscale, functional coatings on nanorod arrays. Nanoscale Horiz. 2017 2(2):110–7.

3. Hoye RLZ, et al. Synthesis and Modeling of Uniform Complex Metal Oxides by Close-Proximity Atmospheric Pressure Chemical Vapor Deposition. ACS Appl Mater Interfaces 2015;7:10684−10694.

4. Masse de la Huerta, C., et al. Influence of the Geometric Parameters on the Deposition Mode in Spatial Atomic Layer Deposition : A Novel Approach to Area- Selective Deposition. Coatings 9, 5 (2018).

5. Masse de la Huerta, et al., Gas-phase 3D printing of functional materials, Advanced Materials Technologies, 5, 2000657 2020.

ALD Applications
Room Arteveldeforum & Pedro de Gante - Session AA-TuP

ALD Applications Poster Session

AA-TuP-1 Atomic Layer Deposition of MoS_2 Decorated TiO_2 Nanotubes for Photoelectrochemical Water Splitting*, Chengxu Shen,* *E. Wierzbicka,* Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany*; T. Schultz, R. Wang, N. Koch,* Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany*; N. Pinna,* Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

MoS_2, a prototypical two-dimensional (2D) transition metal dichalcogenide (TMD) material, has been widely applied on multifarious applications such as transistor, catalysis, and energy storage.[1-3] In this work, a low-temperature atomic layer deposition process for MoS_2 thin film is successfully demonstrated by using cycloheptatriene molybdenum tricarbonyl ($C_7H_8Mo(CO)_3$) and H_2S as precursors. The as-deposited MoS_2 films are amorphous while they can be crystalized *in-situ* by sulfurization with H_2S at 300 °C. Moreover, MoS_2/TiO_2 heterostructures are facilely synthesized by depositing MoS_2 onto anodized TiO_2 nanotubes. Photoelectrochemical (PEC) water splitting test have been carried out and our heterostructures exibits a superior PEC performance than pure TiO_2 nanotubes under visible irradiation. This improved PEC performance is attributed to an enhanced light-harvesting ability of MoS_2 and an improved separation of the photo-generated charge carriers. The band structure of the MoS_2/TiO_2 heterostructures is further studied to understand the photoelectrochemical mechanism.

[1] T. Jurca, M. J. Moody, A. Henning, J. D. Emery, B. Wang, J. M. Tan, T. L. Lohr, L. J. Lauhon, T. J. Marks, *Angew. Chem. Int. Ed. Engl.* **2017**, 56, 4991.

[2] C. Shen, M. H. Raza, P. Amsalem, T. Schultz, N. Koch, N. Pinna, *Nanoscale* **2020**, 12, 20404.

[3] L. Guo, Z. Yang, K. Marcus, Z. Li, B. Luo, L. Zhou, X. Wang, Y. Du, Y. Yang, Energy Environ. Sci. **2018**, 11, 106.

AA-TuP-2 Impact of ALD-TiO_2 Overlayer on Hematite Nanorod Arrays for the Photoelectrochemical Water Splitting*, Jiao Wang,* Humboldt University Berlin, Germany*; L. Liccardo,* Ca' Foscari University of Venice, Italy*; H. Habibimarkani, E. Moretti,* Ca´Foscari University of Venice, Italy*; N. Pinna,* Humboldt University Berlin, Germany

Hematite (α-Fe_2O_3) is an attractive photoanode candidate for solar water splitting because of its favorable bandgap to absorb solar light, nontoxic and abundant. However, the short hole-diffusion length, poor carrier conductivity, and high electron-hole recombination rate especially at surface states significantly limit its practical applications in photoelectrocatalysis. The surface treatment of photoanodes with passivation overlayers have been used to modify the surface states, which can improve the separation and transfer of the photo-generated carriers. Here, hydrothermal grown hematite nanorod arrays were coated with an ultrathin TiO_2 layer by atomic layer deposition for achieving an improved photoelectrochemical performance. Compared to a bare Fe_2O_3 photoanode, the photoelectrochemical water oxidation performance of TiO_2-modified Fe_2O_3 photoanodes is dramatically improved. This improvement is attributed to the surface modification of Fe_2O_3 with the TiO_2 overlayer, which can passivate the surface states, suppress the electron−hole recombination and increase the photogenerated voltage. The effect of TiO_2 overlayer thickness on the overall water splitting efficiency of hematite photoanodes has been systematically investigated. This study demonstrates that a surface treatment with a TiO_2 overlayer is effective and might be extended to other high-performance photoelectrodes for solar water splitting.

AA-TuP-3 Improvement of the Performance of III-IV Multi-Junction Solar Cells Using Atomic Layer Deposited Antireflective Coatings*, Mantas Drazdys,* *D. Astrauskyė, R. Drazdys, T. Paulauskas,* Center for Physical Sciences and Technology, Lithuania

Multi-junction solar cells composed of group III-V semiconductor alloys are widely employed in space and concentrated-sun photovoltaic applications. For the devices to achieve high power conversion efficiency, the reflection losses must be minimized over a wide 400 – 1600 nm spectral range in which they typically operate. Therefore, the design and deposition techniques of antireflection coatings (ARC) play an important role.

The atomic layer deposition (ALD) technique offers several advantageous properties: resulting films are highly conformal, which ensure surface passivation of the structure and protection of the window layer from atmospheric conditions and oxidation. Also, the depositions can be conducted at low temperatures, which prevents unintentional solar cell contact alloying or hardening of photoresist for subsequent device testing. Finally, very high precision thickness control of multilayer ARCs can be achieved, which is a result of self-limiting ALD reactions.

In this work, two different antireflective coatings were deposited on GaAs and AlGaAs subcells and fused silica (FS) glass. The optical design of an ARC typically uses a sequence of layers with high and low refractive indices. For a low refractive index material, Al_2O_3 can be used, since ALD thermal deposition of Al_2O_3 is well known and does not require a complex reactor design. The first ARC was deposited using exclusively thermal ALD and consisted of two layers – TiO_2 and Al_2O_3. To minimize reflection losses over a wide spectral range even further, materials with higher refractive index contrast could be used. Silicon dioxide (SiO_2) is one of the most widely employed materials in the manufacturing of optical coatings owing to its low refractive index and large bandgap. However, it has been shown that the deposition of SiO_2 using a thermal process, where oxidant is water, is not sufficient. Therefore, the second ARC was deposited using a combination of thermal and plasma enhanced ALD and consisted of three layers: Al_2O_3 (thermal), HfO_2 (thermal), and SiO_2 (plasma enhanced).

Here, we present optical coating modelling and deposition results, including reflection spectra, surface morphology, and photovoltaic characteristics comparison of the cells with different coatings.

AA-TuP-4 Li-Nb-O Protection Layer for Li-ion Battery Electrodes *via* Atomic-Layer-Deposition*, Dae Woong Kim,* *W. Hong, J. Park,* Hyundai Motor Company, Korea (Republic of)*; S. Oh,* Hyundai Motor Comp, Korea (Republic of)*; M. Lee, S. Noh, T. Park,* Hanyang University, Korea

Recently, various active materials are being developed as anode/cathode to enhance the performance of next-generation lithium-ion batteries. However, due to the high reactivity occurring at the electrolyte/electrode interfaces, the active material requires a protective layer to improve durability.[1] Unlike general metal-oxide materials, lithium compounds have high ionic conductivity as well as electrochemical stability, so they are considered as one of the ideal solutions for active material protection. Although various technologies are used for coating processes, it is an issue to apply a nano-scale coating to the active material due to thickness control, uniformity, and intrinsic defects of the film. Owing to the attainment of uniform, conformal, ultra-thin, pin-hole free, and thickness controlled deposition of sub-nanoscale films, atomic layer deposition (ALD) is one of the most promising techniques to realize a stable, high-performance thin-film protection layer.

In this work, we have demonstrated Li-ion conductive ALD Li-Nb-O thin films with various compositions were grown by repeated sub-cycle of LiOH and NbOx *via* ALD, and thickness was measured by ellipsometry. The composition of thin films was estimated by XPS and ICP The ionic conductivity of thin films was measured by electrochemical impedance spectroscopy. The experimental results will be presented in detail.

AA-TuP-5 ALD Ge-Se-S Amorphous Chalcogenide Alloys via Post Plasma Sulfurization for OTS Applications*, Myoungsub Kim,* *S. Park, T. Kim, S. Seo, M. Lee, S. Chung, T. Lee, H. Kim,* Yonsei University, Korea

The 3D cross-point memory using chalcogenide amorphous material with ovonic threshold switching (OTS) selector is already required future scaling study for storage class memories and neuromorphic computing systems. The cross-point memory of today`s planar 3D structure is expected to change to a vertical 3D cross-point structure, as in the history of NAND flash, so it is necessary to study chalcogenide ALD for OTS application.[1] We present an ALD study of ternary Ge-Se-S thin films, motivated by the expectation of superior OTS properties over binary Ge-Se and Ge-S, recently published in ALD research.[2,3] Here, we performed DFT calculations and ALD experiments comparing $HGeCl_3$ and $GeCl_4$ precursors based on Se(SiMe3)2 precursors. The ALD $GeSe_2$ thin film with self-limiting behavior is showed to be able to synthesize the novel Ge-Se-S alloys through post-sulfurization process. By changing the temperature and time of the low-temperature plasma sulfurization process, the compositional change of 10 nm-thick Ge_x-Se_y-S_z thin films were controlled along the $GeSe_2$-Ge_2S pseudo binary line. It was confirmed that the $Ge_5Se_3S_2$ alloys through the two-step process maintained the amorphous phase and excellent step coverage similar to ALD $GeSe_2$. Finally, we compared the OTS electrical characteristics of ALD $GeSe_2$ and $Ge_5Se_3S_2$ amorphous chalcogenide thin films in a mushroom-type device with a 50 nm bottom electrode. The novel $Ge_5Se_3S_2$ exhibited lower off current and superior cyclic endurance up to 1E6 cycles than $GeSe_2$. The achievement of ALD research on novel ternary Ge-Se-S amorphous chalcogenide will contribute to development the future 3D cross-point memory scaling.

Acknowledgments

This paper was result of the research project supported by SK Hynix Inc. We would also like to thank Merck for providing Ge, Se precursors.

References

[1] Kim, T. & Lee, S. Evolution of Phase-Change Memory for the Storage-Class Memory and beyond. *IEEE Trans. Electron Devices***67**, 1394–1406 (2020).

[2] Yoo, C. *et al.* Atomic Layer Deposition of Ge xSe1- x Thin Films for Endurable Ovonic Threshold Selectors with a Low Threshold Voltage. *ACS Appl. Mater. Interfaces***12**, 23110–23118 (2020).

[3] Myoungsub Kim *et al.* PE-ALD of Ge 1−x S x amorphous chalcogenide alloys for OTS applications. *J. Mater. Chem. C***9**, 6006–6013 (2021).

AA-TuP-6 Low-Temperature ALD for Electronic Applications*, **Jun Yang**, A. Bahrami, S. Mukherjee, S. He, S. Lehmann, K. Nielsch,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science Dresden, Germany

Atomic layer deposition (ALD) is an advanced thin film deposition technique, based on self-limited surface reaction, to dose in the chamber with two or more separated gaseous reactant pulses at a low temperature. The development of semiconductor thin films with good performance may be a true enabler for a variety of applications, such as displays, sensors, photovoltaics, memristors, and electronics. In this poster, a variety of thin films, including ZnO, SbO_x, and Sb_2Te_3 were developed. The quality of the thin film was evaluated using XRD, XPS, and ERDA. Finally, these thin films were successfully integrated on field-effect transistors (FETs) or photodetectors and the performance of devices was discussed.

AA-TuP-7 Atomic Layer Deposition, Annealing and Characterization of FeS_x Layers*, **Zsofia Baji**, I. Cora, Z. Fogarassy, B. Pécz,* Centre for Energy Research, Hungary

Iron sulphide is an important member of the transition metal chalcogenide group which is presently less researched, although it can be used for a number of different applications. Novel rechargeable batteries, e.g. rechargeable lithium-air (Li-air/O_2) batteries have gained a great deal of attention recently, however, the kinetics of air/O_2 electrodes still pose a problem. Recent research focused on transition metal mono- and di-sulfides, such as FeS as they may be promising electrocatalysts for proton exchange membrane fuel cells, water oxidation, zinc-air battery, and deinsertion/insertion material for Li-ion battery applications.

Transition-metal chalcogenide catalysts have also attracted significant interest recently, due to their activity toward proton reduction to produce molecular hydrogen from water iron sulfide nanoparticles can achieve electrocatalysis for molecular hydrogen evolution with no structural decomposition. FeS can be used as a catalytic material for CO_2 adsorption and the purifying of groundwater and soil.

The atomic layer deposition of iron sulfides promises a number of technological advances, such as precise composition and the possibility to grow few-monolayer thick films and nanostructured layers. However, there is so far only one report on the ALD of FeS using the precursor Bis(N,N'-di-t-butylacetamidinato)iron (II). This work focuses on a further investigation of this deposition process by changing the deposition temperature pulse lengths and by applying different annealing procedures. We examined the composition and structure of the prepared layers by transmission electron microscopy and found that by optimising the deposition parameters, high quality epitaxial FeS films can be grown, moreover, with slight changes in the parameters, the stoichiometry can slightly be influenced, through which the electrical and magnetic properties of the material may be changed.

The layers were deposited in a Picosun Sunale R-200 reactor using Bis(N,N'-di-t-butylacetamidinato)iron (II) and H_2S. The used substrates were sapphire and silicon. The depositions were performed at temperatures between 250 and 450°C. Some layers were treated by post-deposition annealing for an hour performed in the same ALD reactor at 500°C in H_2S atmosphere.

AA-TuP-8 N-Doped TiO_2 Nanotubes Synthesized by Atomic Layer Deposition for the Degradation of Acetaminophen*, **Syreina Alsayegh**,* Institut Européen des Membranes, France*; M. Bechelany,* Institut Européen des membranes, France*; M. ABID, F. TANOS,* Institut Européen des Membranes, France*; G. LESAGE, F. Zaviska,* Institut Européen des membranes, France

Titanium dioxide is widely used in photocatalysis applications for wastewater treatment due to its benefits. However, its wide band gap and fast electron-holes recombination limits its use under visible light. Many techniques have been used for elaboration and modification of this catalyst. Investigations demonstrated that Titanium dioxide (TiO_2) structure plays a major role on enhancing the degradation efficiency of different micropollutants present in wastewater. Titanium dioxide (TiO_2) nanotubes have attracted much interest in photocatalytic degradation due to their large specific surface area and highly ordered structure. Atomic Layer Deposition (ALD) proves to be very suitable for elaboration of well-structured photocatalysts. In this work, N-doped TiO_2 nanotubes (NTs) were successfully prepared by ALD followed by a thermal treatment for nitrogen doping. The photocatalytic efficiency of these nanotubes was compared to TiO_2 nanofibers (NFs) for the degradation of acetaminophen (ACT). Therefore, the acetaminophen degradation performance on the nitrogen-doped photocatalyst is much enhanced and superior to that of TiO_2 nanofibers prepared by electrospinning. The morphology and structure of these materials were investigated by several characterization techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Photolumiscence measurement were also achieved, and TiO2 NTs shows a lower PL intensity than TiO_2 NFs. The lowest PL intensity correspond to a lower recombination of electron-holes, consequently higher degradation efficiency. The nanotubes were doped with Boron and/or nitrogen in order to enhance its photocatalytic activity for acetaminophen degradation. Among the different doping, nitrogen doped TiO_2 demonstrated the best catalytic properties. The degradation efficiency of N-TiO_2-NTs was 5 times higher than TiO_2-NFs with a degradation rate of 0.05 and 0.01 mg.L-1 .min-1 , respectively. In addition, the photocatalyst has shown a high stability after 4 repetitive cycles, then the stability slightly decreased after the fifth cycle. Acute toxicity assays confirm the release of high toxic sub-products during the first hours of ACT degradation but the toxicity decreased markedly to lower values than initial ACT toxicity after 5 hours irradiation

AA-TuP-9 Iron-Nickel Oxide and Iron-Nickel Sufide Deposited by Atomic Layer Deposition for the Oxygen Evolution Reaction in Alkaline Media*, **Estelle Jozwiak**,* Humboldt University Berlin, Germany*; N. Pinna,* humboldt University Berlin, Germany

Iron-Nickel alloys in their oxides and sulfides form have already made their proof as electrochemical catalysts for the oxygen evolution reaction. In those alloys both nickel and iron atoms play a different and a complementary role regarding the OER activity: The nickel ones act as active sites while the iron atoms act as an electron relay during the oxygen production. Regarding to the sulfide ions their role is more indirect. They will be exchange by oxide ions during the OER leading to the creation of defaults that will reveal new active sites and so increase the catalytic activity. In this study iron-nickel oxides and sulfides alloys were deposited by atomic layer deposition on carbon nanotubes using nickelocene and ferrocene as metallic sources, and, ozone and hydrogen sulfide as co-reactants. Different ratios of metals were used during the deposition which showed a morphological variation of the final deposited layer. The co-reactants choice also led to a variation of the final morphology. All the samples were tested as catalyst for the OER by using a rotating disc electrode in order to improve the catalysts performance.

AA-TuP-10 Forming-Free Non-Linear Resistive Switching Memory Devices With ALD-Grown HfO_X/TaO_X Bilayers*, **Mari Napari**, F. Simanjuntak, S. Stathopoulos, T. Prodromakis,* University of Southampton, UK

Resistive switching random access memories (RRAM) have been extensively studied in recent decades because they could potentially be the future of data storage and replace the NAND flash memory when its scaling ends [1]. Several challenges in the RRAM design still remain such as the necessity of electroforming operation to activate the devices with high voltage, and sneak-path issues in the array [2]. Here, we present our work on RRAM devices with HfO_x/TaO_x bilayers grown by thermal and plasma enhanced atomic layer deposition. These devices with ultra-thin switching layer thickness (< 10 nm) are able to perform electroforming-free with non-linear characteristics. The insertion of the HfO_x layer induces the switching behaviour in the single-layer TaOx Zener diode. We also confirmed that this phenomenon persists with both the Pt/Ti and TiN electrodes. We discuss the multi-bit operation of the devices and the factors impacting their stability (retention & endurance), uniformity and scalability. This discussion on the device performances is supported by X-ray photoelectron spectroscopy characterisation of the thin films and their interfaces.

[1] J. Prinzie, F.M. Simanjuntak, P. Leroux, and T. Prodromakis, Nat. Electron. **4**, 243 (2021).

[2] H. Wang, F. Meng, B. Zhu, W.R. Leow, Y. Liu, and X. Chen, Adv. Mater. **27**, 7670 (2015).

AA-TuP-11 Film Properties of Al_2O_3 on Si and Graphene substrates deposited by UV Enhanced Atomic Layer Deposition

***Geonwoo Park**, J. Shin, D. Go, J. An,* Seoul National University of Science and Technology, Korea (Republic of)

Atomic layer deposition (ALD) is a technology that can deposit a very thin, uniform, high-quality and dense film. Due to these advantages, ALD technology is being applied to various energy storage and conversion devices such as fuel cells, capacitors, and batteries. Graphene is one of the well-known 2-D materials consisted of strong carbon bonding, and it shows interesting materials properties, e.g., mechanical flexibility, high carrier mobility and surface to volume ratio, and therefore has been widely adopted in energy storage and conversion devices. However, basal plane of graphene is inert due to the strong sp2 carbon bonding, which can inhibit the facile nucleation ALD layer because ALD process is based on chemical reaction with the surface of the substrate. There have been many attempts to functionalize graphene surface such as oxygen plasma, UV-ozone, thermal oxidation treatments, etc. For instance, plasma treatment is well-known method to functionalization of the graphene, but the high ion energy of plasma can etch the graphene, so the intrinsic properties of graphene can be damaged. On the other hand, UV light energy has the advantage of having a directionality (possibly desirable for selective functionalization), mild energy level (a few eV), and easy controllability.

In this study, we incorporated UV-light source into ALD system, i.e., UV-enhanced ALD, and deposited Al_2O_3 film on silicon and graphene substrates. UV irradiation (10mW/cm^2, 3-4 eV) was conducted with control during the reactant pulse & purge step, and the characteristics of the deposited thin film were analyzed. We show that the film quality of the Al_2O_3 thin film on Si and graphene substrates was changed by UV irradiation during the ALD process. As a result, it was confirmed that, as the UV irradiation time increased, the carbon contamination level of the Al_2O_3 thin film decreased with the density increment on the Si substrate. However, when UV-enhanced ALD was performed on graphene substrates, the film density and uniformity were controlled depending on the UV irradiation time. The uniformity and density of the Al_2O_3 thin film increased when UV was irradiated for up to 5-s, while,in turn, the uniformity of the thin film decreased when the UV irradiation time was exceeded over 5-s. We speculate that UV light promotes neucleation site on the silicon substrate, but adversely affects the neucleation on the graphene substrate. This is because O-H bonds on graphene substrate have smaller bonding energy than that on silicon substrate, which can be more easily removed by UV irradiation energy.

AA-TuP-12 Atomic Layer Deposition of Ruthenium Using a Zero-Valent Precursor

***Ella Rimpila**, J. Hamalainen, P. King,* Picosun Oy, Finland

Ruthenium (Ru) thin films have multiple applications in the microelectronic industry. For example, Ru films can be used as a barrier layer for copper interconnect lines in integrated circuits or as electrode material in dynamic random access memory (DRAM) capacitors, and in the future possibly as interconnect material itself.[1–3]In such applications, conformality and precise thickness control of ALD are advantageous. In some cases, the thickness of the films is required to be in the range of only afew nanometres. Uniformity of the Ru films across the substrates is also essential in industrial applications.

According to literature, numerous Ru precursors have been used in ALD during the last two decades.[4,5] The precursors can be classified based on the oxidation state of Ru, for example. Many of the newer precursors are zero-valent, which means that Ru has the oxidationstate of zero. It appears that zero-valent Ru precursors generally have the benefit of shorter nucleation delays compared to Ru precursors with higher metal valences.[5]

In this work, a Ru ALD process using a zero-valent precursor was examined for a 200mm wafer scale Picosun R-200 Advanced single wafer ALD tool. Several process conditions, such as deposition temperature and precursor pulsing time, were varied. Electrical properties of the obtained Ru films were analysed with a four-point probe (4PP), and thicknesses of selected samples were measured by XRR, and resistivities were then calculated based on the resulting data. Nonuniformity of the films was evaluated by 4PP sheet resistance mapping. Additionally, SEM, XRD, and ToF-ERDA analyses were done.

Ru was deposited both directly on native oxide (thermal SiO_2), and on in-situ grown Al_2O_3, which were compared in terms of film resistivity, uniformity, and estimated nucleation delay. Of these, SiO_2 proved to be a more suitable surface for ALD of Ru using this zero-valent precursor. Nucleation delay of Ru growth on SiO_2 was estimated to be negligible.

Conductive and continuous Ru films were grown at a range of deposition temperatures between 230 and 350 °C. Relatively low resistivities were obtained: for example, the resistivity of a 20 nm thick Ru film grown on SiO_2 was 22 $\mu\Omega$cm. At best, nonuniformities (1σ) of under 5% were achieved. Furthermore, a conductive film with a thickness of 2.4 nm was deposited.

Refs.

[1] C. Adelmann et al., IEEE, 2014, pp. 173–176.

[2] L. G. Wen et al., ACS Appl. Mater. Interfaces 2016, 7.

[3] C. H. An et al., J. Phys. Chem. C 2019, 123, 22539–22549.

[4] K. Kukli et al., J. Electrochem. Soc. 2011, 158, D158-D165.

[5] S.-H. Kim et al., Electrical & Electronic Materials 2015, 28, 25–33.

AA-TuP-13 Wake-Up-Free Metal-Ferroelectric-Metal Capacitor Consisted of $Hf_{0.5}Zr_{0.5}O_2$ and Tin(200) Bottom Electrode

***Dong Hee Han**, A. Lee, M. Nam,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)*; T. Moon,* Inorganic Material Lab, Material Research Center, Samsung Advanced Institute of Technology, Korea (Republic of)*; W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

KEYWORDS: Ferroelectric, $Hf_{0.5}Zr_{0.5}O_2$, wake-up, local-epitaxy

Wake-up effect in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) based ferroelectric thin films is reported to be due to the stabilization of the orthorhombic phase following the redistribution of oxygen vacancies present at the interface between the electrode and the ferroelectric layer during electric field cycling. [1] This effect adversely affects device reliability of the metal-ferroelectric-metal (MFM) capacitor. To improve the reliability characteristics of ferroelectric-based memory devices, it is necessary to prevent the wake-up effect.

In this study, the ferroelectric properties of HZO according to the crystallographic orientations of the TiN bottom electrode (BE) were investigated. The wake-up-free was shown in the MFM capacitor in which HZO was grown on TiN(200) BE. To clarify the reason of wake-up-free, the crystalline structure of MFM capacitors which were consisted of TiN(111) and TiN(200) BEs were carefully compared. High resolution transmission electron microscopy revealed that HZO film was epitaxially crystalized on TiN surface. Crystallographic orientation of HZO film on TiN(200) was more favorable to form orthorhombic phase than that on TiN(111) considering effective tensile stress on lattice. Therefore wake-up-free and higher remnant polarization of HZO film on TiN(200) were ascribed to prominent portion of orthorhombic phase in the film. Accordingly, controlling preferred orientation of TiN BE will enable robust the ferroelectric characteristics of HZO based MFM capacitors.

Reference

[1] Kim *et al.*, ***Nanoscale***, 2016,**8**, 1383-1389

Acknowledgments This work was supported by by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

AA-TuP-14 Investigating the Y-Doped HfO_2 Thin Film for the Metal-Insulator-Metal Capacitor Application Using a Cocktail Precursor

***YoungUk Ryu**, H. Seol,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)*; H. Oh, I. Hwang, Y. Park,* SK trichem Co. Ltd., Korea (Republic of)*; W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

In recent years, HfO_2 has been attracting a lot of attention as high dielectric constant material utilized to gate insulator and capacitor dielectric. However, the pristine HfO_2 tends to have a monoclinic phase, which has a relatively lower dielectric constant. To demonstrate the tetragonal phase, employing yttrium (Y) dopant has been reported because the Y allows both tetragonal phase formation and enhancing the crystallinity, simultaneously. [1, 2] The Y-doped HfO_2 thin film exhibited dielectric constant as high as 40, and strong dependency in the Y concentration, indicating that a deposition process for homogeneous dopant distribution in the thin film is required.

In this presentation, the atomic layer deposition (ALD) process using a cocktail precursor with a liquid delivery system (LDS) was investigated for the Y-doped HfO2 thin film deposition with homogeneous Y dopant concentration. Also, the change in the electrical properties of Y-doped HfO_2 according to the Y concentration was confirmed and compared with the crystal structure. The optimized yttrium concentration where HfO_2 grows into a tetragonal phase was identified, and the fraction with the highest dielectric constant was found. Using this, a metal-insulator-metal capacitor with improved performance was developed by constructing a ZrO_2 / Y-doped HfO_2heterostructure. In this study, we developed ZrO_2 / Y-doped HfO_2 structure with a higher dielectric constant than the $ZrO_2/Al_2O_3/ZrO_2$ (ZAZ) structure adopted in the current DRAM structure, which is expected to have high process suitability for the current DRAM fabrication.

Reference[1] J Kim et al. Y-doped HfO_2 deposited by Atomic Layer Deposition using a Cocktail Precursor for DRAM Capacitor Dielectric Application, 2021, ceramic international. [2] J.S.Lee et al. Atomic layer deposition of Y_2O_3 and yttrium-doped HfO_2 using a newly synthesized $Y(iPrCp)_2(N\text{-}iPr\text{-}amd)$ precursor for a high permittivity gate dielectric, 2014, appl.surf.sci.

Acknowledgments This work was supported by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

**AA-TuP-15 Atomic-layer-deposited Molybdenum Dioxide Thin Films as Promising Electrode Candidates for Application to Next-generation-dynamic-random-access-memory Devices*, Yewon Kim,* *A. Lee, D. Han, S. Moon, T. Youn, M. Lee, W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

In dynamic random-access memory (DRAM) devices, TiO_2 one of promising-high dielectric canstant (*k*) materials has been studied to increase the capacitance density. However, TiO_2 deposited by atomic layer deposition (ALD) on TiN whichismainlyusedasanelectrodeinDRAMexhibited an amorphous or anatase phase, which has a low *k* value of less than 40. Meanwhile,by using RuO_2 electrode, TiO_2 can be crystallized into rutile phase, which has higher *k* value of 100, even at as-deposited state by a template effect due to its low lattice mismatch. [1,2] However, RuO_2 electrode have a difficulty applying real devices due to poor thermal stability.

Thus, MoO_2 has been proposed as an alternative oxide electrode for DRAM capacitor.[3] The crystal structure of MoO_2 has similar lattice constant with rutile-TiO_2, resulting in the rutile-TiO_2 formation as does as the RuO_2. Moreover, MoO_2 has an adequate thermal stability even after annealing process. However, developing the MoO_2 deposition process is a challenging issue because the formation energy of MoO_2 is higher than that of MoO_3 throughout the temperature range.

In this study, we used the template effect to develop an atomic layer deposition process for MoO_2 thin films exhibiting high crystallinity and a very high work function. By employing MoO_2, a rutile TiO_2 thin film exhibiting a *k* value as high as 150 was obtained. The high work function was also attributed to leakage current suppression in the metal-insulator-metal capacitor. Eventually, the minimum equivalent oxide thickness of 0.35 nm, the lowest ever reported, was achieved. Therefore, the proposed MoO_2 ALD is applicable to developing next-generation dynamic-random-access-memory devices.

Acknowledgments This work was supported by by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

References [1] Seong Keun Kim etal, Applied Physics Letters, Volume 85, 4112-4114 (2004). [2] Seong Keun Kim etal, Applied Physics Letters, Volume 99, 022901 (2011). [3] Woongkyu Lee etal, Journal of Materials Chemistry C, Volume 6, 13250-13256 (2018).

**AA-TuP-16 Improving Properties of Atomic-layer deposited ZrO_2 Thin Film by Employing the Discrete Feeding Method with Various Zr-based Precursors*, Aejin Lee,* *M. Nam, Y. Kim, W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

ZrO_2 is a representative high dielectric constant (*k*) material for dynamic random-access memory (DRAM) capacitors because it has a relatively high dielectric constant (*k*~40) and a sufficient band gap.[1] The conventional atomic layer deposition (ALD), which is well known to be used to deposit ZrO_2 for DRAM capacitors, can secure step coverage and uniformity,[2] but the full saturation required an extremely long feeding time. In addition, the ALD saturated growth rate is affected by a screen effect, in which the physisorbed precursor molecules screen the active adsorption sites for the following precursor.[3] To eliminate the screen effect, the discrete feeding method (DFM) has been investigated. The DFM-ALD was performed by dividing the Zr feeding and purge steps of the conventional-ALD process into shorter several steps (shorter feeding + cut-in purge).[4] The DFM effectively removes the physisorbed precursor through the cut-in purge during precursor feeding and improves the growth rate by 10 %.[5] In addition, since the size of the physisorbed precursor molecules affects the extent to which the active adsorption sites are covered, the effect of DFM differs depending on the size of the precursor molecule.

In this study, the growth behavior and electrical properties of ZrO_2 deposited via ALD with a conventional process and DFM were compared, and the extent to which the precursor size affected the DFM effect was analyzed. Through DFM, it was confirmed that the growth rate of Cyclopentadienyl Tris(dimethylamino) Zirconium (Cp-Zr) and Tetrakis(ethylmethylamino) Zirconium (TEMAZr), which are Zr-based precursors of different size, was increased by 16 and 23 %, respectively. Unlike Cp-Zr, which still has a steric hinderance even when physisorbed precursors are removed by cut-in purge, TEMAZr with a small size has excellent DFM effect by securing enough active sites by cut-in purge. When DFM was applied to both precursors, the crystallinity and density were improved, and in the case of TEMAZr, which had excellent DFM effect, the density was 5.68 g/cm^3, which is the literature value. By securing a high-density thin film, the interfacial properties were also improved.

Acknowledgments This work was supported by by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

References [1] D Panda et al, Thin solid films 531, 1 (2013). [2] M. Gutsche et al, Future Fab, 213-217 (2003). [3] M. A. Alam et al, J. Appl. Phys. 94, 3403 (2003). [4] Dae Seon Park et al, ACS Appl. Mater. Interfaces 13, 23915 (2021). [5] Tae Joo Park et al, Chem. Mater. 23, 1654–1658 (2011).

AA-TuP-17 Atomic Layer Deposition of AlN Films With and Without Plasma Piezoelectric Effect*, Noureddine Adjeroud,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Summary

- Low temperature processes from 180 °C to 250 °C for growing AlN with (002)-preferred orientation by plasma enhanced atomic layer deposition
- High temperature processes 400 °C to 500 °C for growing AlN with atomic layer deposition
- Measurement of piezoelectric coefficient $e_{31,f}$ of AlN films: 0.38 $C.m^{-2}$ for 590 nm-thick (002) AlN film

Motivation and results

Aluminum nitride (AlN) thin films have attracted significant attention for optoelectronics, piezoelectrics-based devices as surface-acoustic-wave resonators thanks to its excellent properties such as wide band gap of 6.2 eV, piezoelectricity along c-axis and high phase velocities of acoustic waves. Those applications, however, require the control of the c-axis (002) crystalline orientation of AlN in order to achieve the highest piezoelectric effect and surface acoustic velocity [1]. Many efforts have been devoted to grow (002)-oriented AlN films. For instance, (002) oriented AlN film can be synthesized by pulse laser deposition, chemical vapor deposition, plasma assisted physical vapor deposition and plasma enhanced atomic layer deposition (PEALD). Nevertheless, those techniques require either elevated temperatures of substrate from 300 to 1000 °C and/or long period of plasma treatment during each cycle [2, 3]. In this study by carefully adjusting parameters of PEALD we were able to tailor preferred orientations of AlN thin films from a preferred (100) orientation to the (002) orientation at low substrate temperature from 180°C to 250 °C (figure 1). In addition, X-ray photoelectric spectrometry surveys (figure 2) confirmed high quality AlN films with low impurities level of 1% of carbon and 6-7% of oxygen, which are comparable to the literatures [4, 5]. The direct piezoelectric coefficient $e_{31,f}$ measurements (4-point bending method, aixACCT), which were rarely reported on AlN films grown by PEALD, revealed a strong correlation between crystallographic orientations and $e_{31,f}$value of AlN films; *i.e.* $e_{31,f}$ coefficient of (100) AlN film was almost "zero", whereas that of (002) preferred orientation film was measured to 0.38 $C.m^{-2}$ (figure 3). In addition, we synthesized 2-2 magnetoelectric composites by depositing (002) oriented AlN film of 500 nm thickness on nickel foil with an excellent interface coupling by the highly conformal coating of ALD technique. Though, AlN film is grown at temperature as low as 250 °C, the properties of the AlN film are utmost promising for energy harvesting and sensing applications on silicon-based as well as flexible-organic-substrate-based micro-electro-mechanic-system (MEMS) devices.

AA-TuP-18 Growth of Rutile TiO_2 on VO_2 by Atomic Layer Deposition for DRAM Capacitor Application*, Seungwoo Lee*, *D. Han, M. Nam, Y. Kim,* Kyung Hee University, Korea (Republic of)*; D. Kim, K. Kim, Y. Park,* SK Trichem Co. Ltd., Korea (Republic of)*; W. Jeon,* Kyung Hee University, Korea (Republic of)

Among binary transition metal oxides, titanium dioxide (TiO_2) has been widely studied for application to next-generation DRAM capacitor because it has a relatively high dielectric constant (*k*). TiO_2 has different *k* values depending on the crystalline phase. The anatase structure has a *k* value of about 40, and the rutile structure has a higher *k* value of 86 and 170 along the a-and c-axis, respectively.[1, 2] However, rutile TiO_2 is a stable phase at high temperature and requires a subsequent annealing process at very high temperature.[3] Alternatively, it can be formed under epitaxial growth conditions on materials such as RuO_2 which have similar crystal structures to rutile TiO_2.[4] Vanadium dioxide (VO_2) undergoes a reversible phase transition from the low-temperature monoclinic VO_2 to the high-temperature rutile VO_2 at about 67 °C.[5] Rutile VO_2 has less lattice mismatch with rutile TiO_2 than RuO_2.[6] It has also been reported that when TiO_2 was grown on VO_2, oxygen ionic transport to TiO_2 occurred due to the difference in the chemical potential for oxygen between the two materials, which facilitates the crystallization of rutile TiO_2.[7]

Therefore, in this presentation, crystallization of TiO_2 to rutile phase on VO_2 films using the crystal structure similarity between rutile TiO_2 and VO_2 was demonstrated. VO_x film was deposited by atomic layer deposition (ALD) and monoclinic VO_2 was formed using rapid thermal annealing under appropriate O_2 partial pressure. TiO_2 ALD on VO_2 substrates was carried out at a temperature (250 °C) higher than the phase transition temperature of VO_2. The crystalline property of TiO_2 and VO_2 films was investigated by X-ray diffraction. In addition, it was confirmed that TiO_2 grown on VO_2 has a rutile structure by electrical properties analysis.

Acknowledgments This work was supported by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

References [1] JY Kim et al., Jpn. J. Appl. Phys. 44, 6148 (2005). [2] U Diebold, Surf. Sci. Rep. 48, 53 (2003). [3] C Jin et al., Nanoscale Res. Lett. 10, 95 (2015). [4] SK Kim et al., Electrochem. Solid-State Lett. 9 F5 (2006). [5] A. Cavalleri et al., Phys. Rev. B 70, 161102(R) (2004). [6] Ziyang Yu et al., Ceram. int. 46, 8, 12393 (2020). [7] Y Park et al., Nat. Commun. 11, 1401 (2020).

AA-TuP-19 Superconducting Nbn: Sputtered Versus Plasma ALD With Bias*, Tania Hemakumara*, *Y. Shu,* Oxford Instruments Plasma Technology, UK*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands*; R. Renzas,* Oxford Instruments Plasma Technology*; V. Gauthier, V. Giglia, S. Nicolay,* Université de Sherbrooke, Canada*; M. Weides,* University of Glasgow, UK*; M. Pioro-Ladrière, D. Drouin,* Université de Sherbrooke, Canada*; R. Sundaram,* Oxford Instruments Plasma Technology, UK

High quality superconducting metal nitrides are crucial for the fabrication of quantum devices. NbN, specifically has been widely used due to its favourable critical temperatures (T_c), where PVD has been the traditional route for the deposition of NbN. However, ALD offers many advantages compared to PVD, including superior reproducibility, composition, and thickness control. For these films to be used in quantum applications, information on film quality and composition are essential. Comparison of sputtered and ALD films enable us to understand how these properties differ and their impact on T_c and crystal orientation. Here we report the potential of ALD with bias based on these studies for various quantum applications. To this end data on electrical, chemical and physical characterisation of the ALD and sputtered films will be provided.

NbN has been deposited using TBTDEN and H_2/Ar plasma at 250ºC using RF substrate bias. Sputtered films were deposited using a pure Nb target and N_2/Ar gas mixture. 50 nm of both sputtered and ALD NbN were deposited on intrinsic Si samples. Sample resistance measurement were performed in a 4-point probe configuration as a function of temperature from 300 K down to 2 K and T_c was extracted by taking the intercept of the slope at the resistance drop point with the temperature axis. In addition, XRD and SIMS analysis were also performed on the ALD film to obtain the crystal orientation and composition of the NbN film.

Sputtered NbN resulted in a T_c of 12 K, this is lower than values stated in literature and is possibly due to the challenging nature of optimizing sputtered nitrides or due to the formation of defects at the Si/NbN interface during the sputtering process. ALD NbN on the other hand has resulted in a $T_c$of 14.5 K. In addition, a (111) crystallographic orientation has been observed on the XRD measurements of the ALD NbN film, which is indicativeof the cubic phase leading to superconductivity. Further, SIMS analysis confirmed low O content on the NbN films proving high quality ALD deposited films.

The enhanced T_c, XRD and SIMS data of ALD NbN with bias is encouraging for the realisation of devices for quantum application.

This work is supported by NSERC Canada and Innovate UK project, “Advanced Manufacturing Toolkit for Quantum Sensing and Quantum Computing”.

AA-TuP-20 Membrane Design by ALD/MLD for Hydrogen Sensing*, S. Sayegh, M. Drobek, A. Julbe,* ***Mikhael Bechelany,*** European Institute of Membranes, France

Hydrogen (H_2) is one of the energy vectors essential for the success of the energy transition. In less than twenty-five years, hydrogen is expected to represent 18% of the total energy consumed on the planet thus leading to possible CO_2 emissions reduction by 6 gigatonnes compared to current levels. At the same time, hydrogen energy technologies involve major environmental, research and industrial challenges. In this work, we will address our research implication in the area of hydrogen detection.

The explosive and flammable nature of hydrogen hampers a widespread deployment of this energy vector without an efficient securing production, storage and implementation facilities and equipment, both in industrial or general public sectors. In this respect, hydrogen selective gas sensors are recognized as essential links in this security chain. Depending on the operating conditions, such sensors should fulfill very precise specifications in terms of sensitivity, selectivity, response time, temperature range etc. In our research group, different original approaches in detection and sensor design are currently studied. For instance, gas sensors based on zinc oxide (ZnO) nanowires encapsulated in MOF (Metal Organic Framework)-based molecular sieve membrane have been developed for the selective detection of H_2 in gas mixtures up to 300 °C [1]. Attractively, this concept is applicable to various sensors geometries which could be further functionalized with metal nanoparticles (e.g. palladium)by Atomic Layer Deposition [2] in order to confer the hydrogen sensors with additional sensitivity. The same approach has been applied using ALD of boron nitride as selective membrane for increasing both sensor sensitivity and stability [3]. Moreover and for the sake of enhancing the sensors humidity resistance, Molecular Layer Deposition (MLD) has been recently used to deposit a humidity-resistant nanomembranes on ZnO semiconductor nanowires [4].

[1] ACS applied materials & interfaces, 2016, 8, 8323−8328 & Sensors and Actuators B: Chemical, 2018, 264, 410-418

[2] ACS applied materials & interfaces,2018, 10, 34765-34773

[3] Journal of Materials Chemistry A, 2019, 7, 8107-8116

[4] Sensors and Actuators B: Chemical 2021, 344, 130302

AA-TuP-21 Schottky Diodes to Gallium Nitride Prepared by Plasma-Enhanced Atomic Layer Deposition*, Suzanne Mohney*, *I. Campbell, A. Molina, A. Agyapong, M. Thomas,* Penn State University

Transition metal nitrides are attractive candidates for Schottky diodes and gate metallizations for group III nitride devices. Many of them are unreactive with gallium nitride and aluminum gallium nitride at elevated temperatures. In addition, some transition metal nitrides are already accepted in typical nanofabrication laboratories, and they can be integrated into processes where dry etching is preferred for patterning. However, transition metal nitride Schottky diodes on gallium nitride reported in the literature are typically prepared by sputter deposition, which can introduce defects in the semiconductor, resulting in high currents under reverse bias and ideality factors much greater than unity. We have fabricated Schottky diodes to n-type gallium nitride by plasma enhanced atomic layer deposition using a remote N_2-H_2 plasma in a Fiji Gen II reactor. Film composition was measured by x-ray photoelectron spectroscopy and energy-dispersive x- ray spectroscopy. When layers with the composition $MoC_{0.3}N_{0.7}$ were prepared usingbis(tertbutylimino)bis(dimethylamino)molybdenum, diodes to n-GaN had rectifying characteristics as deposited. After they were annealed at 600°C in N_2, the Schottky barrier height increased to 0.87 ± 0.01 eV with an ideality factor of 1.02 ± 0.01. Since the barrier height was measured by the current-voltage technique, the ideality factor will always be slightly greater than unity due to image force lowering of the barrier height. X-ray diffraction and transmission electron microscopy revealed that these films were a single phase, which is beneficial for creating homogeneous diodes. More carbon-rich films with the composition $MoC_{0.8}N_{0.2}$ also displayed rectifying characteristics, but the films contained two phases, the ideality factor of the diodes was higher, and the barrier height was lower. We have also successfully prepared diodes with another precursor (molybdenum carbonyl) and will report the effect of precursor and deposition conditions on the performance of diodes in this presentation. The authors thank ONR for support through N000141812360 (Approved, DCN# 43-9072-22) and A. Allerman (Sandia National Laboratories) for gallium nitride epilayers.

**AA-TuP-22 Development of High-k Gate Insulator Deposition Process for Next-Generation Thin Film Transistor Using Atomic Layer Deposition*, Min Kyeong Nam*, *A. Lee, D. Han, S. Lee, W. Jeon,* Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Korea (Republic of)

Currently, thin film transistor (TFT) based on transparent oxide channel such as amorphous InGaZnO (a-IGZO) has being widely studied as switching devices for liquid crystal displays (LCD) and flexible active matrix organic light emitting diode (AM-OLED) displays.[1] To demonstrate high speed and high resolution display, operation speed and dimension of TFT should be enhanced. In this regard, a gate insulator application of the high dielectric constant (k) materials has been attracted a lot of attentions. Moreover, for deposition of the high-k materials, the atomic layer deposition (ALD) process, which allows relatively low process temperature with adequate thin film quality, is required.

In this study, ALD process of ZrO_2 on IGZO as the gate insulator of TFT was developed using Tetrakis(ethylmethylamino) Zirconium (TEMAZr) and Cyclopentadienyl Tris(dimethylamino) Zirconium (Cp-Zr) as the Zr precursors. The thin film growth behavior and electrical properties of deposited ZrO_2 were strongly affected to the difference in chemistry of TEMAZr and Cp-Zr. The crystallinity of the ZrO_2 film and the formation of an interfacial layer were examined through x-ray diffraction, x-ray reflectometry, and x-ray photoelectron spectroscopy analysis. We demonstrated the possibility of developing a high-performance TFT device capable of low-voltage driving for next-generation displays by evaluating the TFT characteristics of the metal-insulator-semiconductor structure.

References [1]X Wang et al., Membranes, 11(2), 134 (2021). [2]YH Lin, JC Chou, J. Nanomater., 2014, (347858)5 (2014).

Acknowledgments This work was supported by by the Technology Innovation Program (No. 20016813 and 20017216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea)the BK21 Plus program.

**AA-TuP-23 Co-Coated Si X-Ray Optics With Atomic Layer Deposition*, Yukine Tsuji*, *A. Fukushima, D. Ishi, Y. Ezoe, K. Ishikawa, M. Numazawa, T. Uchino, S. Sakuda, A. Inagaki, Y. Ueda, H. Morishita, L. Sekiguchi, T. Murakawa,* Tokyo Metropolitan University, Japan*; K. Mitsuda,* National Astronomical Observatory of Japan

We have been developing an ultra-lightweight Wolter type-I X-ray optic using MEMS technologies for X-ray astronomical observations (Ezoe et al., 2010, Microsys.Tech.2010, 16, 1633) In this paper, we present our first Co atomic layer deposition (ALD) test on a test optic and evaluation of its X-ray reflectivity which is to our knowledge the first demonstration of the Co-coated X-ray optic with ALD.

The MEMS X-ray optic is made of 4-inch Si (111) wafers (300-500-micrometer thickness). The Si wafer is firstly etched to have micropores (20-micrometer width) by deep reactive ion etching, and sidewalls are used as X-ray reflective mirrors. Using high-temperature hydrogen annealing process, we then smooth the sidewalls. With chemical mechanical polishing process burr structures on edges of the sidewalls which block incidence of X-ray are removed. Finally, the wafer is plastic-deformed into a spherical shape to focus parallel X-ray beam from celestial objects. Two wafers deformed to different curvature radii are stacked to form a Wolter type-I optic.

Si is easy to be etched, but its X-ray reflectivity at large reflection angle and high energy becomes significantly lower than those of heavy metals such as Au, Pt and Ir. Therefore, we use ALD to coat heavy metals thin film to the sidewalls of the micropores. We have already demonstrated Ir and Pt film formation (Ogawa, et al., 2013, Applied Optiics, 52, 5949, Ishi, et al., 2020 Applied Express, 13, 087001). For our future space applications (Ezoe et al., 2018，J. Astron. Telescope, Instrum, 4，046001), we need to increase X-ray reflectivity around 1 keV. We thus tested to form a Co film with ALD, which has excellent reflection characteristics in this energy band.

First, we coated a Co film on the surface of a bare Si wafer as a test. Then, we evaluated the reflectivity of the Co-coated surface at the Al K_α characteristic X-ray (1.49 keV) using the 30 m beamline at JAXA and confirmed a significant improvement in reflectivity at large angles (>1 degrees). Furthermore, the roughness of the Co-coated surface was estimated to be about 1 nm rms by comparison with the theoretical reflectivity. This roughness satisfies the requirement in our future space mission (< 1 nm rms) and can be expected as a candidate for a new film deposition material. Similarly, Cu L_α (0.93 keV) and C K_α (0.28 keV) were also evaluated, and it was found that the surface roughness was 1-2 nm rms, which was close to the required performance. In the near future, we plan to deposit Co film on our micropore optical system and evaluate the performance.

AA-TuP-24 Optimization of High-Performance P-Channel Sno Thin Film Transistor Using Atomic Layer Deposition*, Myeong Gil Chae,* *J. Kim,* Seoul National University of Science and Technology, Korea (Republic of)*; B. Park, T. Chung,* Korea Research Institute of Chemical Technology (KRICT), Korea (Republic of)*; S. Kim,* Korea Institute of Science and Technology (KIST), Korea (Republic of)*; J. Han,* Seoul National University of Science and Technology, Korea (Republic of)

Up to date, oxide semiconductor-based electronics are limited to unipolar devices consisting of n-type oxides owing to the challenges in achieving high-performance p-type oxide counterparts. P-type oxide semiconductors show inferior carrier transport characteristics than n-type oxide owing to localized oxygen orbitals with large hole effective mass at valence band maximum (VBM). Among p-type oxides, SnO regarded as a promising candidate with low defect formation energy of Sn vacancy (V_{Sn}) that produces hole carriers and delocalization of VBM by hybridization of Sn 5s and O 2p orbitals, leading to low hole effective mass and high hole mobility. Meanwhile, atomic layer deposition (ALD) allows precise control of thickness and composition based on self-limiting reaction and layer-by-layer growth by alternately injecting precursor and reactant. Therefore, in this work, we have introduced high quality SnO film as a channel layer of p-type TFT by ALD using $Sn(dmamp)_2$ and H_2O. The strategic probing of key parameters such as the deposition temperature and thickness of ALD SnO film for high performance TFTs resulted in the SnO TFT with field-effect mobility (μ_{FE}) of 6.13–7.24 $cm^2/V{\cdot}s$ and on/off current-ratio (I_{on}/I_{off}) of 10^4–10^5 without post-annealing processing. Moreover, back-channel passivation with ALD Al_2O_3 film further improved the switching characteristics of the SnO TFT, exhibiting enhanced subthreshold swing (SS) of 3.18 V/dec.

AA-TuP-25 Intense Pulsed Light Annealing of Low-temperature Atomic-layer-deposited SnO Thin Films for P-channel Thin Film Transistor*, Jina Kim*, *M. Chae,* Seoul National University of Science and Technology, Korea (Republic of)*; B. Park, T. Chung,* Korea Research Institute of Chemical Technology (KRICT), Korea (Republic of)*; J. Choi, K. Cho,* Korea institute of industrial technology (KITECH), Korea (Republic of)*; W. Lee,* Myongji University, Korea (Republic of)*; J. Han,* Seoul National University of Science and Technology, Korea (Republic of)

SnO is promising p-type transparent semiconducting oxide known for excellent hole transport property. Its high p-type conductivity is driven by the unique valence band maximum structure composed of Sn 5s–O 2p hybridized orbitals and low formation energy of Sn vacancies generating hole carriers. Especially, atomic layer depositon (ALD) is a suitable process to grow SnO because the oxidation state and film thickness can be finely controlled through the self-limited surface reaction. However, crystalline SnO could be obtained only at >150 ℃ using ALD [1], which would hinder the application of ALD SnO to polymer-based plastic substrates. Therefore, it has been required to develop low-temperature post-crystallization technology to achieve crystallized SnO films without deformation of the flexible substrates. Intense pulsed light (IPL) annealing is considered as useful post-annealing tool with insignificant thermal impact.

Herein, amorphous SnO films were grown by ALD with Sn(dmamp)$_2$ and H_2O as the Sn precursor and reactant at a low temperature of 120 ℃. The IPL annealing was employed to successfully crystallize the SnO films with maintaining oxidation state of Sn^{2+}, resulting in excellent hole transport characteristics. Amorphous SnO film was start to be crystallized at IPL pulse number of 200−300, and the crystallinity was increased with increasing the pulse number. The various properties such as crystallinity, surface morphology, and chemical states of SnO films were characterized by X-ray diffraction (XRD), raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The bottom-gate staggered-structured thin-film transistors (TFTs) were fabricated with Al_2O_3 passivation layer. With SnO films after 200 IPL pulses, remarkable p-type transistor property was achieved with field-effect mobility of 2.49 cm^2/V·sec, subthreshold swing of 2.85 V/dec, on-off current ratio of 8.2×10^4.

Acknowledgments This Research has been supported by the KOREA RESEARCH INSTITUTE of CHEMICAL TECHNOLOGY (KRICT) and National R&D Program through the National Research Foundation of Korea (NRF) funded by Ministry of Science and ICT (NRF-2020M3H4A3082126)

References [1] J. H. Han et al., Chem. Mater., vol. 26, no. 21, pp. 6088−6091 (2014).

AA-TuP-26 Hafnium Zirconium Oxide-Based Ferroelectric Field Effect Transistor With Atomic-Layer-Deposited Indium Gallium Tin Oxide Channel Layer*, **Hyeonhui Jo**, J. Won, P. Youn, J. Kim, H. Jang, W. Jo, J. Han,* Department of Materials Science and Engineering, Seoul National University of Science and Technology, Korea (Republic of)

Ferroelectric field effect transistors (FeFET) have received increasing interest as synaptic devices because they can easily imitate the synaptic weights update behavior through analog conductance modulation of the channel layer. In particular, the conductance of the channel layer can be controlled by the multiple polarization states of the ferroelectric layer, which is determined according to the applied gate voltage pulse. Hafniumzirconium oxide (HZO) commonly used in the ferroelectric layer of FeFET has various advantages such as low deposition temperature, ALD capability, and good ferroelectric characteristics despite a thickness of ~10 nm. Also, indium gallium tin oxide (IGTO) is a promising material as the channel layer because it has high mobility despite the amorphous phase and minimizes the formation of the interfacial layer between IGTO and HZO, which induces high operating speed and low power consumption. Moreover, the field effect mobility of IGTO can be improved by increasing In and Sn compositions because both the In-5s and Sn-5s orbitals form the main channel of the electron conduction.

In this work, ferroelectric HZO layer was deposited by ALD at 300 °C using CpHf(NMe$_2$)$_3$ and CpZr(NMe$_2$)$_3$ as Hf and Zr precursor, respectively. ALD IGTO channel was deposited at 200 °C using 3-(dimethylamino)propyl]dimethyl-Indium (DADI), dimethyl(N-ethoxy-2,2-dimethylcarboxylicpropanamide)gallium (Me$_2$Ga(edpa)), and tetrakis(dimethylamido)tin (TDMASn). The growth characteristics of ternary HZO and quaternary IGTO films were examined and film properties were analyzed using XPS, XRD, and SEM. FeFET devices were fabricated using HZO and IGTO films as the ferroelectric layer and channel layer and the synaptic characteristics of FeFET devices were investigated by conductance modulation behavior.

Acknowledgments: This research has been performed as a cooperation project of “Basic project(referring to projects performed with the budget directly contributed by the Government to achieve the purposes of establishment of Government-funded research Institutes)” and supported by the KOREA RESEARCH INSTITUTE of CHEMICAL TECHNOLOGY (KRICT) and by National R&D Program through the National Research Foundation of Korea(NRF) funded by Ministry of Science and ICT(NRF-2020M3H4A3082126).

AA-TuP-27 Interface and Electrolyte Design to Enable Stable Zn Metal Anode for Aqueous Zn-ion Batteries*, **Jian Liu**,* University of British Columbia, Canada

Rechargeable aqueous zinc-ion batteries (ZIBs) have attracted increasing attention as energy storage technology for large-scale applications because of low cost, inherent high safety, and high capacity of Zn metal (820 mAh g^{-1} and 5854 Ah L^{-1}). However, the poor rechargeability of Zn anodes limits their development, which is attributed to the dendrite growth, passivation, and hydrogen evolution issues in the zinc anode. This talk will introduce recent progress in addressing these problems associated with zinc anodes by using nanoscale interface engineering and developing novel electrolytes to enable durable and high-performance ZIBs [1]. First, a nanoscale Al_2O_3 coating by atomic layer deposition was applied to modify the zinc-electrolyte interface [2]. The Al_2O_3 coating effectively suppressed the zinc dendrite formation, improved wettability, and inhibited zinc corrosion. As a result, the surface-coated Zn has been verified in Zn-MnO_2 batteries using layered δ-MnO_2 as the cathodes and consequently superior electrochemical performance with a high capacity retention of 89.4% after over 1000 cycles. In the second part, the performance of zinc metal was further improved by using a hybrid organic-inorganic coating (alucone). With the optimal coating thickness (12 nm), an over 11-fold enhancement in the running lifetime (780 *vs.* 70 h) and a reduced overpotential (84.3 *vs.* 110.3 mV) were achieved compared to bare Zn at a current density of 3 mA cm^{-2} [3]. Thirdly, an acetonitrile/water-in-salt (AWIS) hybrid electrolyte was developed and found to prolong the lifespan of Zn|Zn cells from 150 to 2,500 h [3]. More importantly, the AWIS hybrid electrolyte increased the upper cut-off voltage of Zn-MnO_2 batteries from 1.8 to 2.2 V, leading to enhanced energy and power densities. This series of work will provide insights into the design and development of high-performance ZIBs for grid applications.

References

[1] H. He, H. Qin, J. Wu, X. Chen, R. Huang, F. Shen, Z. Wu, G. Chen, S. Yin, J. Liu. Energy Storage Mater., 2021, 43, 317.

[2] H. He, H. Tong, X. Song, X. Song, J. Liu. J. Mater. Chem. A, 2020, 8, 7836.

[3] H. He, J. Liu. J. Mater. Chem. A, 2020, 8, 22100.

[3] X. Song, H.He, M. H. Aboonasr Shiraz, H. Zhu, A. Khosrozadeh, J. Liu. Chem. Commun., 2021, 57, 1246.

AA-TuP-28 ALD-Coated Mesoporous Films for Electrocatalysis*, **Nicola Pinna**, M. Raza,* Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany*; M. Frisch, R. Krähnert,* Department of Chemistry, Technische Universität Berlin, Germany

Water splitting electrocatalysts are in need because of the growing demand for renewable energy and simultaneous depletion of fossil fuels. There are different types of catalytically active oxides used as electrodes for the electrochemical water splitting, both in acidic and alkaline conditions. The catalytic performance of those materials strongly depends on surface composition and morphology. It is possible to increase the catalytic efficiency of such electrodes by increasing the number of active surface sites. Here we report the synthesis of novel electrode with template-controlled mesoporosity and their modification with highly active catalytic species. The improved utilization of active species relies on the synthesis of soft-templated metal oxide supports, and a subsequent well-controlled and conformal modification *via* atomic layer deposition (ALD). The composition, morphology, and crystallinity of the deposited film were controlled by varying different deposition parameters. The structural and morphological properties, as well as the mass activity and stability in the electrocatalytic oxygen evolution reaction were investigated in the order to propose clear structure-properties correlations.

AA-TuP-29 Nanoscale Energy Transport Processes in Chalcogenide-Based Phase Change Materials*, **Kiumars Aryana**, P. Hopkins,* University of Virginia

Modern computing relies on the processing of information by constantly shuttling the data back and forth between the storage and the processing units1. This computing architecture, known as von Neumann, leads to huge traffic jams between the memory and processor, incurring considerable costs in terms of latency and energy. Phase change memory (PCM) is a rapidly growing technology that not only offers advancements in storage-class memories but also enables in-memory data processing to overcome the von Neumann bottleneck. In PCMs, data storage is driven by thermal excitation. However, there is limited research regarding PCM thermal properties at length scales close to the memory cell dimensions. Our work uses the knowledge of carrier dynamics to experimentally identify an optimal thickness for the phase change material based on a balance of thermal conductivity and crystallographic-phase-dependent interfacial thermal resistance in order to improve memory device performance. We present evidence of ballistic transport of energy carriers as the characteristic length of the device is decreased to less than the mean free paths of the electrodes carriers. In addition, we investigate the thermal properties of $Ge_2Sb_2Se_4Te$, one of the most promising material candidates for integrated photonics, and show that upon substituting tellurium with selenium, the thermal transport transitions from an electron dominated to a phonon dominated regime. By implementing an ultrafast mid-infrared pump-probe spectroscopy technique that allows for direct monitoring of electronic and vibrational energy carrier lifetimes in these materials, we find that this reduction in thermal conductivity is a result of a drastic change in electronic lifetimes of $Ge_2Sb_2Se_4Te$, leading to a transition from an electron-dominated to a phonon-dominated thermal transport mechanism upon selenium substitution.

AA-TuP-30 Comparison of the Insulating Properties of Aluminum Oxide (Al_2O_3) High-K Layers at the Early Growth Stages of by Thermal- and Plasma-Enhanced Atomic Layer Deposition on AlGaN/GaN Heterostructures, ***Raffaella Lo Nigro**, E. Schilirò, P. Fiorenza, G. Greco, F. Giannazzo, F. Roccaforte,* CNR-IMM, Italy

A comparative study of the early growth stages of aluminium oxide (Al_2O_3) thin dielectric layers deposited by thermal and plasma-enhanced atomic layer deposition (i.e. T-ALD and PE-ALD) methods on AlGaN/GaN heterostructures is presented and two different nucleation processes have been identified. Investigation has been carried out at nanoscale by morphological and leakage current maps, which showed that the Al_2O_3 thin films deposited by the PE- ALD possess excellent insulating properties, conformal interface with AlGaN/GaN substrate, low oxide trap charges and good dielectric permittivity of k≈8. By contrast, a not conformal and uniform insulating behaviour has been recorded on T-ALD Al_2O_3 films. The different insulating behaviour and its evolution upon increasing the film thickness is indication that two different growth mechanisms are running and chemical characterization by X-ray Photoelectron Spectroscopy provided evidence that the PE-ALD process occurs under an ideal layer-by-layer growth because of the efficiency the O_2-plasma agent which acts directly on the Al precursor. The T-ALD process by contrast, shows a behaviour similar to the island growth model because of the formation of undesirable Al-N-O bonds. The origin of interface defects, whose limitation is crucial for the correct operation of the device, has been discovered and studied, as well as, the proper deposition process has been defined.

AA-TuP-31 Amorphous ALD Alumina On a Quartz Plate Enables Significant Cost of Ownership (CoO) Reduction in Metal Plasma Etch Chambers, ***Jeff Young**,* Intel Corporation; *G. Mata-Osoro, P. Spring,* INFICON Ltd., Liechtenstein; *J. Delle Donne,* Ultra Clean Technologies (UCT); *R. Parise,* Ultra Clean Technologies; *V. Venkatesan,* Ultra Clean Technologies (UCT)

Crystalline Al_2O_3 by-product and trace metals deposited on quartz parts in metal etch chambers are a problem. They peel off and cause particle problems leading to unscheduled downtime of chambers. It is therefore important to remove these by-products and trace metals from the quartz parts on a regular basis during preventive maintenance (PM). However, stripping crystalline Al_2O_3 (and trace metals) from quartz without attacking the quartz substrate is a challenge. In order to address this problem, these quartz parts with a specified surface roughness were coated with 200 nm of amorphous ALD Al_2O_3 films. After processing in chamber, these coated parts with by-products were taken out during PM. They were grit blasted to loosen the surface, a proprietary chemical strip developed to remove the ALD Al_2O_3 film and by-product deposition. Quartz substrate showed no degradation as characterized using XRF, particle level and roughness measurements. This process is now qualified, and the recycled quartz parts provide > 75% reduction in Cost of Ownership (CoO) compared to that of new parts.

Fig.1 Shows a TEM cross-section of the stack on top of the quartz plate used in the metal etch chamber after etch residue by-product deposition.

Fig.2 Depicts the process flow for recycling the quartz plate.

Fig.3 Shows the XRF characterization of post-strip and clean surface showing no trace of coating and by-products.

See attached document for the figures.

AA-TuP-32 Application of Powder Atomic Layer Deposition to Solid Oxide Fuel Cell Electrodes, ***Sung Eun Jo**, H. Kim, B. Yang, J. An,* Seoul National University of Science and Technology, Korea (Republic of)

Atomic layer deposition(ALD) can uniformly coat conformal films on complicated structures with atomic-level thickness controllability. ALD is being widely used in the semiconductor industry but is also showing high potential as an effective technique for upgrading electrochemical energy devices' performance and durability by precisely and conformally overcoating their components. For example, the electrodes of solid oxide fuel cells (SOFCs) usually adopt nano-porous and complex structures for fast electrochemical kinetics; to fabricate such porous structures, SOFC electrodes are fabricated by sintering powder materials. Lanthanum strontium cobalt ferrite (LSCF) powder, for instance, is a popular material for SOFC cathode. In LSCF-based electrodes, strontium in perovskite material segregates at elevated temperature (e.g., the operating temperature range of >600C for SOFCs). Exsolution of Sr forms SrOx at the surface of the cathode, which diminishes ORR activity and escalates polarization resistance by blocking active sites at electrodes' surface. Therefore, the conformal and ultra-thin protective coating of LSCF powders is crucial for the stable operation of SOFC electrodes at elevated temperatures.

In this study, we report on the use of powder ALD process to conformally coat LSCF powders for SOFC cathodes. Bare LSCF powders are ball-milled, situated in the rotary module assembled with the ALD station, and are coated with ALD ZrO_2. As powders have an extremely high area-to-volume ratio, static exposure mode for precursor infiltration between nanoscale air gap. In the electrochemical test, the cells with bare LSCF cathodes (no ALD), LSCF cathodes with conventional ALD (C-ALD), and with powder ALD (P-ALD)-coated ZrO2 overcoats are compared. Powder ALD treated cell effectively suppress Sr ex-solution in the entire location of the electrode, and eventually result in the highest maximum power density among cells.

AA-TuP-33 Evaluation of Temporal vs. Spatial Atomic Layer Deposition Techniques for the Production of Ceramic Nanofiltration Membranes, *J. Peper,* University of Twente, Netherlands; *H. Jain,* TNO/Holst Cent, Netherlands; *M. Nijboer, A. Nijmeijer, F. Roozeboom, A. Kovalgin,* ***Mieke Luiten-Olieman**,* University of Twente, Netherlands

Today's bulk chemical separation and purification is mainly driven by thermal processes like distillation, drying and evaporation. Examples are in hydrocarbon separation from crude oil feedstocks, surface and wastewater purification and desalination. These processes account for 10–15 % of the global energy consumption [1].

As an inherent non-thermal process, membrane-based separation can cause a paradigm shift in worldwide energy consumption since this alternative requires 2 up to 10 times less energy, and will offset carbon emissions correspondingly [1]. However, the challenges in manufacturing large-scale membrane systems are manifold. Bulk wastewater streams can contain solvents that make polymeric membranes unsuitable due to the destructive solvent-membrane interactions. In addition, the production of ceramic membranes for nanofiltration applications with pore sizes typically ranging from ~1 to a few nm is challenging [2,3]. Therefore, new methods for upscalable production of robust ceramic nanofiltration membranes are required.

The potential of applying Atomic Layer Deposition (ALD) in order to narrow down ceramic membrane pores to the nanofiltration range is studied. The aim was to get a better understanding of ALD on 3D porous substrates compared to the state-of-the-art process on planar silicon wafers. Experiments were performed to tune the most important process parameters using different types of ALD reactors – temporal (PICOSUN® R200) and spatial [4]. The advantage of temporal ALD in the production of ceramic membranes is that process recipes proved to be easily tunable, whereas the spatial ALD benefited from high throughput.

A decrease in pore size of γ-alumina membranes was observed for recipes with an increasing number of s- and t-ALD cycles; from 2.5 nm to <0.5 nm within 25 ALD cycles. We also observed a higher growth rate for porous γ-alumina substrates as compared to the reference silicon wafers (GPC 0.14 vs 0.10 nm/cycle).

This study showed the potential of ALD for the production of ceramic nanofiltration membranes by narrowing ceramic ultrafiltration membranes. Furthermore, this exploratory work provides a starting point for further research into the method and showed the importance of directly characterizing the porous substrates. New ALD process recipes specifically aimed at porous substrates can lead to further improvement of the method.

[1] Nature, 532, pp. 435–437 (2016)

[2] Membrane Technology, 2003(11), pp. 5–8 (2003)

[3] Separation and Purification Technology, 219, pp. 159–168 (2019)

[4] Advanced Materials, 22(32), 3564-3567 (2010)

AA-TuP-34 Robust YF$_3$ Batch ALD Process With a Novel Precursor for Plasma Etch Tool Component Protection*, J. Kalliomäki, E. Manninen, J. Mariam,* ***Peter King****, R. Ritasalo,* Picosun Oy, Finland

Atomic layer deposited corrosion barrier solutions have been of high interest lately in the semiconductor industry. The main driver for this has been the need to protect plasma etching tools used in several manufacturing steps from self-damage and contamination. Traditionally, thick ceramic coatings applied with spray coating have been used but these techniques suffer from low conformality, which makes it unable to protect parts with complex geometries like showerheads. [1]

The most sought-after materials, like Y_2O_3 and YF_3 are very etch resistant [2], but are difficult to scale to large ALD tools, while retaining good conformality and repeatability [3]. YF_3 especially has been problematic from a tool maintenance and health & safety perspective as available processes involves HF as a reaction by-product.

We present process development and scale up results from a new precursor (*Y-Beta', Air Liquide*), which can produce pure YF_3 films using O_3 as co-reactant. The process is scaled up to Picosun P-1000 class tool with maximum usable chamber volume 0.2 m^3, which can be used to deposit several full-sized showerheads. In wafer batch tool (P-300B) the process can reach a GPC of ~0.6 Å and cycle time <5 s. With 20 s cycle time a Chip-2-Chip uniformity of 3% can be achieved (statistics extracted from mapping spectroscopic ellipsometry measurements). The compositional purity of the resulting films were determined with ToF-ERDA along with structural characterization by XRD.

The general ALD process portfolio has been wanting for a simple, convenient, and robust alternative for YF3 deposition in addition of the two existing ones [4-5]. This new precursor answers directly to this need by allowing the YF3 to be deposited in industrial scale without HF.

[1] Shih (2012), ISBN: 978-953-51-0467-4

[2] Kim et al. (2011), doi:10.1111/j.1551-2916.2011.04589.x

[3] Abdulagatov et al. (2019), doi:10.1134/S1063739719010025

[4] Wallas et al. (2018), AVS 65th International Symposium & Exhibition

[5] Pilvi et al. (2008), doi:10.1002/cvde.200806721

AA-TuP-35 Surface Modification of Atomic Layer Deposited Metal Oxides: Vapor-Phase Grafting of Functional Silanes*,* ***Vepa Rozyyev,*** University of Chicago*; R. Pathak, R. Shevate,* Argonne National Laboratory, USA*; J. Murphy,* University of Chicago*; A. Mane,* Argonne National Laboratory, USA*; S. Sibener,* University of Chicago*; J. Elam,* Argonne National Laboratory, USA

Covalent surface modification of oxides with alkyl silanes is one of the most commonly used method to prepare well-defined functional surfaces. Using alkyl silanes with functional groups at the alkyl chain will produce functional surfaces for various applications such as water treatment, biosensing, and anti-fouling surfaces. Atomic layer deposition (ALD) is a highly versatile surface functionalization technique that can conformally coat both planar and porous substrates. Surface modification of ALD films with organic species is an ideal way to tailor the surface properties. Here we demonstrate the vapor-phase grafting of various bifunctional silanes on ALD metal oxides. We investigate the grafting of six different silanes with amine, thiol, nitrile, and ester functionalities at 100 °C, 150 °C, and 200 °C temperatures. In situ quartz crystal microbalance (QCM), Fourier-transform infrared (FTIR) spectroscopy measurements, ex-situ atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) measurements show the uniform monolayer silane formation through self-limiting reactions. It is shown that the density of reacted silanes and surface hydrophobicity can be tuned by using different bifunctional silane agents, on different metal oxides, at different temperatures.

AA-TuP-36 Developing ALD RuO$_x$ Process for Coating Porous Current Collectors for Supercapacitor Applications*,* ***Sakeb Hasan Choudhury,*** LAAS-CNRS, France*; G. Vignaud,* Université Bretagne Sud, France*; P. Dubreuil, D. Pech,* LAAS-CNRS, France

Atomic Layer Deposition (ALD) is considered to be one of the most conformal thin film deposition techniques. In literature, its self-saturated growth mechanism and atomic layer control has been studied in various methods [1]. However, the permeation of ALD into different research fields has brought new challenges in front of us and we investigate such a scientific issue in this work. The application of independent autonomous microelectronic devices has revolutionized the IoT (Internet of Things) based industry [2]. Therefore, the development of onboard micro-energy storage has become one of hot research topics in the scientific community. In recent years, it was evident that the 3D micro-supercapacitors are shaping up to be capable of serving such purposes. One of the remarkable aspects of 3D micro-supercapacitors was the emergence of dynamic hydrogen bubble template (DHBT). It provided the necessary 3D architectures of micro-supercapacitors for satisfying the energy storage requirements of high-power onboard devices. However, the efficient utilization of these highly porous DHBT structures still remains a challenge when it comes to coat them with active materials [3]. Here, in this work, we channel our efforts to utilize the conformal coating capabilities of ALD to handle such challenges. To investigate the scheme, we propose to deposit a hydrous $RuO_2.xH_2O$ as the active materials on DHBT samples. In order to develop the conformal ALD growth, we used $Ru(EtCp)_2$ and O_2 as precursors [4]. The temperature for ALD deposition was kept at 200 C to avoid losing the electrochemical area of the DHBT samples. From our initial experiments, we observed that a capacitance value of 7mF can be achieved from 500 ALD cycles of RuO$_x$ on an Au DHBT template. To study and optimize the conformality of RuOx deposition, an additional trap timing was introduced during the pulsing of the $Ru(EtCp)_2$ precursor.

[1] Steven M. George, Atomic Layer Deposition: An Overview, Chem. Rev. (2010), 110, 1, 111–131, https://doi.org/10.1021/cr900056b.

[2] N.A. Kyeremateng, T. Brousse, D. Pech, Microsupercapacitors as miniaturized energy-storage components for on-chip electronics, Nat. Nanotechnol. 12 (2017) 7–15, https://doi.org/10.1038/nnano.2016.196.

[3] A. Ferris, D. Bourrier, S. Garbarino, D. Guay, D. Pech, 3D interdigitated micro-supercapacitors with record areal cell capacitance, Small 15 (2019) 1901224, https://doi.org/10.1002/smll.201901224.4.

[4] S Park, W Kim, W. Maeng, Y. Yang, C. Park, H Kim, K Lee, S Jung, W. Seong, 3D interdigitated micro-supercapacitors with record areal cell capacitance, Thin Solid Films 516 (2008) 7345, https://doi.org/10.1016/j.tsf.2008.02.011.

AA-TuP-37 Defect Engineering in Corrosion Protected Semiconductor Photoanodes by Atomic Layer Deposition of Titania*,* ***Oliver Bienek****, B. Fuchs, M. Kuhl, D. Silva, T. Rieth, A. Henning, I. Sharp,* Walter Schottky Institute and Physics Department, Technische Universität München, Germany

Protection layers are important for enabling stable and efficient photoelectrochemical energy conversion, especially for photoanodes operating under highly oxidizing conditions. Although TiO_2 protection layers have been intensively investigated, there are conflicting interpretations regarding the mechanism of charge transport through the films, with some studies indicating hole transport through a defect band in "leaky" titania (TiO_x) and other studies suggesting electron injection from the electrolyte into the conduction band followed by recombination at the Si/TiO_x interface. To shed light on the interfacial transport pathway, as well as elucidate the role of interfacial insulating oxide between absorber and protection layer, we have systematically investigated the effect of ALD process parameters on interfacial charge injection and photoelectrochemical function. In this context, six different ALD processes were established using two Ti precursors, TDMAT and TTIP, both in thermal (H_2O) and two plasma-enhanced (OP) processes, wherein oxygen plasmas of 300 W and 5 W power are applied. To investigate the defect properties of the TiO_x films, optical absorption coefficients were determined using photothermal deflection spectroscopy. The obtained absorption spectra vary over three orders of magnitude in the sub-bandgap region, implying a significant variation of the mid-gap defect concentrations in these films. TiO_x deposited using H_2O as oxidant yields substantially higher sub-bandgap absorption compared to PE-ALD films. XPS measurements not only deliver a direct proof of these mid-gap defects but also reveal a significant amount of Ti^{3+} states for the most defective layer, which suggests that oxygen vacancies are the dominant defect type. Photoelectrochemical characteristics of Si-based electrodes with TiO_x protective coatings, onto which Ni oxygen evolution reaction catalysts have been applied, were determined in 1 M KOH under 1 Sun illumination. While the Ni/TiO_x/Si photoanodes formed using both H_2O and 5 W oxygen plasma as the oxidant feature relatively low onset potentials and light-saturated photocurrent densities, the samples made from 300 W oxygen plasma processes have large onset potentials and shallow slopes indicative of a high series resistance due to oxidation of the Si substrate, as determined by in situ spectroscopic ellipsometry. Among the other samples, which possess comparably thin silica interlayers, we find that the photoelectrochemical onset potentials are correlated with the mid-gap defect concentrations within the ALD layers, providing a route towards rational defect engineering of protective photoelectrode coatings.

AA-TuP-38 Film Characteristics of Lanthanide Oxide Thin Film by Using Atomic Layer Deposition Method*, **Suin Kim**, M. Kim,* EMD Performance Materials, Korea (Republic of)*; S. Ivanov,* EMD Performance Materials

Lanthanide oxide films possess a wide variety of functional properties. In particular, using them as insulators in MIM structures offers a number of advantages over silicon dioxide. Lanthanide oxide based thin films can be used as gas sensors or hard mask. They are potentially attractive materials for the fabrication of multi layer optical coatings, beam splitters, passive components of integrated circuits, and heat based laser recording devices. Among them, terbium oxide (Tb_2O_3) and gadolinium oxide (Gd_2O_3) have proven to be promising materials for conventional silicon dioxide replacement in nano device applications. It has a relatively high dielectric constant (14 ~ 20) and a large band gap. Our research examines the electrical and physical characteristics of TbO_x and GdO_x thin films by atomic layer deposition (ALD) with as-deposited and post rapid thermal annealing (RTP) to improve dielectric characteristics and optimize performance for potential application in nano devices.

Here, we report thermal ALD of TbO_x and GdO_x thin films using high purity Tris(iso-propylcyclopentadienyl) terbium(III) ($Tb(^iPrCp)_3$) and Tris(iso-propylcyclopentadienyl)gadolinium(III) ($Gd(^iPrCp)_3$). Deposition of both films was investigated by thermal ALD process with ozone reactant at 150-350 °C on Si and TiN substrates. After film deposition, RTP was conducted to observe post annealing effects. ALD thermal window, and the film properties were very similar to the two films. In both films, amorphous phase with no XRD peak was observed at 200 °C samples, but crystallization peak was observed above 250 °C. The film density of GdO_x film was ~ 15% higher than the TbO_x film. XPS results showed that carbon is detected in 200 °C samples, but it is not detected at temperatures above that. Both samples showed a good step coverage of more than 90% at 200°C, but step coverage was deteriorated rapidly in samples of more than 250°C. Dielectric constant was measured using TiN/TbO_x or GdO_x/TiN (MIM) structures.

In conclusion, we conducted atomic layer deposition of TbO_x and GdO_x films and analyzed those properties. Both processes showed thermal ALD at 200 °C withgood step coverage. The films are expected to be used in applications such as high-k gate insulators or hard mask for complex pattern.

AA-TuP-39 Advanced 3D Mxene ALD Assembly Through Precious Metal Conformal Coating for Clean Energy Applications*, **Debananda Mohapatra**, Y. Kim, Y. Park, S. Kim,* Yeungnam University, Korea (Republic of)

MXenes are a large family of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides, with similar and better overall physicochemical properties than one of the most studied 2D graphene. Notably, its electronic and electrochemical properties are massively affected by how these MXene materials are synthesized and processed wet chemically. To eliminate one of the pressing face-to-face staking issues of these MXenes, we try to introduce an atomic layer deposition (ALD) technique to introduce the precious metals conformally. Precious metal like iridium is quite rare and expensive; hence, precise quantity and quality control are desired. These ALD processed precious metals could be fascinating to explore their electrochemical activity along with the novel engineered MXene host material. We also discuss another exciting fullerene family of carbon materials such as carbon nano-onions (CNO), which are multi-shelled cage-like graphitic structures at an intergraphitic distance of 0.34 nm, mimicking onion morphology is excellent host materials for precious metals. Additionally, we will introduce the role of precious metals such as Ir, Pt, Ru ALD induced electrochemical behavior. The novel proposed MXene-ALD noble metal nanostructures could be potential electrocatalysts for HER/OER applications.

AA-TuP-40 Toward a Rational Surface Texture Designof FBR-ALD Pt/CCatalyst to Enhance PEMFC Performance*, **Ji-Hu Baek**, S. Kwon, S. Lee,* Pusan National University, Korea (Republic of)

Proton exchange membrane fuel cell (PEMFC) is an efficient electrochemical energy conversion device that directly generates electricity from the chemical energy of fuels without the emission of greenhouse gases. The most reliable catalyst in PEMFC is Platinum (Pt) metal nanoparticles (NPs) that exhibit excellent electrochemical activity and stability compared to other catalysts. However, using of Pt catalyst is limited due to its very high cost and low abundance on Earth. Therefore, it is important to use Pt catalyst efficiently for making the PEMFC economically viable. In this regard, several synthesis techniques have been developed to reduce the loading and uniform distribution of Pt NPs on carbon support with high electrochemically active surface area (ECSA). One of the most efficient techniques to uniformly deposit Pt NPs with a controllable size on carbon support is to use a fluidized bed reactor (FBR) atomic layer deposition (ALD). Our group recently demonstrated that FBR-ALD Pt/C catalysts can exhibit high fuel cell performance and high endurance even with low Pt NPs loading by optimizing the surface of carbon supports combined with proper ALD process parameters [1]. However, it is still challenging to further improve the fuel cell performance by rational designing the Pt NPs surfaces in order to make FBR-ALD into a viable commercial production.

In this study, a unique way to improve the fuel cell performance was suggested to design and optimize atomic scale surface textures of Pt NPs. During the FBR-ALD of Pt NPs, in-situ surface modulation of Pt NPs were applied via a proper protective oxide deposition and etching. A careful surface studies was performed to analyze the surface morphology, distribution and uniformity of Pt NPs. Electrochemical performances were evaluated and optimized by measuring cyclic voltammetry (CV) and oxygen reduction reaction (ORR). Finally, a fuel cell performance was studied through membrane electrode assembly (MEA) characteristics.

AA-TuP-41 Plasma Enhanced Atomic Layer Deposition (PEALD) of Silicon Nitride for FEOL Applications*, **Marco Lisker**, M. Kalishettyhalli Mahadevaiah,* IHP Frankfurt (Oder), Germany

Silicon nitride (SiN) is commonly used for spacer formation for various gate CMOS-architectures and advanced 3D-RF-devices as heterojunction bipolar transistors as wellas a masking layer in high selective wet etching steps in FEOL processes. Standard processes for SiN like low pressure chemical vapor deposition (LPCVD) results in high quality layers but at the cost of a very high thermal budget. Plasma enhanced chemical vapor deposition (PECVD) results in high quality layers as well but comes with a disadvantage of poor step coverage. The deposition temperatures of PECVD SiN can be much lower compared to LPCVD SiN process which results in lower thermal budget. However, PECVD process leads to plasma damage in the underlying device structures due to the ion bombardment during the deposition step using high RF power. As an appropriate alternative the PEALD process make use of several advantages as lower deposition temperatures, uniformity and conformality of the deposited layers and good step coverage. Hence, in this work we investigate the deposition of SiN using PEALD process and the possibility of the process competing with industry standard LPCVD and PECVD SiN processes.

The deposition process of PEALD SiN is carried out using a high vapor pressure precursor Trisilylamine (TSA). The PEALD deposition parameters which could be varied are identified and the design of experiments (DOE) is systematically carried out by varying only one parameter at a time. The process parameters such as deposition temperature, plasma exposure time, precursor feed time, RF power etc. are among the many other parameters which are used for DOE. Further, the SiN deposition process is investigated by using nitrogen (N_2) or ammonia (NH_3) as the reactant gases. The quality of the deposited SiN layers is investigated in terms of the layer uniformity, refractive index, step coverage, conformality, chemical composition of the layers etc. through various metrology techniques. Additionally, the etch rates of the deposited SiN layers are tested in liquid etchants like hydrofluoric acid and hot phosphoric acid to evaluate the potential of the PEALD SiN layers as high selective wet etch mask.

AA-TuP-42 Mechanical and Optical Properties of Alumina Doped Hafnia Deposited by Plasma Assisted Atomic Layer Deposition*, **Taivo Jõgiaas**,* University of Tartu, Estonia

Atomic layer deposited hafnium oxide is known as high-k material, but could be used as an optical coating. The latter could also require a certain mechanical resilience. Doping could induce phase changes, for instance, stabilizing hafnia in a certain crystallographic phase such as tetragonal or cubic.

Alumina doped hafnia thin films were atomic layer deposited using oxygen plasma as the oxygen source, and trimethylaluminium and tetrakis(ethylmethylamino)hafnium as respective metal sources. The processes were conducted mainly at substrate temperatures of 300 °C with some additional depositions at 200 °C or 400 °C. Elemental and crystallographic phase compositions, optical and mechanical properties were characterized. The film thicknesses averaged around 70 nm.

Correlations between compositions, optical and mechanical properties were drawn, which is essential in tuning optical coatings with certain mechanical properties.

AA-TuP-43 Al Doped Zno Thin Film on High Aspect Ration Structure (1:10) by Ald Process for Biomedical Application*, **Po-Tsung Hsieh**, T. Tsai, T. Wang, C. Lin, T. Chen, H. Tu,* Core Facility Center, National Cheng Kung University, Taiwan

The determination of dopamine (DA) has been used as an important biochemical indicator for progressively degenerative diseases in the central nervous system, such as Parkinson’s disease (PD). As compared to the optical sensing techniques for precise DA quantification, electrochemical biosensors provide an attractive technique to analyze the content in a biological sample due to the direct conversion of a biological event to a redox current signal. Based on these categories of procedures occur at the surface of the working electrodes, the enlargement of sensing surface area is a critical factor corresponding to the improvement of sensitivity. The main limitations from insufficient reproducibility and poor stability for the present nanomaterial remain to be solved due to its complicated process of materials coated onto the electrode surface.

For increasing the sensing surface area to enhance the sensitivity, an ultra-sensitive electrochemical biosensor can be realized by the three-dimensional (3D) nano-rod architecture with a remarkable conductive material on it. Nano-rod with high aspect ratio of 1:10 was fabricated. Aluminum-doped zinc oxide (AZO) thin-film with a prominent electrical conductivity is selected for depositing on the surface of nano-rod. The uniformity issue is the key concern especially for the 3D nano-rod structure among many depositing techniques. The uniformity of AZO film will have great impact on the sensitivity of electrochemical sensor. To overcome such issue, atomic layer deposition (ALD) technique was selected for depositing AZO thin film on the nano-rod structure. ALD is a chemical deposition technique relied on the saturated surface reactions and self-limiting which can provide excellent conformality for the deposited thin film. Then AZO thin film was deposited at 250℃ by ALD technique. Trimethylaluminum (TMA) and diethylzinc (DEZn) were used as the precursors for AZO film by ALD process. The deposition sequence (1:9, 1:19, 1:29) of TMA and DEZn was designed for seeking the optimal doping ratio. The processing cycle is 500 times for obtaining the expected AZO thickness of 50nm. After ALD processing, the thickness and uniformity of AZO thin film were continually measured for confirming the thickness at the top and the bottom of the nano-rod. And the doping ratio was also examined for understanding the ALD depositing parameter. The results shows that the resistivity can be obtained by the doping ratio of 1:29 (TMA:DEZn) is 5E-4 ohm-cm. The sensitivity will then be tested on the electrochemical sensor. This study proposed microfabrication would be further conducted into the other electrochemical sensors in the future.

AA-TuP-44 H_2 Separative Membrane Fabricated by Thermal Atomic Layer Deposition*, **Clémence Badie**,* Aix-Marseille University, France*; M. Drobek,* CNRS- Univ. Montpellier, France*; M. Bechelany,* CNRS/Univ. Montpellier, France*; J. Decams,* Annealsys, France*; L. Santinacci,* Aix-Marseille University, France

To provide affordable H_2 with high purity for energy applications, new strategies as H_2-selective membranes gained in interest. This technology presents valuable benefits as it is cost-effective and have a reasonable environmental impact. In addition, a large variety of materials is available, thus, the composition of the membrane can be adapted to the working conditions. This study focuses on the fabrication of dense membranes able to operate at the high temperatures required in industrial processes (400-800°C). The specificity of the present approach is to fabricate new nanocomposite devices that combine the stability of a ceramic matrix, titanium nitride, with the catalytic effect of palladium nanoparticles used as nanofillers. Both TiN films and Pd nanoparticles are deposited onto a hetero-porous alumina tubular membranes by thermal Atomic Layer Deposition (ALD). The composite membrane is optimized to reach the highest H_2-selectivity (purity) and permeation (flow), by finely tuning the thickness and the chemical composition of the TiN/Pd coating. ALD is an original technique in this field, but it is well adapted because it allows for coating nanostructured substrates with an excellent control of the thickness and composition.

The fabrication of the membrane follows two steps. First, the TiN deposit fills the alumina porosity. The coating forms a dense layer on the nanoporosity at the inner part and penetrates into the macroporosity of the outer part, covering the alumina grains. Afterwards, the Pd nanoparticles are deposited. The selectivity and the permeation of the TiN-Pd membrane are assessed using H_2, He and N_2. The increase of the temperature up to 400°C allows for achieving an encouraging H_2 ideal selectivity and permeance of 35 and 258 GPU (Gas Per Unit), respectively. Moreover, these values increase during the measurement: the selectivity and the permeance rises up to 109 and 718 GPU, respectively, after 4.5 h at 400°C. These performances are promising as a similar pure Pd membrane presents an ideal selectivity of 23 and a permeance of 991 GPU at 188°C [1]. The investigation of the thermal evolution and the stability of the present membrane is then required. Complementary results will therefore be presented.

[1] Weber et al., Hydrogen selective palladium-alumina composite membranes prepared by Atomic Layer Deposition, *J. Membr. Sci*. ***2020**, 596*, *117701*.

AA-TuP-45 Universal Relationship between Spontaneous Polarization and Coercive Field of HfZrO Ferroelectric*, **Min Liao**, J. Xiang, X. Wang,* Institute of Microelectronics, Chinese Academy of Sciences, China

The discovery of ferroelectric characteristics in doped HfO_2 films strongly supports the ferroelectric transistors as a nonvolatile memory device. The ferroelectric characteristic is key. However, this issue is still not completely understood. In this work, we investigate the relationship between the spontaneous polarization and the coercive field of HfZrO ferroelectric. We grew the HfZrO film by changing atomic stoichiometry, annealing temperature and time, insertion dielectric material (HfO_2, ZrO_2, TiO_2, Al_2O_3) by ALD method. We find a universal relationship between spontaneous polarization and coercive field of HfZrO ferroelectric, regardless of growth condition and ferroelectric/dielectric structure. This is helpful to understand the HfZrO ferroelectric.

AA-TuP-46 Synthesis of Noble Metal Nanoparticles by ALD for Electrocatalysis*, **Sitaramanjaneya Mouli Thalluri**, R. Zazpe, H. Sopha, J. Macak,* University of Pardubice, Czechia

Platinum group metals such as Pt, Ru, Pd, Ir, etc., have superior performance in various catalytic applications.[1] Due to their scarcity efforts were being made to reduce or replace these noble metals. Atomic Layer Deposition (ALD) is one among the best technique that is available to reduce the metal loading of noble metals.[2],[3] ALD is employed to develop continuous thin films of thickness down to single atom. Due to the governing surface energies variations for noble metals with respect to substrate surface, the growth initiates as nanoparticles (NP) and with a further increase in ALD cycles the agglomeration among NP’s dominates over the individual NP size increase, thus developing thin films.

For electrocatalytic applications, it is important to choose the right substrates. Among available substrates, Carbon papers (CP) and Titania nanotube (TNT) layers are best choices considering their properties, availability, vast literature and low costs incurred using these as support substrates in electrocatalysis and photocatalysis. Several surface modifications for CP’s and variations on morphological aspects of TNT layers had received a great attention form applied fields due to their improved surface area, conductivity and stability.[4],[5][6] Anodic oxidation of titanium foils using relevant electrolytes is one of the appropriate method to fabricate TNT layers.[7] Uniformly decorating these CP’s and TNT layers by nanoparticles or thin films of catalysts proved to be highly efficient with no boundaries on applications.[8]

ALD is the most suitable technology that can decorate high aspect ratio and high surface area nano architectures.[9]

The presentation will introduce and describe the synthesis of different noble metals by our ALD tool (Beneq TFS 200) on various aspect ratio TNT layers and CP substrates. It will also include the corresponding physical and electrochemical characterization and encouraging results obtained in electrocatalysis.

References:

1.Huang, Z. F. et al. Advanced Energy Materials vol. 7 (2017) 1700544.

2.Yoo, J. E. et al. Electrochem. commun. 86, (2018) 6.

3.Anitha, V. C. et al. J. Catal. 365, (2018) 86.

4.Sopha, H. et al. Appl. Mater. Today 9, (2017) 104.

5.Macak, J. M., Zlamal, M., Krysa, J. & Schmuki, P. Small 3, (2007) 300.

6.Liu, C., Sun, C., Gao, Y., Lan, W. & Chen, S. 6, (1915).

7.Macak, J. M. et al. Curr. Opin. Solid State Mater. Sci. 11, (2007) 3.

8.Dvorak, F. et al. Appl. Mater. Today 14, (2019) 1.

9.Zazpe, R. et al. Langmuir 32, (2016) 10551.

AA-TuP-47 Protection of Platinum Electrocatalysts for Water Electrolysis Using Atomic Layer Deposited Silicon Dioxide, *Ming Li*, *R. Kortlever, R. van Ommen,* Delft University of Technology, Netherlands

Hydrogen is an important building block for the energy transition because it is a clean renewable energy carrier and an important feedstock for the chemical industry[1]. Among the various methods of producing hydrogen, water electrolysis using electricity from renewable sources such as wind and solar will become a main pathway in the coming years. Platinum is one of the most effective electrocatalysts for water reduction to hydrogen and hydrogen oxidation and is widely used in the PEM electrolyzers and fuel cells. However, its high costs and scarcity limit its application. To use platinum-based electrocatalysis in a cost-effective manner, it is crucial to have a method to protect the platinum catalyst from degradation and prolong its lifetime.

Here, we have applied an atomic layer deposited SiO_2 coating on the surface of platinum electrocatalysts to improve its durability. TEM, XPS, SEM-EDS mapping were used to characterize the catalyst. Linear sweep voltammetry (LSV), cyclic voltammetry (CV), and accelerated durability tests were applied to study the stability of the catalyst. We found that after 1000 cycles of CV scans in the water reduction potential range, the current density at -0.2 V vs. reversible hydrogen electrode (RHE) of the original catalyst was reduced by 34%. By contrast, after applying 2 cycles of ALD SiO_2 deposition, the current density at the same voltage was reduced by 7.3% after the same test procedure. After applying 5 cycles of ALD SiO_2 deposition, the catalyst current density was only reduced by 1.9% after the accelerated durability test. The particle size of the original catalyst increased by 16% after 1000 cycles CV scans, whereas it only increased by 1.6% after 1000 cycles scans protected by 5 cycles of ALD SiO_2 deposition.

41. Cheng, N., et al., *Platinum single-atom and cluster catalysis of the hydrogen evolution reaction.* Nat Commun, 2016. **7**: p. 13638

AA-TuP-48 ALD-Deposition of Cathodic Materials for 3D Li-Ion Micro Batteries - Ongoing Results, *Antoine Peisert*, *G. Lamblin, D. Lenoble, N. Adjeroud,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Since their discovery in the 70's, Li-ion batteries are a hot topic in R&D, driving innovation and investigation of new materials and synthesis routes to meet the market demand. Widely use over a large range of applications (smartphone, laptops, electric vehicles), Li-ion batteries face numerous challenges: enhancement of the electrochemical properties, miniaturization, increase in safety… Among the solutions considered to answers those challenge, the use of 3D microstructures could potentially increase the active specific surface, in regard to a fix volume, thus enhancing the capacity of the battery and its energy density.

The approach presented in this oral presentation is the use of ALD (Atomic Layer Deposition) to deposit a thin film of cathodic material ($LiCoO_2$) onto and into a porous 3D membrane. By utilizing ALD supercycles (a combination of one Li-based ALD process to form Li_2CO_3 and another Co-based ALD process to form Co_3O_4), a thin film of $LiCoO_2$ is obtained, with the numerous benefits of ALD processes, like total covering of the surface, homogeneity, uniformity and conformality on high aspect-ratio structures. A similar approach has been developed in the literature using PE-ALD, but to the best of our knowledge, no other source are using thermally activated ALD processes.

This process would allow the uniform deposition of active electrochemical material on 3D substrate, thus developing 3D Li-ion batteries.

This presentation will gather the results obtain for the fabrication of Co_3O_4 and Li_2CO_3 thin films onto planar substrates by thermal ALD, characterized by Raman spectroscopy, XPS (X-Ray Photoelectron Spectroscopy), and EDX (Energy Dispersive X-Ray), as well as thickness measurements obtain by mean of XRR (X-Ray Reflectivity) measurements. Then, supercycles results combining both previous cycles will be shown, with the same type of physico-chemical characterizations, as well as some of the first evaluations of the electrochemical performances of the developed electrodes

AA-TuP-49 Disentangling the Effect of Diffusion and Solubility in the Gas Barrier Properties of ALD Alumina Thin Films, *S. Bhudia, J. Barbe, M. Gerard,* Luxembourg Institute of Science and Technology (LIST), Luxembourg; *V. Cassio,* MET-LUX S.A., Luxembourg; ***Renaud Leturcq***, Luxembourg Institute of Science and Technology (LIST), Luxembourg

Alumina thin films deposited by ALD have demonstrated very good barrier properties [1] due to the expected low pinhole density as compared to films deposited e.g. by CVD, enabling long-term stability of photovoltaic [2] and OLED devices [3]. However, the obtained permeation properties strongly depend on the deposition temperature and the substrate [4], the origin of which are still not fully understood. In particular, the effect of pinholes as compared to bulk diffusion properties of the ultra-thin film are not fully elucidated. Here we address the potential permeation mechanisms in alumina thin films deposited by ALD by using time-dependent analysis of the helium permeation rate.

We compare two alumina thermal ALD processes, standard process using trimethylaluminium (TMA) and water (H2O) as precursors, and a new process where a diethylzinc (DEZ) injection before the TMA injection provides better properties for films deposited at room temperature. Both films are deposited on standard PET films. To address the permeation mechanisms of alumina thin films, we have first compared the water and oxygen permeation properties measured by usual Mocon® test to helium permeation properties measured using an in-house developed prototype. The good correlation of all measurements for alumina obtained using the standard TMA-H2O process shows the high stability of alumina when exposed to water or oxygen, and that the permeation can be well described by the physical diffusion of the gas through the film. A lower correlation is obtained with the new DEZ-TMA-H2O process, which we attribute to higher density of OH groups.

By analyzing the time dependent helium permeation rate, we disentangle the effective diffusion coefficient of the barrier layer and the solubility, showing that the main improvement is obtained by a reduced solubility with only a weak change in the diffusion coefficient. These results have been compared to analytical models and simulations, using both a continuous bilayer model and a defect permeation model. While both models can reproduce well the observed data, the defect permeation model allows us to extract the product between the pinhole density n and their average diameter d_0. We obtain values 10 to 100 times lower than SiOx and SiN films obtained by PECVD [5].

[1] M. D. Groner et al., Appl. Phys. Lett. 88, 051907 (2006); P. F. Carcia e al., Appl. Phys. Lett. 89, 031915 (2006)

[2] J. A. van Delft et al., Semicond. Sci. Technol. 27, 074002 (2012)

[3] J. S. Park et al., Semicond. Sci. Technol. 26, 034001 (2011)

[4] T. Hirvikorpi et al., Surf. Coat. Technol. 205, 5088 (2011)

[5] A. S. da Silva Sobrinho et al., J. Vac. Sci. Technol. A 18, 149 (2000)

AA-TuP-50 Vapor Phase Infiltration (VPI) on Polymers Fibers and Fabrics for Multifunctional and Antimicrobial Textile, *Natalia Chamorro*, *M. Knez,* CIC nanoGUNE, Spain

For functional textile the relevant industry is seeking materials with a wide range of exciting new applications such as self-cleaning, antibacterial, anti-odor, etc., ideally at the same time. One of the very promising strategies to implement such properties into textile is the application of vapor phase chemistry to the manufactured textile.

In this work, we present our strategy to functionalize textiles with a mixed composition, namely denim jeans (mix of cotton and polyethylene fibers), with TiO2 and ZnO by applying vapor phase infiltration (VPI). The resulting modified textile becomes largely waterproof, antimicrobial properties and can block UV light. Interestingly, the pristine material is hydrophilic and absorbs water rapidly. However, after treatment with TiO2 the wetting properties change to hydrophobic, which is seen in the increase of the water contact angle. We assign the evolving hydrophobicity to the wetting behavior of the rough surface in the textile. This property can be adjusted by controlling some processing parameters, such as the number of VPI cycles or the exposure time of the textile to the metalorganic precursor. Furthermore, the incorporation of TiO2 into the textile as infiltrating and coating inhibits the attachment of both gram-positive bacteria (Staphylococcus aureus) and gram-negative bacteria (Escherichia coli). These results suggest that the increment in roughness and the evolving hydrophobicity have a considerable effect on the binding of bacteria to the textile fibers. In addition, an improvement in the UV blocking capacity of the textiles was observed. In this case the material shows the ability to absorb in the UV region from 280 to 400 nm.

The application of VPI to textile can introduce new features to the materials which can synergistically act and contribute to the development of functional textiles.

AA-TuP-51 Impact of Substrate Bias on the Wear Rate of Plasma Enhanced Atomic Layer Deposited TiVN*, Mark Sowa,* Veeco ALD*; M. Chowdhury,* Department of Materials Science and Engineering, Lehigh University*; K. Van Meter, T. Babuska,* Department of Mechanical Engineering, Florida State University*; A. Kozen,* Department of Materials Science & Engineering, University of Maryland, College Park*; N. Strandwitz,* Department of Materials Science and Engineering, Lehigh University*; B. Krick,* Department of Mechanical Engineering, Florida State University

During Plasma Enhanced Atomic Layer Deposition (PEALD), substrates are typically subjected to alternating exposures of chemical precursors and plasma generated species including: atomic and molecular radicals; atomic and molecular ions (positive and negative); electrons; and photons. Plasma physics dictate a sheath form at surfaces in contact with the plasma. A potential drop across the sheath develops equilibrating the flux of negative (mostly relatively fast moving electrons) and positive (slower, heavier ions) charge to the surface. During PEALD, energy acquired by positive ions accelerated through the sheath is transferred to the surface of the substrate and growing film playing a role in the resulting substrate/film interface and film properties. Through application of RF power to the substrate holder, the energy acquired by positive ions crossing the sheath from the plasma to the substrate is increased. Recent studies have demonstrated variation of PEALD film properties through application of different RF bias levels. Work continues to elucidate how the potentially important RF bias process knob can be leveraged to provide additional control on PEALD film properties.

We have previously reported on the excellent wear rate properties of PEALD TiN and VN.[1] Our continuing studies have shown superior wear properties for mixtures of these two films compared to the pure binary nitrides. In this study we have investigated how low substrate bias voltages during PEALD impacts film characteristics ultimately focusing on the tribological properties of TiVN.

1:1 TiVN films were deposited in a Veeco G2 Fiji Plasma ALD system with TDMAT, TDMAV, and N_2 plasma at 250°C over a range of low RF bias voltages and durations. We will report on the impact of substrate ion bombardment energy and dose on film properties including wear rate, density, crystallinity, roughness, composition, and stress.

1. M. J. Sowa, L. Ju, A. C. Kozen, N. C. Strandwitz, G. Zeng, T. F. Babuska, Z. Hsain, and B. A. Krick, "Plasma-enhanced atomic layer deposition of titanium vanadium nitride," J. Vac. Sci. Technol. A 36(6), 2018.

AA-TuP-52 Thermal and Aqueous Media Stability of $Sr_2Mgsi_2O_7$:Eu^{2+}, Dy^{3+} Phosphors Encapsulated by Al_2O_3 Using Atomic Layer Deposition (ALD)*, Erkul Karacaoglu,* Karamanoglu Mehmetbey University, Turkey*; A. Okyay,* Okyay Technologies and with the Stanford University*; H. Yurdakul,* Kutahya Dumlupinar University, Turkey*; M. Losego,* Georgia Institute of Technology, USA

This study includes the results of thermal stability and aqueous media studies of $Sr_2MgSi_2O_7$:Eu^{2+}, Dy^{3+}blue light emitting phosphorescence powders synthesized from solid-state reaction method and Al_2O_3 encapsulation via atomic layer deposition (ALD). Water immersion studies revealed that the uncoated phosphor powders have good resistance to aqueous media up to 30 days. Along with this resistance, there was also stability in the blue phosphorescence (466 nm) characteristics and structural properties. Thermal stability tests up to 1000 °C showed that these phosphors are unstable and loss afterglow property at elevated temperature, thus limiting their applications in the low to high temperature range. ALD coatings of ~10 nm Al_2O_3 on phosphor powders improved the phosphorescence ability by percentage of ~6 and a significant improvement was also observed in phosphorescence stability at high temperatures. This study will undoubtedly create an opportunity for the use of these long afterglow phosphors in applications that require heat treatment process. Successful encapsulation of $Sr_2MgSi_2O_7$-based phosphors will make them possible to utilize in applications requiring heat treatment or in high and continuous temperature environments.

AA-TuP-53 Fabrication of High-Quality Titanium Nitride Thin Film as a Cu Diffusion Barrier Layer by Hollow Cathode Plasma Atomic Layer Deposition at Low Temperature*, Ha Young Lee,* *J. Han, B. Choi,* Seoul National University of Science and Technology, Korea (Republic of)

Use of the Cu interconnects in CMOS-based demands advancement of diffusion barrier layers which prevent Cu diffusion into the Si based transistors at the elevated temperature.Titanium nitride (TiN) is one of good candidate for Cu diffusion barrier material among the transition metal nitrides due to its high thermal stability and low electrical resistivity. TiN thin film is usually grown by physical vapor deposition (PVD), and chemical vapor deposition (CVD). As scale down of the feature size, TiN barrier layers are required to be thin and conformal. In this regard, the territory of atomic layer deposition (ALD) can be expanded to achieve high step coverage with high quality. Introducing plasma source to ALD equipment, it is possible to fabricate higher quality thin film at a lower process temperature.Hollow cathode plasma (HCP) source is the latest plasma source to alternate inductively coupled plasma (ICP), capacitively coupled plasma (CCP), and microwave plasma (MP). HCP have the advantages of low plasma damage, high radical and electron density, leading to faster growth rates, improved crystallinity, and scalability.

In this study, TiN thin film was grown by HCP-ALD (HCP source by Meaglow, US and ALD by CN-1, Korea). HCP-ALD process was executed at temperature of 230, 250, 300℃, using Titanium tetra chloride ($TiCl_4$) as Ti precursor and ammonia (NH_3) as reactants with 0.5, 0.55, 0.54Å/cyc at each temperature. TiN thin film has face centered cubic polycrystalline structure and uniform thickness confirmed by XRD and TEM. Density of TiN_x thin films was 5.16-5.29g/cm^3, which showed higher density than that of sputtered TiN, which is similar to the theoretical density (5.35g/cm^3) of TiN. HCP-ALD grown TiN showed a surface roughness of about 1.2nm confirmed by AFM and XRR. Resistivity of TiN was decreased by increasing deposition temperature showing about 160μΩ.cm grown at 300℃ with 35nm-thicnkess. HCP-ALD grown TiN was composed of Ti, N, O (3at%), and Cl (0.01at%) by AES depth profile and ToF-SIMS. Through the XPS analysis, TiN film was mainly consisted of Ti-N with a small amount of Ti-O-N, and no Cl peak was identified. Ti:N ratio was confirmed to 1:0.95 by RBS analysis. The diffusion barrier properties for Cu were evaluated by rapid thermal annealing at the temperature range of 200-800℃. The failure temperature was confirmed about 700℃ at 10-nm-thick TiN thin film between Cu and Si. In addition, the step coverage test was executed at trench wafer with aspect ratio of 7:1, which was higher than 95% for sidewall step coverage.

AA-TuP-54 Adjusting Crystal Structure in an In-Zn-O System Deposited by PEALD and its TFT Application*, TaeHyun Hong,* *Y. Kim, J. Park,* Hanyang University, Korea (Republic of)

Oxide semiconductors have been used in various electronic devices because of their low processing temperatures, high mobility (≥ 20 cm^2/Vs), and low off-current characteristics (~10^{18} μA/μm). In particular, since the crystal structure affects electrical properties such as mobility, several studies have been reported for deposit oxide semiconductors with the crystal structure. However, multi-component oxide semiconductors with different crystal structures of each element generally exhibited amorphously, or a high temperature (> 400℃) was required to form the crystal structure. In this study, InZnO (IZO) semiconductors were deposited by plasma enhanced atomic layer deposition (PEALD) at low growth temperature (200℃). The chemical composition ratio was controlled by adjusting each InO and ZnO sub-cycles. By controlling each compositional ratio, the crystal structure of IZO was also influenced. Especially, the c-axis aligned hexagonal structure was also demonstrated in this process. Since the PEALD uses plasma reactants for chemical deposition, we suggest that high plasma energy could induce the crystallization of IZO. For thin film analysis of IZO deposited with PEALD, we conducted X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD). To examine potential use for thin film transistors (TFTs), the IZO film was deposited as an active layer, and inverted staggered- type TFTs were fabricated onto Si substrates.

AA-TuP-55 Pt-coated Si X-ray Optics with Plasma Atomic Layer Deposition for GEO-X Mission*, Masaki Numazawa,* *D. Ishi, A. Fukushima, Y. Ezoe, K. Ishikawa, S. Sakuda, T. Uchino, A. Inagaki, H. Morishita, Y. Ueda, T. Murakawa, Y. Tsuji, L. Sekiguchi,* Tokyo Metropolitan University, Japan*; K. Mitsuda,* National Astronomical Observatory of Japan

We have been developing an ultra-lightweight X-ray optic by using MEMS technologies for future X-ray astronomical missions (Ezoe et al., 2010, Microsys. Tech. 2010, 16, 1633), especially GEO-X (GEOspace X-ray imager) mission which is an 18U CubeSat (~20 kg) project to perform soft X-ray imaging spectroscopy of the entire Earth's magnetosphere from Earth orbit near the Moon (Ezoe et al., 2020, Proc. SPIE 11444, 1144428).

The MEMS X-ray optic is made of 4-inch Si (111) wafer of ~300-µm resultant thickness. The Si wafer is firstly processed by deep reactive ion etching such that they have numerous curvilinear micropores (20-µm width) whose sidewalls are utilized as X-ray reflective mirrors. High-temperature hydrogen annealing and chemical mechanical polishing processes are then applied to make those sidewalls smooth and flat enough to reflect X-rays. After that, the wafer is plastic-deformed into a spherical shape and Pt-coated by atomic layer deposition (ALD) process to focus parallel X-ray lights from celestial objects with high reflectivity. Finally, we stack two optics bent with different curvatures (1000- and 333-mm radius) and complete the Wolter type-I telescope. The telescope is our original micropore optics and possesses lightness (~5 g), a short focal length (~250 mm), and a wide field of view (~4 deg x 4 deg).

We adopted the plasma ALD process to form smooth-thin Pt film on the surface of the micropore on our optic. High-aspect-ratio micropores with 20-µm width and ~300-µm depth were coated with ~20-nm Pt and ~10-nm Al2O3. Measured X-ray reflectivity curves for Al Kα 1.49 keV radiation indicated the surface roughnesses were estimated as 1.2 +0.6/–1.0 and 1.6 ± 0.1 nm RMS before and after the plasma ALD, respectively (Ishi et al., 2020, Appl. Phys. Express, 13, 087001). The surface roughness of the plasma ALD-coated Pt film was comparable with that of the substrate material and better than that of a thermal ALD-coated one in our previous study (Takeuchi et al., 2018, Appl. Opt., 52, 3237). This result and the roughness itself generally satisfied a specification of the telescope for the GEO-X mission. We also optimized the other processes to enable the optics to achieve an angular resolution of ~5.4 arcmins in half-power width (~10 arcmins in half-power diameter required for GEO-X) from the reflective surface figures and the entire wafer shapes. In this paper, we report the enhancement of the Pt-coated Si micropore X-ray optics by using the plasma ALD and the X-ray imaging performance of the telescope as an engineering model for the GEO-X mission (see Fig.1 in Supplemental Documents).

AA-TuP-56 Structural and Optical Properties of Atomically Engineered Ir/Al_2O_3 Heterostructures, *Pallabi Paul, P. Schmitt,* Friedrich Schiller University Jena, Germany*; Z. Wang, W. Li, M. Kling,* Ludwig-Maximilians-University of Munich, Max Planck Institute of Quantum Optics, Germany*; A. Tünnermann,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF , Germany*; A. Szeghalmi,* Fraunhofer Institute for Applied Optics and Precision Engineering, Germany

Recently, the search for nonlinear optical materials has experienced tremendous attention. Due to the continuous requirement of shrinking device sizes, 3D photonic integration, the search for new nonlinear optical materials has become increasingly essential as a substitute to commercially available nonlinear bulk crystals. Owing to the advancement of nano-structuring and coating technologies down to atomically controlled dimension and composition, emerging technologies, such as atomic layer deposition (ALD) has enabled the fabrication of new atomically thin nonlinear optical materials.

In this work, we have explored an effective method to deposit atomically thin interfaces of Ir/Al_2O_3 heterostructures by means of ALD. Atomic layer deposition is a chemical coating technology based on sequential and self-limiting reactions of gaseous reactants with the available functional groups on the substrate surface allowing uniform and conformal films on high aspect ratio structures, 3D substrates, and micro-nano structured objects. The Ir/Al_2O_3 nano-stacks are investigated by spectroscopic ellipsometry, UV/VIS spectrophotometry, XRR, GIXRD, XPS, and HRTEM to obtain the structural, and optical properties. XRR and GIXRD measurements along with HRTEM micrograph demonstrate the growth of amorphous layered heterostructures. Additionally, XPS investigations reveal that for ultrathin Ir contributions, there is a formation of IrO_2 at the interface, in contrast to discrete nanoparticle formation. The optical dispersion profiles (refractive index, and extinction coefficient) of the compositions have been reliably determined employing the spectroscopic ellipsometry technique. Upon increasing the Ir contribution, the whole layered stack undergoes a transition from an effective insulating material towards an effectively metallic system at a critical Ir thickness regime of 2-4 nm.

Initially, iridium nanoparticle systems are examined for their nonlinear optical response. We have experienced the presence of third-order nonlinearities in Ir nanoparticles. Furthermore, nonlinear optical measurements show the enhancement of two orders of magnitude in third-harmonic intensity as compared to pure Al_2O_3 layers by the inclusion of Ir within the heterostructures. Further experimental investigations and theoretical validation of third-order nonlinearities are currently in progress.

AA-TuP-57 Broadband Absorbers by ALD: An Opportunity for Solar-Driven Applications, *Mario Ziegler, V. Ripka,* Leibniz Institute of Photonic Technology, Germany*; P. Cheng,* TU Ilmenau, Germany*; K. Kc, H. Wagner, U. Huebner,* Leibniz Institute of Photonic Technology, Germany*; D. Wang, P. Schaaf,* TU Ilmenau, Germany

The incorporation of nanoparticles in photocatalytic materials improves the absorption behavior and thus, decreasing drastically the necessary thickness of the functional layers. Moreover, the efficiency can be easily increased by absorbing a larger fraction of the incident light due to optical properties of large variety of different nanoparticles. Nevertheless, the incorporation of many different nanoparticles in photocatalytic materials remain challenging. ALD is a versatile and flexible tool with good controllability of the film composition and the deposition itself, leading to new opportunity in layer design.

Here, we report on a plasma-enhanced ALD process on planar and nonstable substrates to fabricate complex 3D hybrid nanostructures with high absorption above 99 % from 220 nm to 2500 nm (Figure 1 (a)) and peak absorption of 99.77 % at a film thickness of only 9 µm [1]. In contrast to classical ALD, this approach utilizes the metastability of planar substrates within the PE-ALD process. The metastable substrate acts as a time-limited precursor container leading to the generation of complex 3D architectures. The geometry of these hybrid structures can be easily adjusted by the applied PE-ALD parameter. So, sponge-like, highly-porous or nanowire-like structures can be generated [2]. The structures consist of nanoparticles, originated from the planar template, and a 3D scaffold originated from the PE-ALD process. By applying silver as template and silica as PE-ALD material, we have shown the formation of high absorption silver-nanoparticle silica nanowire hybrid layers.

We found that the 3D silica-scaffold leads to a preferential forward-scattering while the Ag-NP leads to broader absorption of the incident light. The excellent optical properties as well as the opportunity to generate a variety of different composition setups might be quite promising for solar-driven applications such as plasmonic-induced photocatalysis, photothermal water purification (figure 1 b) or photovoltaics [3].

[1]M. ZIEGLER et al., ACS nano 2020, 11 (14), 15023.

[2]M. ZIEGLER et al., Applied Surface Science 2020, 514, 145770.

[3]P. CHENG et al., Applied Materials Today 2021, 25, 101238.

AA-TuP-58 PE-ALD Synthesis and Characterization of Silver Nanoparticles and Ultrathin Films, *Petru Lunca-Popa,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; S. Guillemot,* ASM, Korea (Republic of)*; R. Leturcq,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Owning its superior optical, electrical and thermal properties, silver is used on wide spectrum of applications ranging from devices based on plasmon resonance (Ag NPs) to optical mirrors infrared reflecting coatings. Nonetheless, the Volmer Weber mechanism governing the growth of Ag films make the synthesis of thin continuous Ag films very challenging as it favours islands morphology. Further, due to self-limiting surface reactions, the ALD is established for its ability to produce an accurate and precise thickness control. In this work we present a thoroughly study on the impact of PEALD parameters on the Ag deposition and consequently we demonstrate the self-saturated regime required for obtaining good control of the deposition and large-scale uniformity. A model explaining the Ag NPs growth mechanism correlated with the experimental results is also suggested. This fine control of the Ag NP morphology is of a great interest for applications based on SPR, as those require precise NP dimensions. Finally, we present an original two-step PECVD-CVD synthesis method for fabricating continuous and highly conductive ultra-thin films. The first step provides a uniform new morphology made of compact Ag NPs that is usually not achieved at low thickness with CVD or ALD. The experimental results suggest that the chemical reaction occurs not only on the surface but also in the gas phase. The second step, consisting in plasma post-treatment enhances the electrical conductivity of silver films by increasing the connectivity between particles. Electrical performances are comparable with those describing sputtered films. This novel leads to a high film conformality on complex lateral high aspect ratio structures, with better coverages than the one reported up to now for ALD of Ag. The presence of an absorbance peak in the visible range is a signature of metallic NP morphology causing localized surface plasmon resonance. By following the film reflectivity spectrum of Ag NP films, a 'continuous-like' behaviour explained by the Drude model is found at low wavelengths whereas higher wavelengths highlight a 'particle-like' behaviour sticking to the oscillator model. This evolution is similar for separated NPs using standard PE-ALD and for the films fabricated using the new approach. The plasma post-processing gives strong increase of the infrared reflectance (up to 97%) and a strong decrease (down to 3%) of near infrared transmittance.

**AA-TuP-59 Bipolar and Unipolar Resistive Switching in HfO_2 Based Films Embedding Ni Particles*, Joonas Merisalu,* *M. Otsus, T. Viskus, T. Kahro, A. Tarre, A. Kasikov, P. Ritslaid, J. Kozlova, J. Aarik, K. Kukli, A. Tamm,* University of Tartu, Estonia

Among various thin metal oxide films, studied as resistive switching (RS) media for memristor cells, HfO_2films have been mentioned as media where both unipolar and bipolar RS could be observed dependently on the cell design [1]. Nanocomposites of HfO_2 and foreign metal particles have also been studied as RS media [2]. However, different types of RS that can co-exist in these structures may destabilize RS and complicate programming-reading operations.

In the present work, changes in RS parameters and direction were studied in HfO_2 based films grown using two different ALD processes, based on $HfCl_4$ and O_3, and $Hf[N(C_2H_5)(CH_3)]_4$ (TEMAH) and O_2 plasma [3] as the precursors. Both sample sets contained cells where Ni particles with sizes of around 70 nm were embedded in HfO_2, as well as cells with particle-free HfO_2 films with the same thickness. All films demonstrated bipolar RS (Figs. 1 and 2). In some cases, clockwise and counterclockwise bipolar RS, and unipolar RS were detected in the same device. During endurance tests of some samples, the RS direction changed after several thousand RS cycles (Fig. 3).HfO_2 films grown from $HfCl_4$ demonstrated all three types of RS (Figs. 1, 3, and 5), whereas HfO_2 grown from $HfCl_4$ with Ni particles showed dominantly bipolar RS (Figs. 2 and 4). The endurance tests of the latter samples allowed recording 33000 RS cycles with the ratio between low and high resistivity states (LRS:HRS) of an order of magnitude (Fig. 4). HfO_2grown from TEMAH with Ni particles exhibited unipolar RS with reset voltage below 0.8 V (Fig. 6). The transition to LRS could place gradually. In the latter case intermediate current-voltage loops could be recorded before final transition to LRS (Fig. 6). This could indicate the possibility of multilevel switching.

References:

[1] F. Zahoor, T Zainal, A. Zulkifli, F. A. Khanday, Resistive random access memory (RRAM): an overview of materials, switching mechanism, performance, multilevel cell (mlc) storage, modeling, and applications. Nanoscale Res. Lett.15, 2020, 90.

[2] Y. Li, J. Tang, B. Gao, W. Sun, Q. Hua, W. Zhang, X. Li, W. Zhang, H. Qian, H. Wu, High-uniformity threshold switching HfO_2-based selectors with patterned Ag nanodots. Adv. Sci. 7, 2020, 2002251.

[3] M. Cortez-Valadez, C. Fierro, J.R. Farias-Mancilla, A. Vargas-Ortiz, M. Flores-Acosta, R. Ramírez-Bon, J.L. Enriquez-Carrejo, C. Soubervielle-Montalvo, P.G. Mani-Gonzalez, Comparison of $HfCl_4$, HfI_4 , TEMA-Hf, and TDMA-Hf as precursors in early growing stages of HfO_2 films deposited by ALD: A DFT study. Chem. Phys. 472, 2016, 81.

AA-TuP-60 Novel Sulfide and Nitride Materials by Plasma Enhanced Atomic Layer Deposition*, Jakob Zessin,* SENTECH Instruments GmbH, Germany*; M. Hagel, T. Reindl,* SF Nanostructuring Lab, Max Planck Institute for Solid State Research, Germany*; K. Küster,* SF Interface Analysis, Max Planck Institute for Solid State Research, Germany*; P. Plate,* SENTECH Instruments GmbH, Germany

The preparation of thin sulfide and nitride films for electronic applications attracts an increasing interest. Atomic layer deposition (ALD) is an advanced method used to deposit uniform thin films with precisely controlled thickness in the sub-nanometer range, on large surface area substrates and with complex 3D-geometries, which makes ALD an important technique in thin film and device manufacturing.

In this work, we investigate the deposition of Molybdenum disulfide (MoS_2) and Niobium nitride (NbN) as representative layers for sulfides and nitrides, respectively, which are used as active layers in electronic devices. MoS_2 is a 2D–material, which consist of a layered structure and the layers can be exfoliated to a single layer. Vice versa to exfoliation, a defined number of layers could be deposited by ALD. The properties of MoS_2 depend on the number of layers. For example, the band gap changes from 1.3 V (indirect) to 2 V (direct) when reducing the number of layers from bulk to a single monolayer.[1] MoS_2 can be used in manifold applications such as thin film transistors (TFTs), photovoltaic devices and as a catalyst for hydrogen evolution reaction due to its optical and electronic properties. NbN is a superconductor and has a critical temperature of up to 13.8 K.[2] Therefore, it has potential for application in single photon detectors.

The depositions have been carried out in a SENTECH plasma enhanced ALD (PEALD) tool. A PEALD process has been developed for MoS_2 and NbN films by using in-situ ellipsometry (SENTECH ALD Real Time Monitor). Furthermore, the films have been analyzed by ex-situ ellipsometry and X-ray photon spectroscopy to determine the optical parameters and the exact film composition. The film morphology of MoS_2 was investigated by means of scanning electron microscopy.

It is observed that MoS_2 features a saturated growth in the precursor half-cycle, but a clear saturation was not found during the plasma treatment step. The temperature window was determined between 200°C and 300°C. The first XPS results revealed the formation of MoS_2, however, there are some contaminations of carbon and oxygen present in the film.

The NbN film properties were investigated depending on the used gas species, i.e. nitrogen and hydrogen. A correlation between the obtained electrical properties of the films and the used plasma gases was observed. Tuning the plasma gas mixture allows to deposit high quality films at different substrate temperatures.

In conclusion, we show successful PEALD processes for the deposition of MoS_2 and NbN.

[1]Daleep et al. *J. Appl. Phys.***2016**, 119, 114309.

[2]Linzen et al. *Supercond Sci Technol***2017**, 30, 035010.

AA-TuP-61 Atomic Layer Deposition of Epsilon Near Zero Transparent Conducting Oxides*, Emily Duggan,* Tyndall National Institute, University College Cork, Ireland*; D. Ghindani,* Tampere University, Finland*; J. Lin,* Tyndall National Institute, University College Cork, Ireland*; H. Caglayan,* Tampere University, Finland*; I. Povey,* Tyndall National Institute, University College Cork, Ireland

An epsilon-near-zero (ENZ) material, in which the real component of the permittivity vanishes, exhibits distinct optical features such as large nonlinearity, near-zero refractive index, decoupling of electricity and magnetism, and infinite phase velocity. Furthermore, it has been shown that the refractive index of these transparent conductive oxides can be altered dramatically when light, with a large enough intensity and close to the plasma-resonance frequency (ENZ frequency), impinges on a layer of a few tens of nm-thickness, these changes are rapid and reversible, with the material being excited and returning to its original state on a timescale of a few picoseconds. Such properties give ENZ materials the potential to revolutionise ultrafast photonic devices.

In this study we have used atomic layer deposition (ALD) to realise ENZ characteristics in doped ZnO. All growth was performed in a Picosun R200 in thermal mode, using Diethylzinc, Tetrakis(dimethylamino)titanium and Trimethylaluminium as the metal sources, and water as the co-reagent. Doping was performed using a laminate methodology. The ENZ frequency was tuned by varying growth parameters, thickness, and doping ratios to optimise the response at the communication wavelength of 1.6 micron. The use of ALD to generate an efficient ENZ material is a significant step to realising manufacturable materials that enable efficient light-light interaction-based device technologies.

AA-TuP-62 Magnetic Domain Creation by Local Reduction of Nickel Oxide Films*, Gabriele Botta,* BRTA CIC nanoGUNE, Italy*; M. Knez,* Nanomaterials Senior Scientists Ikerbasque professor in BRTA CIC nanoGUNE, Croatia

We propose an experimental route for locally modifying the magnetic properties of a ALD deposited NiO thin film (paramagnetic) by isothermal gas phase reduction in presence of hydrogen. Continuous NiO films were deposited by alternately pulsing Ni(Cp)2 and ozone at a temperature of 220 °C. In the present work it will be shown that a thin film of Al_2O_3 (5nm), deposited with TMA and ozone as co-precursor, can be used as a mask to prevent the diffusion of the reductant gas (H_2/Ar mixture) in the underlying NiO thin film and suppress its reduction to metallic nickel.

By patterning with eBeam lithography and anisotropic etching the aluminium mask and finely controlling the gas phase reduction step, this method can be utilized to fabricate nanostructured thin films of ferromagnetic domains (Ni) embedded in a paramagnetic medium (NiO).

The optimization of the reduction step will be discussed and the parameters which influence the creation of the magnetic nanostructures will be highlighted. It will be shown that the Al_2O_3 mask thickness and H_2/Ar pressure, play a crucial role on the diffusion of the gas into the masked areas and how they can be optimized to produce magnetic domains with a high degree of control.

This method will be employed for fabricating two different types of devices for testing the magneto-optical and electronic properties of the ALD materials. The magneto-optical characterization will be carried out by measuring the Magneto Optical Kerr Effect (MOKE) response of nickel nanoarrays produced in different annealing conditions (varying temperature, and reductant pressure). The transport measurement of the ferromagnet will be carried out on a Hall Bar device and the results will be compared with literature demonstrating that this methodology can be used to produce devices with novel functional designs.

AA-TuP-63 Optical and Electrical Device Properties of Plasma-Ald Grown β-Ga$_2$O$_3$

A. Rezk, Khalifa University of Science, Technology & Research, United Arab Emirates*; I. Saidjafarzoda,* University of Connecticut*; **Ali Kemal Okyay**,* Stanford University*; A. Nayfeh,* Khalifa University of Science, Technology & Research, United Arab Emirates*; N. Bıyıklı,* University of Connecticut

Wide bandgap (WBG) semiconductors, such as GaN and SiC make the backbone of high-power high-frequency electronics. However, production complexity and high-cost of these materials make such technologies less widespread. Gallium oxide (Ga$_2$O$_3$) is an emerging WBG semiconductor recently attracting great attention due to its superior electrical properties in this regard. To compete against the mature WBG materials which are grown typically at >1000°C, a substantially lower temperature deposition technique for crystalline Ga$_2$O$_3$ is critical, particularly for its integration with temperature-sensitive substrates. In this study Ga$_2$O$_3$ films were grown on Si, sapphire, glass, and Kapton substrates via hollow-cathode plasma-assisted atomic layer deposition. Films were deposited using triethylgallium and Ar/O$_2$ plasma as metal precursor and oxygen co-reactant, respectively. Growth experiments have been performed at 150-240°C substrate temperature and 30-200W rf-power range. Additionally, each unit AB-type ALD-cycle was followed by an *in-situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20sec varied over 50-300W rf-power. X-ray diffraction showed that Ga$_2$O$_3$ films grown without *in-situ* plasma annealing exhibited amorphous character irrespective of both substrate temperature and rf-power. Though, with the incorporation of the *in-situ* Ar-annealing step the films grown on Si and glass displayed polycrystalline *β*-Ga$_2$O$_3$ crystal phase with further improving crystallinity and film density (from 5.07 to 5.60g/cm^3) with increasing Ar-annealing plasma power. However, XRD analysis of samples deposited at 240°C on sapphire revealed epitaxial monoclinic *β*-Ga$_2$O$_3$.

Conductive atomic force microscopy (CAFM) is used to investigate the structural and electrical characteristics of *β*-Ga$_2$O$_3$films. CAFM is used to generate the electrical I-V response of the grown films on Si. For the electrical measurements and topography, Au coated AFM tips with a 146 kHz resonance frequency and force constant of 1.2-29N/m are used. The used Asylum Research MFP-3D cAFM utilizes a probe holder (908.036) which is capable of measuring currents from ~1 pA to 20nA. During all electrical measurements the tips were grounded, and a bias was applied to the substrate.

Optical properties of the *β*-Ga$_2$O$_3$films were evaluated by building metal-semiconductor-metal photodetectors. The devices were illuminated by UV light (254nm) and photoresponse and dark current behavior were extracted. The reflection and the transmission spectra were measured using a UV–VIS spectrophotometer as a function of the incident wavelength, ranging from 250nm to 1500nm.

AA-TuP-64 The Electrical and Physical Characterization of n-type MoO$_X$ Thin-Film Fabricated by Plasma-Enhanced Atomic Layer Deposition

D. Wang, Feng Chia University, Taiwan*; **Pi-Chun Juan**, C. Tou,* Ming Chi University of Technology, Taiwan*; W. Cho, C. Chen, C. Kei,* National Applied Research Laboratories, Taiwan

The MoOX thin films have been successfully fabricated by PE-ALD technique with Mo(CO)$_6$ as the precursor. The physical and electrical properties as functions of film thickness and plasma power are studied. The intensity of crystallization increases with increasing film thickness of MoO$_x$, while decreases with increasing plasma power. The crystalline belongs to monoclinic b-MoO$_3$ phase. The transmittance is lower at thicker samples which show more crystallization than thinner films. Similarly, lower intensity of x-ray diffraction patterns at higher plasma power behaves low transmittance, which is corelated to the refractive index. In order to understand the current transportation of oxygen-deficient MoO$_x$ in our case, the Hall measurement equipped with precision pA-level source meters has been performed. We found that MoO$_x$ films prepared are semiconductor n-type conducting materials. The carrier concentration increases with increasing film thickness, but slightly decreases with increasing the plasma power. Though the concentration variation is small by different power, the resistivity shows five times increase as the plasma power changing from 50 W to 150 W. The formation of oxygen vacancies during ALD process, which induce n-type conductivity may play an important role in current behavior. When the thickness of film increases, the amount of oxygen vacancies is expected to be increased, which leads to a lower resistivity. On the other hand, the increase in plasma power, no matter what the carrier concentration or conductivity decreases, which is due to less oxygen vacancies formed in MoO$_x$ with more reaction with oxygen reactant.

AA-TuP-65 Enhanced Self-Assembled Monolayer Surface Coverage by ALD NiO in P-I-N Perovskite Solar Cells

N. Phung, M. Verheijen, A. Todinova, K. Datta, M. Verhage, Eindhoven University of Technology, Netherlands*; A. Al-Ashouri, H. Köbler, X. Li, A. Abate, S. Albrecht,* Helmholtz Zentrum Berlin, Germany*; **Mariadriana Creatore**,* Eindhoven University of Technology, Netherlands

Perovskites have attracted tremendous attention due to their excellent opto-electronic properties, enabling perovskite solar cells (PSCs) with a record efficiency of 25.5%[1]. ALD has been used widely in the perovskite field to deposit contact layers, buffer layers, and encapsulation layers. Notably, ALD NiO has been used successfully as hole transport layer (HTL) in PSCs.[2] In this contribution, we further investigate the application of ALD NiO, in combination with self-assembled monolayer (SAM) using MeO-2PACz ([2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid)in p-i-n PSCs.[3] We fabricate 8 nm ALD NiO to use in PSCs by bis-methylcyclopentadienyl-nickel (Ni(MeCp)$_2$) as precursor and O$_2$ plasma as co-reactant at a substrate temperature 150°C. Specifically, we focus on the surface coverage of SAM on ALD NiO/ITO and compare with the coverage directly on ITO.[4] Surface coverage is highly relevant in contacts for photovoltaic devices, since non-covered areas can result in electrical shunts, thus reducing the device efficiency.

Herein, we adopt TEM and analyse the ITO/(NiO/)SAM interface. Processing SAM directly on ITO results in an inhomogeneous layer, with areas exhibiting low molecular density. In contrast, the presence of NiO induces a homogenous SAM formation, characterized by a higher optical density (via spectroscopic ellipsometry) compared to ITO/SAM. This improvement of surface coverage is due to a higher hydroxyl group concentration on the NiO surface when compared to ITO, as revealed by XPS. Moreover, conductive AFM mapping reveals exposed ITO areas due to insufficient SAM coverage on ITO. Instead, ITO/NiO/SAM layer exhibits a uniform and low current map indicating a good coverage of SAM on NiO, and conformality of NiO on ITO. This difference in surface coverage translates into different devices efficiency spread when using the layers as HTL in PSCs using CsFAMAPb(I$_{0.83}$Br$_{0.17}$)$_3$ with FA and MA being formamidinium and methylammonium, respectively. Specifically, a larger efficiency spread with standard deviation of 1.1% is observed for ITO/SAM devices. Instead, the implementation of ALD NiO, by improving the SAM surface coverage, leads to a narrower distribution of efficiency, with a standard deviation down to 0.5%. This study indicates that the bi-layer ALD NiO/SAM can enable highly efficient large area PSCs, which is relevant for upscaling the technology.

1. Lee, *et al.*(2021). *Nature*, *598*, 444-450

2. Koushik, *et al.*(2019). *J. Mater. Chem. C7*, 12532–12543

3. Al-Ashouri, *et al.*(2019). *Energy Environ. Sci.*, *12*, 3356–3369

4. Phung, *et al.*(2022). *ACS Appl. Mater. Interfaces, 14*, 1, 2166–2176

AA-TuP-66 Direct Chemical Vapour Deposition of Graphene on Atomic Layer Deposited Functional Nickel Oxide

***Geedhika Poduval**, D. Ji, S. Bremner, R. Joshi, B. Hoex,* UNSW Sydney, Australia

The rise of graphene-based devices has generated enormous scientific attention to directly synthesize high-quality graphene onto insulating substrates. Currently, graphene layers are synthesized by chemical vapour deposition (CVD) at high temperatures on transition metals Cu and Ni. The graphene layer is subsequently transferred to the desired substrates for device applications. Conventionally, the transfer process involves a solution-based approach, which results in its chemical and physical denaturing. The transferability and quality of the graphene layer significantly influence the final device performance, meaning device yield remains a significant challenge.

Here, a new method is reported to directly synthesize graphene films on a functional layer - NiO_x without the need for an additional metal catalyst. In contrast to the conventional approach, where hazardous gases methane and hydrogen are used, here, ethanol, a non-toxic, liquid precursor, is used to directly grow graphene on atomic layer deposited (ALD) NiO_x. The first successful graphene growth is demonstrated, and its growth mechanism is investigated in detail. The reduction of the surface atomic layers of NiO_x to metallic Ni is found to be key to catalyzing graphene growth. This process resulted in bilayer graphene flakes. Further, the impact of physical vapour deposited (PVD) NiO_x and varying NiO_x thickness on graphene growth is studied. It is found that the PVD NiO_x layer is completely reduced during the CVD process. Whereas the dense layers afforded by ALD seem to be required to limit the reduction of the metal oxide film to the top surface resulting in the preservation of the metal oxide film at the substrate. The capability to directly grow graphene on a functional oxide layer that also acts as the catalyst using a nontoxic liquid precursor enables seamless integration of graphene into next-generation solar cells and optoelectronic devices.

AA-TuP-67 The Role of Defects in Tuning the Properties of Highly Conductive Cuprous Oxide Thin Films Revealed Through Positron Annihilation Spectroscopy*, **Abderrahime Sekkat,*** LMGP/IMEP-LAHC/SIMAP, France*; M. Oskar Liedke,* HZDR, Germany*; V. Huong Nguyen,* Phenikaa, Viet Nam*; M. Butterling,* HZDR, Germany*; F. Baiutti, J. de Dios Sirvent,* IREC, Spain*; M. Weber, L. Rapenne, D. Bellet,* LMGP, France*; G. Chichignoud,* SIMAP, Grenoble-INP, CNRS, France*; A. Kaminski-Cachopo,* IMEP-LAHC, France*; E. Hirschmann, A. Wagner,* HZDR, Germany*; D. Muñoz-Rojas,* LMGP, France

Cu_2O, being a non-toxic and abundant p-type semiconductor, is drawing a lot of attention for several energy applications. So far, the lowest resistivity values have been obtained for films deposited by physical methods and/or at high temperatures (~1000 °C), limiting their mass integration. In this work, Cu_2O thin films with record resistivity values of 0.4 Ω.cm were deposited at only 260 °C by atmospheric pressure spatial atomic layer deposition, a scalable chemical approach. The carrier concentration (7.10^{14}-2.10^{18} cm^{-3}), mobility (1- 86 cm^2/V.s), and optical bandgap (2.2-2.48 eV) can be simply tuned by varying the deposition parameters. Our results show that the transport properties of the films are correlated to the nature and concentration of defects, as revealed by positron annihilation spectroscopy (PAS) studies and density functional theory calculations. This study reveals the existence of large complex defects and the evolution of the overall defects concentration and transport properties evolving with varying deposition conditions, opening prospects for the adoption of Cu_2O.

AA-TuP-68 Highly Conformal CoO_X Layer Formed by Atomic Layer Deposition for High Performance Supercapacitors*, S. Adhikari, G. Noh,* Chonnam National University, Korea (Republic of)*; **do heyoung kim,*** 5-404, Engineering Building 5,, Korea (Republic of)

Binary metal sulfides (BMSs) have attracted great attention over the decades for electrochemical energy storage systems. In particular, BMSs acts as a promising electrode material for supercapacitor application. Compared to their individual sulfide counterparts, BMSs exhibit enhanced electronic conductivity with faster redox reactions. However, stability and capacity retention are the bottlenecks that restricts their applicability. In this regard, atomic layer deposition (ALD) has emerged as an advanced deposition technique, which can tune the performance through atomic level conformal deposition contributing in stable surface reactions for prolonged time-period. In addition, the specific capacitance is influenced by the ALD thickness, leaving more room to understand the electrode-electrolyte interactions. Therefore, the present work will demonstrate the supercapacitor performance of ALD CoO_x on hydrothermally grown and sulfurized $MnCo\text{-}_2S_4$ nanoneedles. The effect of ALD thickness on performance, stability, and capacity retention will be understood and evaluated.

AA-TuP-69 Ultra-low Resistivity Molybdenum Carbide Thin Films Deposited by Plasma-Enhanced Atomic Layer Deposition Using a Cyclopentadienyl-based Precursor*, **Min-Ji Ha,** J. Choi, J. Ahn,* Hanyang University, Korea (Republic of)

As memory devices become ultra-miniaturized, the increase in the resistance of the metal line due to the decrease in the line width has become a very critical issue. Mo-based materials have been studied as candidates for next-generation metal line materials because of their low resistivity at low thickness and excellent oxidation resistance. However, the development of precursors suitable for vapor deposition methods (such as atomic layer deposition) is immature. In this study, we propose an ultra-low resistivity MoC_x thin film using a cyclopentadienyl-basedprecursor as a new metal line candidate. Using a halogen-free liquid precursor, MoC_x thin films were successfully deposited by PEALD in a wide process window of 200-300 ºC. We confirmed that uniform and continuous films were deposited on the SiO_2 substrates without any significant incubation period. The most important result of this study is that as-deposited MoC_x thin films exhibited an ultra-low resistivity of 8-20 μΩ·cm,and such ultra-low resistivity was maintained even with a thickness as thin as 4.25 nm and after rapid thermal annealing up to 600 ºC. This is the lowest resistivity value of reported metal line candidate materials available at the sub-10 nm device scale level. The ultra-low resistivity at a very thin thickness and excellent thermal stability suggest the possibility that the MoC_x thin films proposed in this study can be applied in various applications as a next-generation metal line material in the semiconductor industry.

AA-TuP-70 A Simple Strategy to Realize Super Stable Ferroelectric Capacitor via Interface Engineering*, **Hyo-Bae Kim,*** Hanyang University, Korea (Republic of)*; K. Dae, J. Jang,* Korea Basic Science Institute (KBSI), Korea (Republic of)*; J. Ahn,* Hanyang University, Korea (Republic of)

Fluorite-structure ferroelectric thin films have been extensively studied as promising candidates for next generation non-volatile memory. However, these ferroelectric thin films have fatal issues such as low cycling endurance, and wake-up and fatigue during cycling endurance tests. These problems are reportedly caused by oxygen vacancies, which form due to the interface reaction between the thin films and bottom electrode during deposition and the post-annealing process. Therefore, we expected that the critical problems of fluorite-structure ferroelectric thin films can be solved by controlling the amount of oxygen vacancies by preventing unwanted interface reactions. In this work, the enhanced ferroelectric characteristics of $Hf_{1-x}Zr_xO_2$ thin films that control the oxygen vacancies in thin films through interfacial pre-treatment were investigated. Interfacial pre-treatment using an oxygen source can reduce oxygen vacancies and improve crystallinity through intentional oxidation of the bottom electrode. As a result, the remanent polarization value was increased by about 1.6 times by applying the optimized pre-treatment condition, and the measured $2P_r$ value of 73 μC/cm^2. Furthermore, it exhibited very stable ferroelectric properties without a wake-up effect or significant fatigue, up to 10^8 cycles even under a severe electric-field of 3.5 MV/cm. This simple strategy provides a new avenue to effectively improve the performance and cycling endurance of devices with ferroelectric thin films.

AA-TuP-71 Area-Selective Atomic Layer Deposition Brings Plasmonic Biosensors Into the Electronic Age*, **Corbin Feit,*** University of Central Florida*; P. Rathi, S. Singamaneni,* Washington University in St. Louis*; P. Banerjee,* University of Central Florida

Label-free biosensing platforms based on refractive index sensitivity of localized surface plasmon resonance (LSPR) hold significant importance in healthcare as diagnostic tools. Colorimetric biosensors use plasmonic nanostructures that exhibit significant light-matter enhancement in the nanoscale. Upon a specific biomarker binding event, optical shifts of the LSPR are detected through spectrophotometry. Point-of-care is limited by the bulky, expensive, and labor-intensive use of spectrometers. Efforts to miniaturize instrumentation diminishes the spectral resolution, which in turn compromises the limit of detection for shifts of the LSPR.

To overcome the limitations that arise from current state-of-art optical readout technologies, we present detailed results of a “plasmo-resistor" sensor that electronically monitors the photocurrent generated by hot electrons (HE) emitted from plasmonic gold nanorods (AuNRs). Nanoscale engineering is required to deposit conductive films for transferring hot electrons through a vicinal medium, while maintaining viable plasmonic nanostructures for conjugation with biomarkers. Area-selective atomic layer deposition (AS-ALD) remains the only suitable technique capable of meeting this constraint. The fabrication and viability of partially embedded AuNRs in AS-ALD of zinc oxide (ZnO) on a two-electrode device is probed by UV-Vis and Raman spectrometry, AFM, and TEM. We investigate the electronic properties of the AuNR-ZnO nanocomposite and demonstrate the excitation of HE mirrors the optical response of the LSPR. Through coupled Raman microspectroscopy and laser beam induced current (LBIC) measurements a change in photocurrent caused by shifts in the LSPR is linked to an aminothiolphenol binding event. This proof-of-concept plasmo-resistor device is expected to pave the way for detection of biomarkers via the coupling of highly sensitive changes to LSPR to an electronic signal thus, negating the use of expensive, bulky and labor-intensive instrumentation.

AA-TuP-73 Annealed ALD TiN_X Layers for Through-Silicon Superconducting Interconnects, ***Kestutis Grigoras***, *P. Eskelinen,* VTT Technical Research Centre of Finland, Ltd, Finland*; M. Caputo,* VTT Technical Research Centre of Finlandt, Ltd, Finland*; D. Datta,* VTT Technical Research Centre of Finland, LTD, Finland*; A. Ronzani,* VTT Technical Research Centre of Finland, Ltd, Finland*; E. Mannila, J. Govenius,* VTT Technical Research Centre of Finland, LTD, Finland

The unique mechanical, electrical, and chemical properties of titanium nitride facilitate a wide range of applications. TiN layers are employed as drill coating materials, as MOSFET gate electrodes, as diffusion barriers for Cu, as 3D interconnects, and even as gold imitating coatings on watches. Many of those applications can benefit from atomic layer deposition (ALD), which offers conformal coating and precise control of film thickness [1, 2]. During subsequent fabrication steps, or during device operation, the TiN coating can experience thermal cycling. Therefore, understanding the effect of annealing TiN layers at various temperatures is important.

In this work, we investigate the influence of annealing on electrical conductivity, residual stress, and optical properties of TiN_x layers. Layers are grown on 6-inch wafers by a thermal ALD process at 450ºC using $TiCl_4$ and ammonia as precursors and nitrogen as a carrier gas. Pulse and purge times were tuned in order to change film stress and resistivity. The obtained thicknesses are 50 to 150 nm, and the growth per cycle is approximately 0.19 Å. Coated wafers are annealed for 5 to 10 minutes at 700, 800 or 900ºC in nitrogen atmosphere. As grown and annealed samples are characterized by scanning electron microscope (SEM), 4-point probe measurements, ellipsometry, X-ray diffraction (XRD), and laser reflection based residual stress measurement.

We obtain resistivities of approximately 200 to 300 µOhm cm and tensile stresses of approximately 1.5 GPa for as deposited layers. Tests show that TiN films are sensitive to annealing conditions: presence of humidity or oxygen results in degradation: resistivity increases to the MOhm-cm range, also visually layers change and partly peel off from the substrate (Fig. 1). Minimizing pressure and increasing nitrogen flow during annealing results in uniform and bright films, even for different initial thicknesses (Fig.1). The resistivity also decreases, by a factor of 2 to 3 for layers annealed at 900ºC. This may be explained partly by a change in crystallinity (Fig. 2) and by possible additional nitridation of layers: our earlier investigations by ToF ERDA showed that the main impurity of as grown layers was oxygen [3]. An important result is the increase of the critical temperature of the superconducting phase T_c from 100 mK to 3 K after annealing.

42. Grigoras et al, Nano Energy 26 (2016) 340-345
43. Grigoras et al, 21st Electronics Packaging Technology Conference (2019) 81-82
44. Grigoras et al, ALD2016, Technical Program & Abstracts American Vacuum Society (2016)

AA-TuP-74 Plasma-Enhanced Atomic Layer Deposition of Crystalline NiO Films Using Nickelocene and O2 Plasmas for BEOL p-Channel Devices*, S. Ilhom, A. Mohammad, M. Niemiec, D. Zacharzewski, P. Chardavoyne, S. Abdari,* ***Necmi Biyikli,*** University of Connecticut

In contrast to the relative abundance of as-grown unintentionally doped n-type semiconductor materials, there are only a few alternative alloys showing p-type conduction without needing extra high-temperature doping processes. Among them, CuO, Bi_2O_3, SnO, and NiO represent the most widely studied metal oxides which exhibit native p-type properties. NiO is of particular interest mainly due to its stability and promising performance as hole-transport layers in emerging solar cell device structures. However, to broaden the NiO application domain towards potential back-end-of-the-line (BEOL) transistor devices as potential p-type channel layers, the transport properties of NiO needs to be improved significantly. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have resulted in p-type NiO films with atomic-level precision and large-area uniformity, the hole mobility is far from being sufficient, typically lower than 1 cm^2/Vs.

In an attempt to enhance the hole transport properties in low-temperature as-grown NiO layers, in this study we have carried out a systematic study on plasma-enhanced ALD (PEALD) of NiO films on Si and glass substrates using nickelocene ($NiCp_2$) and O_2/Ar plasma mixture in two separate plasma reactors equipped with inductively coupled and hollow-cathode plasma sources. Detailed saturation studies using in-situ ellipsometer monitoring were carried out in the HCP-ALD reactor, scanning for $NiCp_2$ pulse time, O_2 plasma exposure time, purge time, and plasma power. Optimal growth conditions were identified as 90 ms NiCp2 pulse / 5 s purge / 10 s O_2-plasma@ 100W / 5 s purge. To check the growth linearity and obtain thicker films for materials characterization, 800 cycle runs were conducted to evaluate the substrate temperature impact (100 - 250 °C) on growth-per-cycle (GPC) and film properties. The last growth parameter studied was the plasma gas composition, where several O_2/Ar mixtures (20/0, 20/20, 20/50, 50/20 sccm) were tested at the optimal substrate temperature.

The resulting NiO films are characterized for their optical, structural, and electrical properties. Film grown at optimal conditions exhibit refractive index values within a range of 2.1 - 2.2, which is in good agreement with reported values in the literature. NiO films deposited on both Si and glass substrates exhibit polycrystalline single-phase cubic structure (c-NiO). Initial electrical measurements confirm p-type conductivity of the as-grown NiO layers on glass substrates, with resistivity values about 40 and 150 ohm-cm for HCP and ICP samples, respectively. Hall measurements will be carried out, analyzed, and presented in detail as well.

ALD for Manufacturing
Room Arteveldeforum & Pedro de Gante - Session AM-TuP
ALD for Manufacturing Poster Session

AM-TuP-1 Atmospheric Pressure Plasma Enhanced Spatial ALD for Energy Applications*,* ***Corne Frijters****, V. Tielen, R. Pals, J. Smeltink, K. Driessen, H. Heezen, P. Poodt,* SALDtech B.V., Netherlands

One of our greatest challenges for the coming decade is the transition to a sustainable way of generating, storing, and converting energy. High performance batteries, fuel cells, electrolyzers and solar cells are part of the solution, but still face many challenges that need to be solved. Efficiencies and capacities need to increase, the use of scarce and expensive materials needs to reduce and the life-time needs to improve. There are many examples where ALD has been used to improve on these aspects. For example, by applying thin and highly conformal films on porous substrates using ALD, the lifetime of Li-ion batteries can be improved, the loading of expensive catalyst materials in fuel cells and electrolyzers can be reduced and new devices such as 3D solid state batteries are enabled. In order to enable large-scale mass production of these applications, Spatial ALD can be used for high deposition rates on both large substrates (square meters) and roll-to-roll.

Precise control of film thickness uniformity is essential for a reliable performance of energy devices. We will show that we have used CFD modeling to develop a remote atmospheric pressure plasma source that is integrated in our Spatial ALD tool, demonstrating excellent uniformity of plasma gas flows towards the surface, leading to thickness non-uniformities of less than 2% over more than 30 cm widths.

This plasma source also allows to do maskless patterned deposition, in combination with stripe coating, to only deposit films on targeted active areas and not in between. Not only does maskless patterned deposition mean that no masks are required, it also leads to a significant decrease in precursor use, as precursors are only dosed where and when required. Especially in the case of expensive materials, like platinum-group metals, this is essential to minimize cost. Additionally, there is the option to reclaim unreacted precursor from the Spatial ALD reactor for recycling purposes, further decreasing the overall process costs.

Finally we will show how these components have been integrated in a 300 mm Spatial ALD R&D tool, that can be used to deposit a range of different materials on substrates of various shapes and sizes. This tool can be used to develop and optimize Spatial ALD processes for energy applications, in preparation for future large-area or roll-to-roll manufacturing.

AM-TuP-2 Computational Fluid Dynamics Analysis of Cyclone-Type Vaporizer for Atomic Layer Deposition*, D. Shin,* ***Cha-Hee Kim,*** Sejong University, Korea (Republic of)*; S. Seo, Y. Lee, K. Jeong, D. Kim,* GO Element Co. Ltd., Korea (Republic of)*; W. Lee,* Sejong University, Korea (Republic of)

Due to the three-dimensionalization of semiconductor devices, the substrate surface area for atomic layer deposition (ALD) increases, requiring high-capacity precursor delivery systems. The commercial liquid delivery system (LDS) has a vaporizer with complicated pathways to secure a sufficient vaporization area. However, since it is difficult to control the inner wall temperature of the vaporizer precisely, there are concerns about line clogging and particle generations due to the condensation or decomposition of the precursor [1]. The development of vaporizers has relied heavily on experimental trial-and-error methods. Computational fluid dynamics (CFD) can analyze the gas flow and temperature distribution inside the vaporizer, which enables the prediction of potential issues and the optimization of the vaporizer structure. In this study, we proposed a cyclone-type vaporizer structure for a high-capacity LDS. We performed CFD analysis for cyclone-type vaporizers with different design parameters, such as inlet guide pipe diameter, outlet length, cylinder length, and total length. The optimized model that maximizes the gas flow path and minimizes the temperature nonuniformity was selected based on the CFD results. The optimized model showed better characteristics than the conventional Lapple-type cyclone structure [2].

[1]K. Erickson et al, Advanced Semiconductor Manufacturing Conference, (2019)

[2] C. E. Lapple, Chemical Engineering, (1951)

AM-TuP-3 Lightweight, Modular Model for Multizone Spatial ALD*, Angel Yanguas-Gil,* *J. Elam,* Argonne National Laboratory

Spatial ALD is a promising route for transitioning ALD processes into manufacturing that has long been explored by the research community and that is compatible with a wide range of applications, from photovoltaics to energy storage and separations membranes. As part of our development of an atmospheric pressure spatial ALD tool, we developed a simple model to explore the evolution of surface coverage and film thickness as a moving web or substrate passes through a series of spatially-separated precursor zones. Our simulation approach solves the reactive transport and surface reaction of ALD precursors under realistic conditions all the way from the precursor insertion point to the upstream and downstream exhaust regions, tracking the evolution of surface coverage and precursor concentration at each point on the substrate surface. By coupling multiple zones, we were able to simulate experimental configurations involving multiple ALD cycles in a single pass.

To benchmark this simple model, we compared the model results with those of 2D computational fluid dynamic (CFD) simulations that computed the reactive transport of precursor and the evolution of surface coverage as the substrate moves through a single ALD zone. The agreement between the simple model and the CFD simulation is excellent under conditions where precursor transport is efficient and the gap above the substrate is small enough to prevent the formation of significant mass boundary layers. We then applied these simulations to model the evolution of surface coverage and film thickness over multiple precursor/co-reactant zones. Our results show that after two cycles the growth per cycle achieved by passing through a single zone reaches a steady state value. Depending on the web velocity, substantial growth can take place in the inert gas purge regions upstream and downstream of the precursor insertion point.

This research was funded through Argonne's LDRD program.

AM-TuP-4 Effect of Surface Treatment of Tan for Rapid Nucleation and Growth of ALD Ru Films*, Corbin Feit,* *U. Kumar, L. Tomar, Z. Caribe, N. Berriel , S. Seal , P. Banerjee,* University of Central Florida

Ruthenium (Ru) is a promising alternative to copper interconnects due to its improved electromigration with reducing line width and excludes the need for diffusion barriers compared to copper interconnects. Atomic layer deposition (ALD) is the industry standard for ultra-thin film deposition. However, the challenges of depositing ultra-thin films of Ru remain. Current Ru ALD processes proceed through island-like growth as a result of poor nucleation, especially on industrially relevant tantalum nitride (TaN) surfaces. This growth behavior hinders coalescence in the ultra-thin (i.e., < 10 nm) regime, which ultimately leads to increased surface roughness, resistance, and diffusion. Through surface engineering of TaN surfaces, improved nucleation and growth can be achieved.

This work investigates the effect of pretreatments on TaN surfaces on inducing Ru nucleation and growth to achieve early coalescence of ultra-thin films using Ru-dimethyl butadiene tri-carbonyl ($Ru(DMBD)(CO)_3$) and H_2O (growth rate = 0.1 nm/cy).Pretreatments include UV-ozone, hydrogen plasma, and strong reducing agents such as trimethyl aluminum. The film nucleation and roughness are monitored by atomic force microscopy. The Ru thickness is measured by spectroscopic ellipsometry. The interface chemistry is probed by X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. Finally, electrical probing elucidates the film coalescence via conductivity.

The as-deposited TaN surfaces induced a significant nucleation delay and roughness of Ru ALD (> 0.5 nm). Alternatively, UV-ozone pretreatment on TaN shows no indication of island-like growth and no marked increase in film roughness of Ru ALD (< 0.3nm). The enhanced nucleation and growth of Ru ALD on UV-ozone treated TaN is attributed to increased wettability. The role of TaN oxidation states on nucleation is understood through XPS. We provide evidence that UV-ozone treatment enhances nucleation and growth of Ru films on TaN without effecting the overall sheet resistance. Ultra-smooth, 2 nm Ru films on UV-ozone treated TaN can be achieved. In addition, the effect of strong reducing agents on inducing nucleation and growth of Ru ALD on TaN surfaces will be discussed.

AM-TuP-5 How to Improve ALD Process Consistency with Optimized Process Valves and Pneumatic Control Systems*, Masroor Malik,* *J. Butler,* Swagelok Company

Atomic layer processes (ALD/ALE) generally rely on specialized high-purity valves for precise chemical dosing. Fast and consistent valve actuation performance is critical for efficient, accurate, and reliable atomic layer processes. Pneumatically actuated high-purity valves offer response times under 10ms with better than 1ms consistency and remain the most effective solution for atomic layer process chemical delivery systems. The performance of these high-performance atomic layer process valves is highly dependent on the pneumatic system that drives them.

The performance and characteristics of pneumatic systems used to operate atomic layer process valves will be analyzed and reviewed. Performance data and design guidelines for optimizing a pneumatic system for fast and reliable chemical dosing will be provided. A poster that highlights the relationship between the many pneumatic system parameters and the process dose output will be submitted.

AM-TuP-6 Spatial Atomic Layer Deposition for the Coating of Tubular Membranes*, F. Toldra-Reig,* Laboratoire des Matériaux et du Génie Physique, LMGP-CNRS, France*;* ***Clément Lausecker,*** Institut Européen des Membranes, IEM-CNRS / Laboratoire des Matériaux et du Génie Physique, LMGP-CNRS , France*; M. Weber,* Laboratoire des Matériaux et du Génie Physique, LMGP-CNRS, France*; M. Bechelany,* Institut Européen des Membranes, IEM-CNRS, France*; D. Muñoz-Rojas,* Laboratoire des Matériaux et du Génie Physique, LMGP-CNRS, France

Highly efficient gas separation membranes represent a promising prospect for the energy sector and the chemical industry, as they are able to significantly reduce cost, energy, and environmental impact of many processes while also being considered as a key element for process intensification. Tubular-shaped membranes are particularly appealing since they offer stronger adaptability, more convenient cleaning, easier sealing, higher pressure resistance, and higher modularity than their planar counterparts. Furthermore, the membrane surface properties has to be precisely controlled during the fabrication process in order to enhance gas selectivity and permeability. In this context, atomic layer deposition (ALD) has become a valuable technique for membrane surface preparation. Recently, spatial ALD (SALD) has gained increasing interest as it enables the possibility to form high quality thin films under atmospheric pressure faster than conventional ALD while keeping high uniformity, excellent conformality, and good thickness control on substrates with high aspect ratios. Moreover, SALD presents the unique asset of being compatible with the use of 3D printed gas manifolds to readily customize the system to different deposition configurations. Therefore, the SALD technique is particularly suited for the preparation and optimization of membrane surfaces, although it has been limited so far to planar substrates.

In this work, we present a novel approach to perform thin film deposition by SALD on tubular surfaces such as tubular membrane supports. A dedicated custom close-proximity SALD gas manifold was designed, where polymer 3D printing was advantageously used for rapid prototyping and optimization. By implementing the 3D printed gas manifold in the SALD system, various materials such as ZnO were successfully deposited on different tubular surfaces including porous Al_2O_3 membrane supports. Furthermore, by optimizing the material and design used to fabricate the 3D printed gas manifold, this approach can be applied to a broad range of chemical precursors and non-planar surfaces. These results thus reveal the great potential of this new versatile approach for membrane applications, and also extends the capability of SALD for the coating of complex substrates with functional materials which could be of high interest for a variety of other applications including electrolyzers and fuel cells.

AM-TuP-7 Hybrid PEALD/PECVD Reactor Design for Depositing Thick GaN Films on Si*, **Birol Kuyel**, J. Marshall, A. Alphonse,* NANO-MASTER, Inc.

Depositing thick GaN on Si wafer using PECVD or CVD will require a thin buffer layer on sapphire wafers. We have presented results showingALD deposited GaN on Si wafer could possibly be a buffer layer for growing thick GaN layer on Si because of Si/GaN interlayer mixing* during ALD deposition. Now we want to show results of depositing a thick GaN film in a PECVD system on a Si wafer having ALD GaN. Furthermore we will show that our new "Hybrid PEALD/PECVD reactor"** can deposit both thin ALD buffer layer and thick PECVD GaN on Si wafer in same chamber without changing the hardware and breaking the vacuum.

*Deposition of GaN using $GaCl_3$ with N_2 plasma using PAALD, 44th ICMCTF conference at San Deigo, Apr 2015.

**Patent pending

AM-TuP-8 Deposition of $CeO_{2-\delta}$ Thin Films by Atmospheric-Pressure Spatial Atomic Layer Deposition*, **Ozden Celikbilek**,* Univ. Grenoble Alpes, CNRS, France*; M. Bianchini,* Catalonia Institute for Energy Research (IREC), Spain*; F. Toldra-Reid,* Univ. Grenoble Alpes, CNRS, Spain*; A. Sekkat ,* Univ. Grenoble Alpes, CNRS, France*; N. Alayo , A. Tarancón ,* Catalonia Institute for Energy Research (IREC), Spain*; D. Muñoz-Rojas ,* Univ. Grenoble Alpes, CNRS, France

With the discovery of nanoscale phenomena in thin films (TFs), such as grain boundary and strain engineering, increases in Solid Oxide Cells (SOCs) performance up to several orders of magnitude have been achieved.(1) Therefore, Thin film Solid Oxide Cells (TF-SOCs) has received considerable attention as alternatives for their thick, powder-based counterparts. In this study, we aim to develop durable and scalable TF-SOC materialsusing Spatial Atomic Layer Deposition (SALD) technique which provides high-quality film growth under atmospheric pressure and at faster deposition rates than Atomic Layer Deposition (ALD).(2) Since our SALD approach works in the open air, i.e. at atmospheric pressure, it is challenging to find sufficiently volatile, reactive and non-toxic precursors. In the case of $CeO_{2-\delta}$ (ceria), this is particularly difficult due to the low volatility and toxicity of standard Ce precursors. In our communication we will show a comparative study of the deposition of ceria films by SALD using non-toxic precursors.

(1)Acosta, M. *et al*. *Adv. Mater. Interfaces*, 1900462, 1–15 (2019).

(2)Muñoz-Rojas, D. *et al.Mater. Today Chem.*,**12**, 96–120 (2019).

AM-TuP-9 Thermoelectric Performance Improvement by Interface Engineering With Atomic-Layer-Deposited ZnO Thin Films on Snse Powders*, **Myeong Jun Jung**, Y. Weon, J. Park, Y. Yun, J. Byun, B. Choi,* Seoul National University of Science and Technology, Korea (Republic of)

Thermoelectric device, one of energy harvesting is a device that converts thermal energy into electrical energy can recycle wasted thermal energy. However, since improvement of thermoelectric performance is still required, various kinds of research are being conducted. In particular, many studies have been reported on the improvement of thermoelectric performance through the introduction of nanostructures. Atomic layer deposition (ALD) on powder materials is one of them. ALD thin film on powders increases interfaces by preventing the growth of grains during the bulking process. ALD-engineered interface between powders and thin films reduces thermal conductivity through phonon scattering, and the energy filtering effect increases the Seebeck coefficient by generating a potential difference. In this study, SnSe and ZnO were selected as the thermoelectric powder and thin film material, respectively. SnSe shows excellent thermoelectric performance under high temperature (>700K). ZnO thin film has superior electrical properties compared to other oxide films, is easy to deposit, and has a difference in bandgap energy from SnSe, making it possible to introduce an energy filtering effect.

SnSe powders were ground by ball mill (250 RPM, 50hr). ALD coating process on SnSe powders was proceeded with rotary-type ALD reactor (CN-1, Korea). For understanding the thickness effect, 10 , 40, and 100 cycles of ZnO thin films were grown with DEZ (diethylzinc) source and H_2O (water) reactant at 100˚C. Uncoated SnSe powder was also used as a control group. SnSe pellets were produced through Spark plasma sintering at 60MPa, 723K for 6 minutes. Scanning and transmission electron microscopy combined with energy-dispersive spectroscopy (EDS) were used to confirm the uniform growth of thin film and its structural and chemical properties. X-ray photoelectron spectroscopy and X-ray diffraction was used to confirm chemical bonding states and structures. Thermoelectric performance was obtained by measuring thermal conductivity, thermal diffusivity, electrical resistivity, and Seebeck coefficient by laser flash analysis and Seebeck and electrical resistivity measurement system. As a result of calculating zT, figure of merit, through the obtained properties, it was demonstrated that the performance improvement up to about 40% was achieved by ZnO coating on SnSe powders.

AM-TuP-10 Mechanical Properties of Atomic-Layer-Deposited Al_2O_3/Y_2O_3 Nanolaminate Films on Aluminum Towards Protective Coatings*, **Barbara Putz**, J. Niemelä,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; G. Mata-Osoro,* INFICON Ltd., Liechtenstein, Switzerland*; C. Guerra-Nunez,* SwissCluster, Switzerland*; K. Mackosz, I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Atomic layer deposition is an appealing deposition technology for the fabrication of protective coatings for various applications, including semiconductor manufacturing chambers and related metallic parts with complex 3D topographies, where a key requirement is (thermo) mechanical robustness of the coatings. Here we study the mechanical properties of atomic layer deposited Al_2O_3, Y_2O_3 and their nanolaminate coatings on Al metal substrate. Tensile straining experiments accompanied with in-situ optical and scanning electron microscopy indicate that the fragmentation onset of 100-nm thick coatings can be tailored in the strain range of 1.3 – 2.1 % by controlling the layer structure and composition of the nanolaminates, such that a higher Al_2O_3 content, denser layer spacing and amorphisation favor higher crack onset strain. Although the fracture toughness of Al_2O_3 and Y_2O_3 are found to be similar, K_{IC} = 1.3 MPa·m$^{1/2}$, the (substantially tensile) intrinsic residual stress for Y_2O_3 is a disadvantage for applications where tensile applied stresses are to be expected. The films adhere well to the Al substrate as significant delamination of the films is not observed in the tensile experiments; the analysis of the fragmentation patterns indicates that insertion of an Al_2O_3 layer at the film/substrate interface can enhance interface toughness. High-temperature (425 ^{o}C) tensile experiments for the Al_2O_3 films indicate good temperature tolerance for the coatings, and in comparison to the room-temperature data, a significant difference is seen in the increase of saturation crack spacing. Moreover, structure and composition of the films are studied in detail through X-ray reflection and diffraction, transmission electron microscopy, Rutherford backscattering spectrometry, and elastic recoil detection analysis. The results are particularly interesting for protective coating applications.

AM-TuP-11 How to Improve Control of Plasma-Assisted Ald/Ale Processes by Accurate Measurement of Ion Flux, Ion Energy Distributions, and Ion-Neutral Ratios in Commercial Plasma Tools Using RFEAs*, A. Rawat, C. Linnane, **Sean Knott**, T. Gilmore,* Impedans Ltd, Ireland

Plasma assisted ALD/ALE processes have demonstrated potential advantages for next-generation semiconductor processes including high-k, multi-patterning and fin doping. However, with more spatially demanding structures and ever-shrinking device dimensions, the need for controllable and optimized plasma processes has never been greater. To fulfill this need, Impedans automated advanced Retarding Field Energy Analyzers (RFEAs) offers researchers, scientists, and engineers a versatile means to measure the ion energies and ion flux measurements [1, 2] at the substrate position, thereby providing deep insight into what happens at the wafer surfaces. *RFEAs* measure the uniformity of ion energies and ion flux hitting a surface, negative ions, and bias voltage at multiple locations inside a plasma chamber using an array of integrated sensors. A novel RFEA, that combines energy retarding grids with an integrated quartz crystal microbalance (QCM) allows measurements of the ion energy and flux properties as well as the ion-neutral ratio and deposition rate. The ion-neutral ratio is a critical control knob for optimizing film properties. A brief theory of operation will be described.

Measurements reported emphasize how the ion energy distribution of the ions impinging on the wafer can be adjusted with a broad range of plasma processing conditions. The data from various Oxford Instruments tools such as FlexAL, AtomFab, PlasmaPro, PlasmaLab will be presented [3, 4]. Some other major contributions to be showcased in this work include the evidence for low-energy ions influencing plasma-assisted ALD of SiO_2 [5], adjustment of the Argon ion energy in controlling an ALE process [6] and the influence of ions and photons during ALD of metal oxides [7] *etc.*, highlighting a few of the many possibilities that exist to gain more control over ALD/ALE processes.

References

[1] Impedans Ltd, Dublin, Ireland [www.impedans.com]

[2] S. Sharma *et al.*, Ph.D. Thesis, Dublin City University (2016)

[3] J. Buiter, Master's Thesis, Eindhoven University of Technology (2018)

[4] H. C. M. Knoops *et al.*, J. Vac. Sci. Technol. A 39, 062403 (2021)

[5] K. Arts *et al.*, Appl. Phys. Lett. 117, 031602 (2020)

[6] S. Dallorto, Ph.D. Thesis, Ilmenau University of Technology (2019)

[7] H. B. Profijt *et al.*, *ECS Trans.*33 61 (2010)

Area Selective ALD

Room Arteveldeforum & Pedro de Gante - Session AS-TuP

Area Selective ALD Poster Session

AS-TuP-1 Thermally Assisted Area Selective Atomic Layer Deposition*, Bart de Braaf,* TU / Eindhoven, Netherlands

In our recent published work, we explore the possibility of achieving area selective ALD by applying temperature gradients on the substrate [1]. In this approach, the majority of the substrate is kept at a low temperature, which suppresses the surface chemical reaction, while a small area is heated to allow the reaction to locally proceed. Controlling the size and the position of the heating spot on the substrate allows for 'writing' on the surface, with potential applications in the bottom-up fabrication of electronic devices like solar panels and OLED displays. We study the feasibility and window of opportunity of this technique by computational modelling. We first model the control of the temperature by various illumination protocols, and then model and simulate the nucleation and growth of spatially localized spots, as well as lines, of deposited material given an inhomogeneous temperature profile. We show that the temperature profile can direct substrate deposition and control the connectivity and size of the pattern deposited on the substrate.

A practical example of this technique is the ALD process of Si_2H_6, where instead of a co-reactant the elevated temperature induced by the laser itself is used to remove the ligands [2]. For this process, it is reported that surface diffusion of deposited molecules also influences growth of the spot that is formed on the substrate. I will present new results from a model that includes this surface diffusion, and study its effect on the deposition on the substrate both at constant temperature and for the case where locally the substrate is heated by a laser. Our model suggest that the absorption rate goes up with increasing diffusivity at constant temperature.

Bibliography

[1] B. de Braaf, C. R. (2021). Modeling the initial monolayer formation in thermally localized surface deposition. *J. Vac. Sci. Technol. B*.

[2] Y. Suda, M. I. (1996). Ar+-laser-assisted subatomic-layer epitaxy of Si. *Journal of Crystal Growth*, 672-680.

AS-TuP-2 An Approach to the Prevention of Chemical Deterioration of Surfaces During Ex-Situ Patterning Steps*, Bernhard van der Wel,* *T. Aarnink, A. Kovalgin,* University of Twente, the Netherlands

Atomic layer deposition (ALD), enabled by sequential self-limiting vapor-solid reactions, is a well-known technique to provide thin films with high conformality, large area uniformity and excellent film thickness control. Applying area-selective ALD (ASALD) allows for reduction of the amount of lithography and critical alignment steps during film patterning for device fabrication [1].

In this work, we propose a novel method for ex-situ thin film patterning, preventing possible chemical deterioration of the surfaces during patterning by chemicals and/or exposure to a reactive chemical ambient. This may be crucial to minimize the effect of undesired interaction of the surface with oxidants, etchants, etc. Preventing or re-establishing required chemical terminations (i.e., functional chemical groups) of the surface is needed to successfully enable a subsequent ASALD process.

After deposition of the material of interest on a substrate, it is capped in-situ (in-vacuo) by amorphous silicon (a-Si) using trisilane (Si_3H_8), protecting the film surface from subsequent possible chemical interactions. The protecting a-Si and underlying layer can be patterned ex-situ, without directly exposing the underlying film to a chemically reactive environment. This allows to prevent the surface of the underlying film from chemical modifications (e.g. by oxidation in the ambient or changing chemical termination of the surface by etching). After stripping the native oxide from the a-Si using hydrogen fluoride (1% HF), the patterned substrate is brought back to the reactor. Next, the substrate is exposed to atomic hydrogen (at-H), generated by letting H_2 interact with a heated tungsten filament, removing the silicon by forming volatile SiH_4 [2]. This opens up the initial film with the originally-present chemical terminations, favoring area-selective deposition by the next in-situ ALD step. A schematic overview of the designed process is given Figure 1, see supplemental document.

[1] A. J. M. Mackus, M. J. M. Merkx, and W. M. M. Kessels, "From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity," Chem. Mater., vol. 31, no. 1, pp. 2–12, 2019.

[2] H. N. Wanka and M. B. Schubert, "High silicon etch rates by hot filament generated atomic hydrogen," J. Phys. D. Appl. Phys., vol. 30, no. 8, pp. L28–L31, Apr. 1997.

AS-TuP-3 Surface Dependence and Selectivity During Atomic Layer Deposition of $Ge_2Sb_2Te_5$*, Jyoti Sinha,* *L. Gallis, J. Clerix,* KU Leuven, IMEC Belgium , Belgium*; L. Nyns,* IMEC Belgium , Belgium*; A. Delabie,* KU Leuven, IMEC Belgium , Belgium

The complex device architecture for Phase change Random Access Memory (PCRAM) has garnered attention towards Atomic Layer Deposition (ALD) for conformal or selective deposition. Ge2Sb2Te5 is one of the promising phase change materials which has been used in PCRAM devices. Ge2Sb2Te5 devices use either W or TiN as bottom electrode and SiO2 or SiN as isolating material for confining heat within the cell [1]. The development of selective deposition processes for such device structures benefits from insight in the growth behaviour of Ge2Sb2Te5 ALD. In this work, we therefore investigate the substrate dependence and selectivity of Ge2Sb2Te5 ALD where TiN and SiO2 were selected as substrates. GeCl2. C4H8O2, SbCl3 and ((CH3)3Si)2Te have been used as precursors to deposit Ge2Sb2Te5 by alternating GeTe and Sb2Te3 subcycles. The growth-per-cycle of Ge2Sb2Te5 ALD is 0.36 nm/cycle. Rutherford Backscattering Spectrometry (RBS) confirmed that Ge2Sb2Te5 layers of ~20 nm has the 2-2-5 composition. We observe linear ALD growth behaviour on both TiN and SiO2 substrates, indicative of fast film formation. Further, both substrates were treated with dimethylamino-trimethylsilane (DMA-TMS) to alter the surface properties for evaluating the selectivity of Ge2Sb2Te5 [2]. The DMA-TMS treatment on TiN shows minor effect on the surface composition and Ge2Sb2Te5 ALD growth behaviour. In contrast, the DMA-TMS treatment on SiO2 substantially inhibits the growth of Ge2Sb2Te5 (figure 1) and no nanoparticles are observed using scanning electron microscopy (SEM) till 64 cycles, while a Ge2Sb2Te5 layer of ~20 nm is obtained on DMA-TMS treated TiN. For higher number of cycles, nanoparticle analysis on DMA-TMS treated SiO2 indicates that growth of Ge2Sb2Te5 follows particle migration and coalescence (figure 2). Thus, the modified surface properties due to chemical treatment provides the selectivity of Ge2Sb2Te5 towards SiO2. This is confirmed by a demonstration of 20 nm of Ge2Sb2Te5 ASD in nanoscale SiO2/TiN line-space patterns.

AS-TuP-4 *In-situ* Surface Cleaning and Area Selective Deposition of SiO_xN_y film on Cu patterns using Anhydrous N_2H_4*, Su Min Hwang,* *J. Kim, D. Le, Y. Jung, K. Tan, J. Veyan,* University of Texas at Dallas*; D. Alvarez, J. Spiegelman,* RASIRC*; J. Kim,* University of Texas at Dallas

Area-selective atomic layer deposition (AS-ALD) has been considered as a prominent technique due to the escalating demands for eliminating the edge placement errors with current top-down approaches in semiconductor processing at the sub-5 nm node.$^{1–3}$. Recently, it has been reported that anhydrous hydrazine (N_2H_4) can be employed as the reduction of the Cu oxide to metallic Cu surface.^{3} By employing the high reactivity of hydrazine, under the ALD environment, the metallic surface condition can be maintained, or the oxidation/reduction of the Cu surface can be repeated under the ALD environment. Eventually, area selective deposition of dielectric material (e.g., ALD-SiO_x on Si, SiN_x, TiN, AlO_x, substrates) can be achieved, whereas nucleation delay and limiting surface oxidation on Cu sample can occur.Additionally, a detailed change of Cu condition with precursor exposures will be studied using *in-situ* surface analysis.

In this study, the consecutive surface cleaning and AS-ALD of SiO_2 process was demonstrated. To identify the substrate dependence on ALD selectivity, Cu, Si, SiN_x, TiN, and AlO_x substrates were loaded in the ALD chamber at the same time. Prior to the ASD process, the samples were pretreated with N_2H_4 at 200 ℃. After that, the ABC-type ALD-SiO_2 was performed. In the Si precursor half-cycle, the tris(dimethylamino)silane (step A), was exposed for 0.2 s, followed by a precursor trapping time for 120 s and purging time of 180 s. In the oxygen reactant half-cycle, the O_3/O_2gas mixture (step B), was introduced for 0.2 s and captured for 120 seconds, followed by purging the chamber with a continuous flow of N_2 carrier gas for 180 seconds. After the ALD-SiO_x cycle, an additional of surface recovery step with N_2H_4 (step C) was introduced. With five supercycle ALD-SiO_x processes, growth of SiO_2 on both bare Si and SiN_xsubstrates, formation of metal-silicates (and/or SiO_x) on TiN_x and AlO_x suggest that the supercycle-based ALD-SiO_xprocess does not impact the growth of SiO_x on top of dielectric substrates. On the other hand, the deposited amount of SiO_x on Cu substrate is approximately 35% less than the AB-typed ALD-SiO_x process. Despite slight detection of SiO_x on Cu (non-growth) substrate, the feasibility of the ASD process with repeating surface oxidation and reduction was demonstrated. The detailed experimental results will be presented.

We thank Rasirc Inc. for funding this project and providing the Brute N_2H_4.

[1] P. Kapur, et al., *IEEE Trans. Electron Devices,***49**, 590 (2002).

[2] M.F.J. Vos et al., *J. Phys. Chem. C,***122**, 22519 (2018).

[3] S.M. Hwang, et al., *ECS Trans*. **92**, 265 (2019).

AS-TuP-5 Inherently Area-Selective Atomic Layer Deposition of SiO_2 through Chemoselective Adsorption of an Aminodisilane Precursor on Oxide versus Nitride Substrates

***Jeong-Min Lee**, J. Lee,* Hanyang University, Korea (Republic of)*; H. Oh, B. Shong,* Hongik University, Korea (Republic of)*; T. Park, W. Kim,* Hanyang University, Korea (Republic of)

Area-selective atomic layer deposition (AS-ALD) offers complementary bottom-up patterning with atomic-level accuracy on pre-defined areas in conjunction with conventional top-down patterning, so it has attracted tremendous interest for enablement of multi-dimensional nanostructures toward sub-10 nm scale technology. In this work, we report a methodology for achieving inherently selective deposition of high-quality oxide thin films through chemoselective adsorption of an aminodisilane precursor, 1,2-bis(diisopropylamino)disilane (BDIPADS), on oxide versus nitride substrates. Density functional theory (DFT) calculations show higher reactivity for adsorption of BDIPADS on OH-terminated SiO_2 compared with NH_2-terminated SiN surfaces, indicating selective growth of SiO_2 films in the SiO_2 area. Applying BDIPADS precursor to both SiO_2 and SiN substrates results in inherent deposition selectivity of ~1 nm even without the use of inhibitory molecules such as self-assembled monolayers. Using this inherent selectivity as a starting point, we further enhance deposition selectivity using combined ALD-etching supercycle strategies in which HF-wet etching step is periodically inserted after 20 cycles of ALD SiO_2, leading to an enlarged deposition selectivity of approximately 5 nm after repeated ALD-etching supercycles. This approach can be envisaged to provide a practically applicable strategy toward highly selective deposition using inherent AS-ALD that can be incorporated into upcoming 3D bottom-up nanofabrication.

AS-TuP-6 Organothiol Inhibitor Instigated Area Selective Deposition of HfO_2

***Summal Zoha**, B. Gu,* Incheon National University, Korea (Republic of)*; F. Pieck, R. Tonner,* Universität Leipzig, Germany*; H. Lee,* Incheon National University, Korea (Republic of)

With continuous progress in the field of nanofabrication and nanotechnology, the semiconductor industry has greatly flourished. However, efforts for further reduction in feature sizes of electronic interconnects in search of better and fancier devices, are still ongoing. The struggle to search for better area selective deposition (ASD) processes has led researchers to manipulate deposition surfaces using different passivation tools. In this regard, surface inhibitors have gained a lot of attention. In this study, an organothiol inhibitor has been utilized for ASD on metal, oxide, and nitride surfaces, Cu, SiO_2, and TiN, respectively. The inhibitor selectively adsorbs on the Cu and SiO_2 surfaces at 400 ºC, while the TiN surface remains unaffected after exposure to the inhibitor. Upon high-temperature exposure, the organothiol inhibitor is capable of decomposing to assist the adsorption of its different parts on the Cu and SiO_2 substrates, thereby simultaneously inhibiting two surfaces through a single inhibitor. The inhibited substrates were examined for adsorption and inhibition using surface analysis tools including water contact angle (WCA) measurements, X-ray photoelectron spectroscopy (XPS), etc. Blocking results revealed promising blocking potential against HfO_2 ALD on Cu compared to SiO_2, whereas the TiN surface did not exhibit any blocking at all. Furthermore, the surface chemistry and reactivity have been explained by theoretical calculation using the Monte Carlo method and density functional theory.

Plenary Session
Room Auditorium - Session PS-WeM1
Plenary Session III

Moderators: Jolien Dendooven, Ghent University, Belgium, Christophe Detavernier, Ghent University, Belgium, Paul Poodt, Holst Centre / TNO

8:45am **PS-WeM1-2 ALD 2022 Innovator Awardee Talk: Prospects of Atomic Layer Deposition for Cell-Stacking Technology of Semiconductor Memory Devices***, **Cheol Seong Hwang**,* Seoul National University, Korea (Republic of) **INVITED**

Atomic layer deposition (ALD) contributed to the scaling down of semiconductor devices for both memory and foundry sectors through its unmatched excellence in controlling the thickness and performance over three-dimensional structures. Furthermore, the types of materials that can be grown by the ALD have expanded from simple binary oxides to diverse and multi-component during the past decades, enabling further exploitation of ALD toward futuristic semiconductor devices. However, one of the biggest challenges in the general semiconductor business is the extremely high cost of fabrication, which is mainly related to the lithography processes requiring extreme-UV scanners. This problem is more severe for the memory business because of the relatively low chip prices than the processors. The memory industry was already aware of this problem, and the NAND flash had evolved from the planar- to the cell-stacked structure when the design rule reached ~ 14 nm. A similar trend may come when dynamic random access memory (DRAM) reaches the ~ 10 nm technology node. It is still unclear when the DRAM industry will hit the ~ 10 nm technology node, but it will come within ~ 10 years. Looking back to the history of cell-stacking technology development of the NAND flash, which took ~ 6-7 years from the first paper publication to the first customer sample fabrication, it is time to focus more on the stackable DRAM cell technology. Besides, the currently suggested cell-stack structure of DRAM indicates several opportunities and challenges for the nano-scale thin film growth area via ALD; it may require an even higher performance of the material, ca. ultrahigh-*k* capacitor dielectrics. Nonetheless, it also offers a chance to use slightly thicker thin films in those structures that are not useful for the planar structures due to the stringent lateral geometry limitations.

This talk will shortly review the status and challenges of the current DRAM and NAND devices, especially from the viewpoints of ALD films. Then, it will cover the suggested or expected memory cell structures based on the cell-stacking technology, in which the NAND is more apparent and DRAM is more obscure. Then, the requirements and challenges for the ALD films for those structures and processing are reviewed. Some of the recent progress achieved in the author's group will be described. The talk will end with remarks on the prospect of memory and the related ALD industry.

9:15am **PS-WeM1-4 ALD Student Award Finalist Talk: Improving Self-Aligned Atomic Layer Deposited Gate Stacks for Electronic Applications***, **Amy Brummer**, D. Aziz, M. Filler, E. Vogel,* Georgia Institute of Technology

Area-selective atomic layer deposition (AS-ALD) is a promising method for the formation of bottom-up structures that can be inherently aligned with the underlying substrate material which would benefit electronics fabrication by reducing the number of photolithography steps and eliminating overlap capacitance. In this work, a previously developed process of forming a self-aligned gate stack [1] is used with various Si oxidation techniques to study methods to improve the semiconductor-oxide interface quality and reduce defect density. A planar adaptation of the SCALES process [2] is combined with AS-ALD to form a self-aligned gate stack based on the underlying Si doping profile. First, a poly(methyl methacrylate) (PMMA) brush is grown from a planar Si surface patterned with regions of light and heavy doping. The PMMA brush is then selectively etched with KOH, which etches lightly doped Si much faster than heavily doped Si, resulting in a patterned PMMA film that covers heavily doped Si with exposed lightly doped Si regions. The patterned PMMA film enables the selective deposition of HfO_2 and Pt on the lightly doped regions via AS-ALD by deactivating the heavily doped Si regions. XPS data confirms selective deposition of HfO_2 and Pt (Figure 1), ultimately forming a metal-oxide-semiconductor (MOS) structure suitable for a MOSFET gate stack. And electrical characterization shows expected C-V behavior for a Pt-HfO_2-Si MOS capacitor structure (Figure 2). To improve electrical performance and reduce defect density, the impact of wet oxidation techniques (e.g. H_2O_2, SC-1 clean, SC-2 clean) prior to HfO_2 ALD on the semiconductor-oxide interface is examined. The MOS capacitor structures are characterized with ellipsometry, XPS and electrical characterization.

This work was supported by DARPA (W911NF2110298), the DOD through the National Defense Science and Engineering Graduate Fellowship Program, and the National Science Foundation (No. CMMI-1916953). This work was performed in part at the Georgia Tech Institute for Electronics and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (No. ECCS-2025462).

[1] Brummer, Amy C., et al. *Applied Physics Letters* 119.14 (2021): 142901.

[2] Mohabir, Amar T., et al. *ACS nano* 14.1 (2020): 282-288.

9:30am **PS-WeM1-5 ALD Student Award Finalist Talk: Towards High Throughput Molecular Layer Deposition of Alucone Films***, **Hardik Jain**,* Holst Centre / TNO, Netherlands*; M. Creatore,* Eindhoven University of Technology, The Netherlands*; P. Poodt,* Holst Centre / TNO, Netherlands

The deposition rate and properties of MLD films are for a large part determined by what happens during the precursor exposure step. In some cases, however, the purge step is of equal importance, for example in the MLD of alucone films using trimethylaluminum (TMA) and ethylene glycol (EG). Due to the porosity of alucone films, the reactants during their exposure step not only react at the film surface but also tend to infiltrate into the film. The subsequent outgassing of the infiltrated reactant can take relatively very long thereby becoming the deposition rate-limiting step. If enough purge time is not provided for the reactant to outgas, it will lead to an additional CVD component alongside MLD in the overall growth. To employ/avoid the CVD component in the deposition process, we have also developed a kinetic model to correlate parameters like exposure times, partial pressures, purge times and deposition temperature to the amount of CVD component in the growth.

Additionally, we also looked into solutions to increase the deposition rate of the alucone films and amongst others found that using a bulkier precursor like DMAI instead of TMA can overcome the problem of precursor infiltration and increase the deposition rate of alucone processes by at least an order of magnitude. In this work, we also present a detailed investigation of MLD of alucone using DMAI as the aluminum precursor. The effect of deposition temperature and reactant purge times on deposition kinetics has been investigated and the DMAI alucone films have been compared with those prepared using TMA for their chemical environment and degradation showing striking similarities between both. The results demonstrate that in some cases less reactive and bulkier precursors like DMAI can indeed be used to increase the deposition rate of an MLD process. We believe that the above work could be extended to other MLD systems and can serve as a guide in designing efficient MLD reactors and processes.

9:45am **PS-WeM1-6 ALD Student Award Finalist Talk: In-situ FTIR Analysis of Selectivity Loss Mechanism of TiO_2 Atomic Layer Deposition on Aminosilane-Passivated SiO_2 and H-terminated Si***, **Jan-Wilem Clerix**,* KU Leuven, NCSU, Imec, Belgium*; G. Dianat,* NCSU*; A. Delabie,* Imec, KU Leuven, Belgium*; G. Parsons,* NCSU

To increase selectivity in area-selective atomic layer deposition (ALD), research is focused on developing passivation layers that inhibit growth on non-growth surfaces. Such passivation layers have a number of requirements: they should form selectively on the non-growth surface, be stable at the process conditions and be unreactive towards the ALD precursors [1]. Different types of passivation layers have been developed, including self-assembled monolayers, small organic molecules and aminosilanes. The last of those show great promise for implementation in area-selective ALD schemes due to their selective reaction with SiO_2, stability at high temperatures and ability to inhibit both metal and metal oxide ALD.

In this study we further develop the understanding of the mechanisms of inhibition of common ALD precursors such as $TiCl_4$ and H_2O by in-situ Fourier-transform infrared spectroscopy. Firstly, the deposition of N,N-dimethylamino-trimethylsilane (DMATMS) is investigated on OH-terminated SiO_2 (SiO_2-OH) and H-terminated Si (Si-H). DMATMS reacts only with hydroxyl sites (-OH) on the surface, with a preference for isolated -OH. Most reactive sites are consumed in the first seconds of exposure. The fast reaction makes DMATMS ideally suited to be implemented in conventional ALD reactors. When the passivated SiO_2-OH is exposed $TiCl_4$, the formation of Ti-O does not coincide with a loss of trimethylsilyl termination of the surface. Instead, the absorption of $TiCl_4$ is due to unpassivated, H-bonded -OH, which is present since the trimethylsilyl coverage is sterically limited and DMATMS reacts preferentially with isolated -OH. The trimethylsilyl termination is stable against H_2O for extended exposures. On the Si-H, DMATMS serves to passivate any remaining -OH. Any passivation loss can be linked to loss of H-termination and adsorption of $TiCl_4$ on siloxane bridges. Encouragingly, we see that the addition of DMATMS creates an even better inhibited surface than pristine Si-H.

Overall, we conclude that DMATMS is an excellent choice for passivating agent due to its ability to inhibit a variety of processes and its applicability in passivation-deposition-etch cycles. Nonetheless, passivation of SiO_2-OH could be improved by combination with an additional, smaller passivating agent to limit the impact of steric hindrance.

[1] J. Yarbrough et al., J. Vac. Sci. Technol. A **39**, 021002 (2021).

10:00am **PS-WeM1-7 ALD Student Award Finalist Talk: Sacrificial Etching Kinetics Control Extent of Pattern Alignment in Area-Selective Atomic Layer Deposition (AS-ALD) via Simultaneous Deposition and Etching***, **Hannah Margavio**, J. Kim,* North Carolina State University*; N. Arellano,* IBM Almaden Research Center*; G. Parsons,* North Carolina State University

By the year 2040, electronic devices are projected to consume ~ 20% of all energy generated on Earth.[1] Therefore, current challenges such as feature misalignment in a semiconductor device, which causes open circuits, excess resistance, and power dissipation and can result in chip failure, must be overcome.[2] Accurate feature alignment from standard lithographic techniques is further hampered by continuous downscaling of integrated circuits, thus bottom-up patterning methods are needed to circumvent inherent variability in lithography. Area-selective atomic layer deposition (AS-ALD) poses a more sustainable patterning alternative to top-down processes by directing precursors to a particular reactive surface chemistry to deposit material only in that region, while preventing growth in an adjacent region.

Our group has previously demonstrated highly selective W-ALD on Si by simultaneously etching a neighboring TiO2 feature with a single precursor set ($SiH_{4(g)}$ and $WF_{6(g)}$) for both reactions.[3] The sacrificial etching reaction maintains selectivity throughout the process by consuming deposition precursors, thereby avoiding unwanted nucleation (Fig. 1). Herein, we show that the extent of selective W growth is controlled by the TiO_2 etching rate. We sequentially dose SiH_4 and WF_6 gases onto 100-nm thick TiO_2 lines patterned on Si (Fig. 2a) and evaluate the extent of selective W growth by scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (STEM-EDS) for various processing temperatures and SiH_4 exposures.

In the initial stages of TiO_2 etching, WF6 diffuses into the bulk of the feature, partially fluorinating it to form a porous oxy-fluoride layer WO_xF_y/TiO_yF_z.[4] We show that at 280 ºC (Fig. 2b), the etching rate is too fast, and the oxy-fluoride layer creates a rough sacrificial feature profile from formation of volatile WF_2O_2 and TiF_4. The subsequent SiH_4 dose remains trapped in the low-density layer after purging, initiating parasitic W growth. We show that selectivity can be maintained by controlling the sacrificial feature profile evolution. At lower reaction temperatures, TiO_2 etches slowly and conformally, thus preventing W nucleation.

The presented mechanism for AS-ALD is a way to perform both selective ALD and CVE with the same chemistry and processing conditions. This process not only improves selective W deposition abilities—a valuable material in semiconductor manufacturing—but also shows the success of an integrable ASD process that can be extended to more materials.

[1] Decadal Plan for Semiconductors; SRC, 2021.

[2] Clark, R. et al. APL Mater. 2018

[3] Song, S. K. et al., ACS Nano 2021.

[4] Lemaire, P. C. et al., Chem. Mater. 2017

10:15am **PS-WeM1-8 ALD Student Award Finalist Talk: Depositing Metal Oxides on Metalcones: Enhancing Initial Growth Through O_2 Plasma Densification***, **Juan Santo Domingo Peñaranda**, M. Minjauw, J. Li, S. Vandenbroucke, J. Dendooven, C. Detavernier,* Ghent University, Belgium

Flexible devices for display/battery applications are gaining traction every day, but moisture sensitivity can be a concern. For this, Thin-Film Encapsulation (TFE) moisture barriers need to be used, but many current technologies rely on rigid barriers that crack and stop performing under flexible stress. As a solution, organic/inorganic thin film stacks are now widely explored for TFE.

In this context, we have studied O_2 plasma densification on MLD alucone[1], titanicone, tincone and zincone. We also investigated the effect of the growth of ALD metal oxides on metalcones with or without prior plasma densification to optimize the deposition of ALD/MLD multilayers.

Upon plasma treatment, all metalcone layers exhibited a similar behaviour. A bilayer structure was evidenced by X-ray reflectivity (XRR), composed of a (~2 nm thick) high-density layer on top of one with metalcone-similar density. The overall film thickness decreased and its evolution in both the dense and less-dense layer could be monitored with in-situ ellipsometry (Figure 1), revealing a saturating behavior. In Fourier-Transform Infrared Spectroscopy (FTIR), plasma-treated metalcones (PT-metalcones) showed a decrease in the C-O region and an increase in the C=O one (Figure 2), similar to aged metalcones. After several months of aging, only an increase in the O-H band was found. X-ray Photoelectron Spectroscopy (XPS) showed a decrease of C content in the top of the layers that did not reach zero. Thus, we conclude that O_2 plasma treatments on metalcones produce a partial densification of the layers. The O_2 radical species oxidise the topmost region of the hybrid film into its corresponding, dense oxide. However, O_2 radicals penetrate deeper down the layer, oxidising the original alcoholic structure into an intermediate ketonic one. According to XPS, a material more similar to an oxycarbide may be formed.

Secondly, metal oxides were grown on top of their respective metalcones, and pristine and PT-metalcones were compared. Using in-situ ellipsometry, growth on pristine metalcones always suffered a delay until the oxide thickness started to increase(Figure 3)[2]. However, an oxide layer immediately started growing on PT-metalcones, from cycle one, offering very accurate oxide thickness control. With this, we hope to have expanded the potential of using stacks of oxides and PT-metalcones for TFE applications. The use of O_2 plasma densifications could hold potential towards film-ratio optimisation for optimum performance at minimal film thicknesses.

45. Santo Domingo Peñaranda et al. *Dalt. Trans.***2021**, *50* (4), 1224–1232
46. Choi et al. *ACS Appl. Mater. Interfaces***2016**, *8* (19), 12263–12271

ALD Applications
Room Baekeland - Session AA1-WeM2

ALD for Optical Applications

Moderators: Parag Banerjee, University of Central Florida, Matti Putkonen, University of Helsinki

10:45am **AA1-WeM2-1 Atomic Layer Deposition of Perovskite K(Ta$_x$,Nb$_{1-x}$)O$_3$ films on Silicon for Integrated Photonics via KOtBu and H$_2$O**, ***Eric Martin,*** Ohio State University; *J. Bickford,* Army Research Laboratory; *H. Sønsteby,* University of Oslo, Norway; *R. Hoffman,* Army Research Laboratory; *R. Reano,* Ohio State University

Photonic integrated circuits (PICs) have advanced significantly over the last decade with a view towards applications in communications, sensing, and computing in the classical and quantum domains.The fabrication of silicon PICs in particular has transitioned from university cleanrooms to foundry supported process design kits by leveraging mature fabrication techniques from the microelectronics industry.The silicon material system exhibits optical properties that are enabling for compact PICs, such as high index contrast and low optical propagation loss at telecommunications wavelengths, allowing for the demonstration of low power nonlinear optical devices in waveguides based on third order susceptibility.An approach to advance the state-of-the-art performance of nonlinear optics in silicon PICs is to pursue heterogeneous integration. A promising material for this purpose is potassium tantalate niobate (KTN).KTN is a solid solution of $KTaO_3$ and $KNbO_3$ perovskites with a Curie temperature (T_c) that is defined by the Ta:Nb ratio.Bulk KTN crystals show record high Kerr nonlinearity when thermally tuned near T_c.KTN thin films can be grown with controllable Ta:Nb ratios via atomic layer deposition (ALD) using potassium tert-butoxide (KOtBu), tantalum ethoxide ($Ta(OEt)_5$), niobium ethoxide ($Nb(OEt)_5$) and H_2O precursors.To date, deposition of KTN films on silicon substrates has not been reported.In this work, we explore several approaches for obtaining perovskite $KTaO_3$ and KTN thin films on silicon using KOtBu, $Ta(OEt)_5$, $Nb(OEt)_5$, and H_2O precursors. Our approaches include varying the ALD process parameters for the metalorganic and H_2O co-precursors, chemically modifying the substrate surface, deposition of interfacial layers, and implementing ALD equipment modifications.We report the K uptake as a function of ALD process parameters using both refractive index obtained from spectroscopic ellipsometry and quantification from X-ray photoelectron spectroscopy (XPS).For a subset of samples, we report the crystal structure of our RTA annealed ALD films using X-ray diffraction (XRD). For the first time, we demonstrate perovskite $KTaO_3$ and KTN films on silicon by ALD.

11:00am **AA1-WeM2-2 Low-temperature ALD Sb$_2$Te$_3$ for Self-powered Broad-band Photodetector**, ***Jun Yang***, *A. Bahrami, S. Mukherjee, S. He, S. Lehmann, K. Nielsch,* Institute for Metallic Materials, Leibniz Institute of Solid State and Materials Science Dresden, Germany

P-type Sb_2Te_3 thin film was deposited by atomic layer deposition (ALD) at 80 °C using $(Et_3Si)_2Te$ and $SbCl_3$ as precursors. The good crystal quality, low defect, and excellent uniformity of low-temperature ALD processed Sb_2Te_3 was supported by Raman, transmission electron microscopy, and XPS. Furthermore, high performance self-powered broad-band photodetectors based on Sb_2Te_3/Si heterostructure were fabricated. The photodetector has a wide detection range of 405 to 1550 nm. Meanwhile, a high responsivity of 4287 mA/W at 405 nm, and a quick response speed of 98 µs (t_{rise}) were obtained under 0 bias voltage, which could be ascribed to the strong built in electric field between p-type Sb_2Te_3 thin film and n-type Si. The temperature dependent performance of Sb_2Te_3/Si photodetector was thoroughly examined. Resistivity, conductivity, and carrier concentration of Sb_2Te_3 were carried out at temperature ranging from 273 K to 473 K to reveal intrinsic mechanism. The Sb_2Te_3/Si heterostructure self-powered photodetector with excellent performance based on ALD process shows the great potential application in optoelectronic devices.

11:15am **AA1-WeM2-3 Preparation of High Mobility Indium Hydroxide Doped by Atomic Layer Deposition and Study on Photoelectric Properties**, ***Liangge Xu,*** Harbin Institute of Technology, China

At present, the industrialization of metal mesh and tin doped indium oxide (ITO) film cannot meet the high transmittance requirements of infrared band. Therefore, how to achieve high carrier mobility has become a hot topic. In order to solve the above problems, In_2O_3:H film is selected, which is a special transparent conductive oxide film. On the one hand, hydrogen has a very small volume and mass, and will not produce impurity scattering in the process of electron transport; On the other hand, hydrogen is distributed in the gap of the indium oxide lattice, resulting in almost no lattice distortion, so it does not increase the number of grain boundaries and reduce the grain boundary scattering. The combined effect of these two factors makes the hydrogen doped indium oxide (In_2O_3:H) thin films have high carrier mobility, which can achieve high infrared transmittance by reducing the carrier concentration on the basis of ensuring the electrical properties.

In this paper, the growth rate, microstructure and photoelectric properties of In2O3:H films were investigated by changing the deposition process parameters. When the deposition temperature is 100 ℃, incomplete reaction occurs during deposition, and the growth rate is slow. The film is amorphous. At this time, the carrier mobility is low, which is only 30.18 cm^2/Vs, and the optical properties are good, the transmittance can reach 80% at 4 µm; With the increase of deposition temperature, the growth rate gradually stabilized at 0.1nm/cycle, the amorphous state gradually changed to crystalline state, the carrier mobility increased sharply, and the highest was 64.05 cm^2/Vs, and the carrier concentration and the optical properties decreased. The ratio of deposition time of InCp / (O_2 + H_2O) and the reaction time of InCp have little effect on the electrical and optical properties. With the increase of deposition period, the carrier mobility can reach up to 80 cm^2/Vs, but the optical performance is very poor, the transmission rate at 4 µm is only 39.5%.

11:30am **AA1-WeM2-4 ALD MgF2 Using (EtCp) $_2$Mg and SF$_6$ Remote Plasma Source**, ***Hoon Kim,*** *. Huang, . Allen, E. Pierce, , J. Wang,* Corning Inc.

Magnesium fluoride (MgF2) is a key material for Deep Ultra-Violet (DUV) and Far UV optics due to its wide bandgap and high resistance of oxidation. ALD process enables conformal coatings and precise thickness control on 3D shape optics. ALD MgF2 has been demonstrated using anhydrous hydrogen fluoride (HF) as fluorine source. However high concentration HF has safety concern in handling and residue in the reactor. Thus, safer fluorine source should be considered for industrial use. Hhfac has also been evaluated, but it requires O3 to activate the fluorine which results in oxygen and carbon incorporation in the film. The impurities are an absorption source for the UV range. SF6 is evaluated as fluorine source for AlF3, but no report for MgF2. In this study, we demonstrated the MgF2 ALD using SF6 remote plasma. The growth rate, impurity level and conformality were evaluated. Optical properties such as dispersion and transmittance were obtained. Hot wall batch reactor with remote plasma source was employed in this study. Fluorine radical was generated by using SF6 flow through Inducted coupled plasma (ICP) source. (EtCp) 2Mg was used as precursor. A prism shape surrogate was used to evaluate coverage on 3D shape. Thickness and reflectance were measured by an ellipsometer. Impurity of the film was measured by XPS and SIMS. Direct reduction of the precursor using SF6 plasma caused high carbon incorporation in the film due to the reaction of Cp ligand and fluorine. XPS results showed that CFx bonds are detected in the film. To address this issue, reducing agent to remove the Cp ligand from adsorbed precursor was introduced before SF6 exposure. This approach effectively removes the carbon incorporation and forms high purity MgF2 film. This ALD film has lower impurity level than that of in-house PVD MgF2. The growth rate of ALD MgF2 is 0.4Å/cycle at 150oC. The refractive index at 550nm is 1.33 which is same as inhouse PVD MgF2. The deposited film is polycrystalline. Other optical properties will be reported.

11:45am **AA1-WeM2-5 Moisture Sensitivity of ALD Metal Fluorides for Far UV Optical Coatings**, ***Robin Rodríguez***, *J. Hennessy, A. Jewell, S. Nikzad,* Jet Propulsion Laboratory (NASA/JPL)

We report on the use of atomic layer deposition (ALD) for the development of metal fluoride thin films relevant to optical coatings operating at far ultraviolet wavelengths (FUV, 90-200 nm). The use of metal fluoride materials like MgF_2, AlF_3, LiF, CaF_2, and LaF_3 is relevant to all FUV optical systems for applications like anti-reflection coatings, dichroic beam splitters, bandpass filters, and reflective mirror coatings. However, many metal fluorides have associated concerns with environmental stability, primarily related to water vapor exposure. For example, LiF-protected aluminum mirror coatings can experience reflectance-losses if stored in modest relative humidity environments (RH ~40%). Initial space-based demonstrations of ALD coatings have shown improved stability by depositing a thin 1–2 nm capping layer of MgF_2 or AlF_3 onto the LiF-protected mirrors. In this work, we have conducted a broader study of the moisture sensitivity of ALD materials. This includes physical vapor deposition (PVD) of AlF_3 mirror coatings capped with ALD MgF_2 layers on Si, as well as stand-alone ALD coatings of MgF_2, AlF_3, CaF_2, and LiF on Si subjected to both long-duration and accelerated aging tests and then characterized by FUV reflectance measurements, spectroscopic ellipsometry, atomic force microscopy, x-ray photoelectron spectroscopy, x-ray diffraction, and secondary-ion mass spectrometry. To the best of our knowledge, this work also reports the first instance of CaF_2 and LaF_3 coatings deposited by ALD using anhydrous HF.

The observed changes in optical properties, surface morphology, and film composition can provide guidelines on storage conditions for these materials for future space instrumentation, and serves as a baseline for the direct comparison of material produced by PVD versus ALD.Finally, we also describe a new test reactor used in the work above that has enabled the deposition of PVD aluminum mirror coatings and ALD metal fluorides within the same vacuum chamber, to prevent oxidation of the aluminum surface and minimizing the time between metal evaporation and ALD encapsulation.

ALD Applications
Room Van Rysselberghe - Session AA2-WeM2
ALD for Memory Applications I

Moderators: Robert Clark, TEL Technology Center, America, LLC, Charles Dezelah, ASM

10:45am **AA2-WeM2-1 Sub 10-nm Ferroelectric HfO_2 Capacitors Doped with Gd**, ***Evgeniy Skopin***, *N. Guillaume, L. Alrifai, A. Bsiesy,* LTM - MINATEC - CEA/LETI, France

Recent discoveries of the ferroelectric properties of doped HfO_2 opens the possibilities of its integration in Ferroelectric-based non-volatile Random-Access Memories (FeRAMs). Replacing memories based on perovskites materials by ferroelectric HfO_2 has many decisive advantages. Indeed, HfO_2 is readily used in CMOS back end of the line, and its use opens the possibility to grow thinner layers of around 10 nm *vs* 70-100 nm for the conventional ferroelectric perovskites. Thinner layers are mandatory for integration in advanced sub 100 nm CMOS technology nodes.

Plasma Enhanced Atomic Layer Deposition (PEALD) allows the synthesis of a different range of materials such as oxides and metals with low surface roughness and precise thickness control. TiN metal (M) layers and Gd doped HfO_2 insulator (I) layer were grown in the same PEALD chamber without contact with the air between depositions to synthesize ferroelectric MIM capacitors. Changing ratios between Hf and Gd PEALD cycles inside one supercycle allows choosing an appropriate Gd doping concentration. In its order, during annealing, Gd doping in HfO_2 (Gd:HfO_2) leads to a crystallization of HfO_2 in a metastable non-centrosymmetric orthorhombic phase, which induces the HfO_2 ferroelectric properties. A decrease of the ferroelectric oxide thickness can allow operating lower switching voltages for the low power circuits.

Continuing our previous work [SB], by using the growth of MIM capacitor by PEALD in one batch (*i.e.* without air break between metal, insulator, and metal layers), we recently demonstrated the ferroelectricity of sub-10 Gd:HfO_2 layers (8.8nm-, 6.6nm, and 4.4nm-thick layers) in TiN / Gd:HfO_2 / TiN stacks and studied the remnant polarization amplitude change with the Gd:HfO_2 layer thickness. Structural measurements (X-ray diffraction and reflectometry) confirmed a HfO_2 transformation to the orthorhombic (ferroelectric) phase. Electrical measurements showed that switching voltage can be decreased for the thinner Gd:HfO_2 layers (hysteresis loop measurements and Positive Up Negative Down measurements). Polarization switching cycling measurements demonstrate ferroelectric endurance of at least up to 10^8 cycles. This work opens the possibilities for the integration of sub-10nm Gd:HfO_2 in the memory device circuits thanks to the unique PEALD deposition capabilities.

References:

[SB] Applied Physics Letters 117.25 (2020): 252903.

11:00am **AA2-WeM2-2 Controlling Stochastic Resistive Switching in Organic-Inorganic Hybrid Memristor by Vapor-Phase Infiltration**, *A. Subramanian,* Stony Brook University*; N. Tiwale, K. Kisslinger,* ***Chang-Yong Nam,*** Brookhaven National Laboratory

Resistive random-access memory (RRAM) is promising for next-generation data storage and non-von Neumann computing hardware. However, tuning device switching characteristics and, particularly, controlling their stochastic variation remain as critical challenges. Here, we report new organic-inorganic hybrid RRAM media whose bipolar switching characteristics and stochasticity can be controlled by vapor-phase infiltration (VPI), an ex-situ organic-inorganic hybridization technique derived from atomic layer deposition (ALD). Hybrid RRAMs based on AlO_x-infiltrated SU-8 doped with sliver perchlorate feature facile tunability of device switching voltages, off-state current, and on-off ratio by adjusting the amount of infiltrated AlO_x in the hybrid, wherein molecular network of AlO_x is homogenously distributed through the polymer free volume by the sequential infiltration of trimethylaluminum (TMA) and water vapor. Furthermore, a significant reduction in the stochastic, cycle-to-cycle variations of switching parameters, such as off-state current and set/reset voltages, was enabled by AlO_x infiltration, driven by the infiltration-induced changes in mechanical, dielectric, and chemical properties of the organic medium and their influence on the dimension and formation characteristics of a conductive silver filament. Finally, we demonstrate multi-level analog switching, potentially useful for neuromorphic applications, by controlling switching compliance current, as well as direct, one-step device patterning ability exploiting the negative-tone resist feature of SU-8. With the demonstrated control over switching characteristics and stochastic variation, combined with analog switching and one-step patterning capabilities, the results not only present a novel hybrid medium for RRAM applications but also showcase the utility of VPI for developing new, high-performance hybrid RRAM devices based on photoresist materials.

11:15am **AA2-WeM2-3 Atomic Layer Deposited Vanadium Oxide Thin Films for Thermocromic and Microelectronic Applications**, ***Zsofia Baji,*** *J. Volk, L. Pósa, G. Molnár,* Centre for Energy Research, Hungary*; A. Surca, G. Drazic,* National Institute of Chemistry, Slovenia

Vanadium oxides are much-researched materials due to their wide range of applications from microelectronics, smart electrochromic and thermochromic windows, metamaterials, gas sensors, programmable critical thermal sensors to battery energy storage. V_2O_5 has been the most widely examined for energy storage and electrochromism, as the Li ions can easily be intercalated between its atomic layers. On the other hand, VO_2 undergoes a reversible transition at 68°C, where a change in light and electrical conductivity occurs, therefore, VO_2 is widely researched as a promising material for resistive switching and thermochromism. Resistive switching is presently at the core of emerging technologies, such as memristors and neuromorphic computing. By the switching between the insulating and metallic phase of VO_2, the switching of signals for nanoelectronical applications becomes possible. Alternative switching mechanisms are also widely researched, such as the field-induced transition. An advantage of the ALD method in the preparation of these films would be the control of the deposition parameters and an easy doping, which allows a better control of material properties (crystallinity, stoichiometry and defects), and, thus, the transition temperature.

The atomic layer deposition of vanadium oxides has been in the focus of much research effort. Several precursors and different reactions can be used for this purpose, but there are some substantial difficulties with all of them. Vanadium oxy-tri-isopropoxide, Tetrakis ethylmethyl-amino vanadium (TEMAV) or VCl_4 are all promising candidates for the process.

Most reports on the ALD of vanadium-oxides present the preparation of V_2O_5 which is the more stable phase and is easier to deposit. An advantage of the ALD method is that the oxidation state of the deposited films can be tuned by the selection of the reactant. More oxidising reagents (e.g. oxygen plasma) will result in films with higher oxidation states, while reactions with hydrogen or ammonia plasma yield lower oxidation states. In this way, by choosing the appropriate reactants and deposition parameters the preparation of VO_2 can be achieved.

The present work examined the ALD process of TEMAV and different oxidants (water, oxygen plasma) a number of annealing procedures in oxidising and reducing atmospheres. The films were annealed to improve the crystallinity and stoichiometry. Their properties were examined with Raman spectroscopy and transmission electron microscopy. The switching properties were analysed electrically and optically, and test structures were demonstrated.

11:30am **AA2-WeM2-4 Brain-Based Inspiration: Towards Neuromorphic Computing With ALD Based Memristive Devices**, *E. Perez, M. Kalishettyhalli Mahadevaiah, E. Perez-Bosch Quesada,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany*; T. Rizzi,* IHP - Leibniz-Institut fuer innovative Mikroelektronik, Germany*;* ***Christian Wenger,*** IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany **INVITED**

Due to its advantages of massive parallelism, high energy efficiency, and cognitive functions, brain-inspired neuromorphic computing is attracting immense interest. As the basic unit cell for learning algorithms, the implementation of synaptic behavior into memristive devices is the key step toward neuromorphic computing.

Recent advances in the performance of resistive random access memory (RRAM) acting as memristive devices have led to a significant interest in neuromorphic applications. Although RRAM based memory arrays demonstrated excellent performance parameters, the variability is still a critical issue. Controlling this intrinsic phenomenon requires employing program-verify schemes. In this talk, an optimized scheme to minimize resistance state dispersion and to achieve reliable multi-bit operation is evaluated.

However, statistical variations can be tolerated in computing applications like neuromorphic networks. The synaptic behavior memristive devices can be evaluated by applying successive algorithms consisting of set or reset pulses. These algorithms can be used to study the synaptic functionality of memristive arrays.

Nevertheless, there is still a huge gap between the physical implementation and the verification of circuits and systems proposed for memristive devices. The first step, required to fill the gap, is the development of analog simulation tools, which are the base for the successful implementation of digital CMOS circuits with memristive elements. New designs and concepts need to be supported up by physical implementation and verification to be reliable. That means, new simulation tools for memristive devices have to address the following issues: device variability, cycling variability, data endurance, data retention as well as device switching speed. Meaning that memristive device models still have a long way to be completed.

Emerging Materials
Room Van Eyck - Session EM-WeM2
Molecular Layer Deposition

Moderators: Arrelaine Dameron, Forge Nano, Ola Nilsen, University of Oslo

10:45am **EM-WeM2-1 Deposition of Copper-based Metal-Organic Framework Thin Film by Molecular Layer Deposition***, **Ben Gikonyo**, C. Journet-Gautier, A. Fateeva, C. Marichy,* Université Claude Bernard Lyon 1, France

Metal-organic frameworks (MOFs) are a class of hybrid materials composed of metal ions/clusters bridged by organic moieties. They have received much attention in recent years as promising porous materials that are highly adaptable to a wide range of applications, such as gas storage or separation, catalysis, sensors, or electrochemistry. In the later field, MOFs are gaining ground for rechargeable batteries, fuel cells, or electrocatalysis. For real breakthroughs, fine-tuning of their structure and thus physico-chemical properties with remarkable precision is required. MOFs have been synthesized mainly as a powder or single crystals but to integrate these hybrid materials into microelectronics, thin films are needed.[1,2] In this regard, molecular layer deposition (MLD) appears as a technique of choice.[3]Based on sequential self-limited gas-surface reactions, it allows fabricating solvent-free films with control of the thickness at the nanoscale level. Although around ten MOFs[4-7] have been successfully grown by MLD, obtaining layers with good porosity and crystallinity remains a major challenge. Nevertheless, amorphous as-grown films have been crystallized by post-deposition treatments that involve exposing the film in a controlled condition with humidity and acetic acid/DMF vapors.[8]

Herein, the direct growth of copper-based MOFs by MLD is presented. Two frameworks are successfully deposited using a homemade reactor: Copper terephthalate (Cu-TP), even though already reported by another group[6]**,**and the porphyrinic MOF, Cu-TCPP (TCPP=meso-tetra(4-carboxyphenyl) porphyrin), attractive for its optical and redox properties. The obtained films are characterized using ellipsometry, UV-Visible, and IR spectroscopies, PXRD and SEM.

On the contrary to the pioneering work,[6] our *as*-deposited Cu-TP film is directly obtained crystallized into the known desolvated phase.[9]Optimum deposition condition and self-limiting property of the precursors/substrate reactions for Cu-TCPP are established. Rough films with a hybrid composition are observed. Hetero-MOF structures made of single DMOF-1 crystals coated with a homogenous Cu-based MOF layer are also reported.

47. J. E. Ellis *et al.,Mater. Adv.* 2, 6169, (2021)
48. O. Shekhah *et al.,* Chem. Soc. Rev., 40, 1081–1106 (2011)
49. C. Crivello *et al.*, *Mater. Horiz.*8, 168–178 (2021)
50. L. D. Salmi *et al.*, *Microporous and Mesoporous Mater.*182, 147–154 (2013)
51. L. D. Salmi *et al.*, *J. Vac. Sci. Technol. A*33, 01A121 (2014)
52. E. Ahvenniemi, M. Karppinen, *Chem. Commun.*52, 1139–1142 (2016)
53. E. Ahvenniemi, M. Karppinen, *Chem. Mater.*28, 6260–6265 (2016)
54. K. B. Lausund, O. Nilsen, *Nat Commun*. 7, 13578 (2016)
55. C. G. Carson *et al.*, *Eur. J. Inorg. Chem.* 2140–2145 (2014)

11:00am **EM-WeM2-2 ALD-Grown ZIF-8 Thin Films : Mechanism Insight Leads to Push Beyond the Current Thickness Limit***, V. Perrot,* Univ. Grenoble Alpes, CEA, LETI, France*; A. Roussey,* Univ. Grenoble Alpes, CEA, LITEN, France*; M. Veillerot, A. Benayad, D. Mariolle, F. Ricoul, V. Jousseaume,* Univ. Grenoble Alpes, CEA, LETI, France*; **Elsje Alessandra Quadrelli,*** CNRS, Univ Lyon IRCELYON , France

Completely vapor phase-based routes for the synthesis of Metal Organic Frameworks (MOF) are recent (see, for example, [1] and [2]). Vapour-phase processes are usually preferred to obtain conformal coatings in the high aspect ratio features of devices but much still remains to be done to control the growth and understand the potential and the limits of these growth methods.

In this work, pinhole-free and crystalline zeolitic imidazolate framework-8 (ZIF-8) layers as thick as 250 nm were grown, by integrating the method previously reported [1]- which typically levels off below 100 nm- in a novel cycling process. Different types of substrates and devices were used, such as silicon wafers, Quartz Crystal Microbalance and silicon micro-pillars arrays, see Figure1).

The material properties as well as the impact of the process parameters on the MOF growth will be reported (data include electronic microscopy, ellipsometric-porosimetry, X-ray diffraction and a study on the influence of water pressure on the final thickness). Molecular-level mechanistic reasons behind the current thickness bottleneck will be discussed through a ToF-SIMS and XPS profil study at different stages of growth.

[1] I. Stassen et al., *Nat. Mat.*, **15**, 304–310 (2016)

[2] E. Ahvenniemi et al., *Chem. Com.*, **52**, 1139-1142 (2016)

11:15am **EM-WeM2-3 Molecular Layer Deposition of Zeolitic Imidazolate Framework 8 Thin Films***, **Jorid Smets**, A. Cruz, R. Ameloot,* KU Leuven, Belgium

Vapor-phase thin film deposition of metal-organic frameworks (MOFs) is required to integrate these materials into electronic devices. Here, we study the molecular layer deposition (MLD) of zeolitic imidazolate framework 8 (ZIF-8), a MOF comprised of zinc nodes connected by 2-methyl imidazolate linkers. In this all-vapor-phase process, thin films are deposited by consecutive self-limiting reactions of diethyl zinc, water, and 2-methyl imidazole. We developed two different methods: (1) Direct ZIF-8 MLD employs only self-limiting reactions resulting in smooth films, crystallinity, and nanometer-scale thickness control, and (2) Two-step ZIF-8 MLD, in which the surface reaction with the linker is completed through a post-treatment step instead of during the MLD deposition. The latter approach resulted in a much faster deposition and an improved MOF quality, *i.e.,* increased crystallinity and probe molecule uptake at the expense of a higher roughness and less precise thickness control. All depositions were performed using a modified commercial ALD reactor, ensuring cleanroom compatibility. *In situ* ellipsometry was employed to monitor the MOF growth and assess the probe molecule uptake. Various *ex situ* techniques, such as atomic force microscopy and grazing incidence XRD were used to supplement the *in situ* techniques and evaluate the coating quality. The critical parameters of the ZIF-8 MLD process were identified, facilitating the adoption of MOF-MLD in other facilities.

11:30am **EM-WeM2-4 Mld of Phosphane-Ene Polymer Thin Films: Bringing Solution Polymer Chemistry to a Gas Phase Process***, J. Lomax,* The University of Western Ontario, Canada*; E. Goodwin, P. Gordon,* Carleton University, Canada*; C. McGuiness,* Solvay*; C. Crudden,* Queen's University, Canada*; S. Barry,* Carleton University, Canada*; **Paul J. Ragogna,*** The University of Western Ontario, Canada

Over the past several years, the Ragogna group has discovered and prepared bulk samples of novel photopolymers from solution via the phosphane-ene reaction, which is the addition of a P-H bond to C-C double or triple bond. These are materials rich in phosphorous content, and the bulk polymers have been used to as precursors to prepare metal-phosphide ceramics and as getters in metal sequestration applications.

Given the unique properties and well-understood reaction chemistry for phosphane-ene materials, we undertook to transfer the phosphane-ene reaction to the gas phase for the deposition of thin films (10-100 nm) via plasma enhanced MLD. Using the commercially available iso-butylphosphine (iBuPH_2 (a.k.a. **IBP**)) and cyclo-tetrasiloxane/silazane (**1**; **2**) as volatile precursors, deposition of thin films of phosphane-ene polymers was achieved. Thermal analysis of the precursors will be discussed, as well as the impact of varying pulse sequences, order of addition and surface priming agents (olefin appended acrylic acids). Pulse sequences of 300 or 600 cycles were employed (0.1 s pulse **IBP**, 10 s N_2 purge | 0.1 – 10 s pulse **1** or **2**, 10 s N_2 purge | 12 s Ar plasma @ 2800 W, 1 s N_2 purge), giving a GPC of 0.31-1.45 Å. All samples were characterized using XPS, ToF-SIMS and AFM. QCM experiments involving O_2 uptake will highlight the potential for these well-controlled polymer thin films for flexible electronic packaging. These results and future directions and opportunities will be discussed.

Key References:

[1] *Chem. Mater.* **2015**, *27*: 1412–1419; **[2]***Angew. Chem. Int. Ed*. **2018**, *57*: 13252-13256; **[3]** 'Photopolymerization of Primary phosphines with olefins to Generate Phosphorous Based Polymer Networks' File date (PCT): September 13, **2018** (PCT/CA2018/051136); Priority No: 62/558,093; **[4]***ACS Appl. Mater. Interfaces***2020**, *12,* 27640–27650; **[5]***Chem. Eur. J.***2020**, *26*, 12751-12757.

11:45am **EM-WeM2-5 Molecular Atomic Layer Deposition of Inorganic-Organic Hybrid Dry Resist for EUV Application***, **Su Min Hwang**, D. Le, Y. Jung, J. Veyan,* University of Texas at Dallas*; A. Subramanian, W. Lee,* Stony Brook University/Brookhaven National Laboratory*; N. Tiwale,* Brookhaven National Laboratory*; C. Nam,* Stony Brook University/Brookhaven National Laboratory*; M. Sung, J. Ahn,* Hanyang University, Korea (Republic of)*; J. Kim,* University of Texas at Dallas

Extreme ultraviolet lithography (EUVL) process is the most promising technique in advanced semiconductor manufacturing with scaling down of device feature size below sub-3nm.[1] However, there are several challenges to apply the EUVL in high volume manufacturing. One of these challenges is the resist performance. Compared to the current polymer-based resist, the development of new resist material is required to meet stringent requirements, such as high EUV absorption, resist thickness, and etch resistance. Among the various approaches, an incorporation of metal into organic resists has been recently reported.[1–3] In particular, hybrid 'dry' resists deposited using molecular atomic layer deposition (MALD) can be a promising approach.

In this study, we demonstrated the feasibility of inorganic-organic hybrid dry resist material comprising trimethylaluminum [$Al(CH_3)_3$] and hydroquinone ($C_6H_6O_2$) via the MALD process. In the temperature range of 150-200 ℃, the TMA/HQ hybrid film exhibited self-limiting growth behaviors (~0.48 nm/cycle) under various HQ exposure and TMA/HQ ratio. In the XPS depth profile with a gas cluster ion beam, the TMA/HQ films show consistent Al, C, and O composition, suggesting the uniform distribution of inorganic elements in the films. After understanding MALD characteristics, a detailed photochemical reaction of TMA/HQ hybrids during electron exposure was studied using a UHV chamber equipped with an *in-situ* FTIR, RGA, and electron flood gun system. The TMA/HQ hybrids with electron exposure above 200 eV exhibited the enhanced wet etch resistance using 0.1% AZ 300 MIF developer, suggesting that the TMA/HQ hybrids show negative-tone resists feature. In *in-situ* FTIR analysis with subsequent electron exposures, aromatic ring (C=C) and Ph–O bond peaks in HQ molecules decreased in intensity. It is expected that the aromatic ring in the HQ is activated via secondary electrons generated by Al, then crosslinked with adjacent HQ molecules. The detailed experimental results will be presented.

This work is supported by SRC-NMP program (task# 3035.001) through SRC.

[1] E.C. Mattson, et al., *Chem. Mater.* **30**, 6192 (2018).

[2] R. Fallica, et al., *J. Micro/Nanolithography, MEMS, MOEMS* **17**, 1 (2018).

[3] N. Tiwale, et al., *J. Mater. Chem. C* **7**, 8803 (2019).

Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS-WeM2

2D Materials I

Moderators: Gregory N. Parsons, North Carolina State University, Henrik Pedersen, Linköping University, Sweden

10:45am **NS-WeM2-1 Atomic Layer Deposition of Layered Chalcogenides***, **Suzanne Mohney**, J. Carter, I. Campbell, A. Agyapong,* Penn State University **INVITED**

Layered chalcogenide materials with van der Waals bonding between layers are fascinating materials. Some are semiconductors with bandgaps suitable for transistors or have been used in atomically thin memory devices, while others are thermoelectrics or topological insulators that are interesting for quantum devices. Antimony(III) telluride has a layered structure with van der Waals bonds between Te atoms in adjacent quintuple layers. We have performed ALD of Sb_2Te_3 using bis(trimethylsilyl)tellurium and antimony(III) ethoxide, which is a pair of previously reported precursors,[1] expanding the set of studied substrates and employing various surface treatments prior to deposition. Growth of a continuous layer is highly dependent on the starting surface through at least the first 500 cycles. Growth on the van der Waals surface of epitaxial monolayers of MoS_2 was difficult, as has been the case for other thermal ALD processes on transition metal dichalcogenides.[2] On SiO_2, we observed incompletely coalesced islands by SEM. Conversely, on amorphous GeTe, single-crystal Bi_2Te_3, or polycrystalline TiN substrates subjected *in situ* toa remote Ar plasma, we grew continuous Sb_2Te_3. On amorphous GeTe and TiN, we measured a pronounced drop in sheet resistance after 500 cycles. X-ray photoelectron spectroscopy confirms the presence of Sb and Te with $3d_{5/2}$ core levels near 527 eV and 572 eV, respectively. Compared to reference spectra, the ratio of intensities matches the expected stoichiometry. Bi_2Te_3 crystals are interesting because they have the same structure as Sb_2Te_3. In our prior study of plasma enhanced ALD on MoS_2, we observed that growth on single-crystal GaN, which has nearly the same lattice parameter in the basal plane, led to much less out-of-plane growth than on other substrates.[3]In reports on ALD of Sb_2Te_3 with the same Te precursor but antimony trichloride instead of antimony(III) ethoxide,[4] or growth of Sb with analogous chloride and alkylsilyl precursors,[5] engineering the hydroxyl groups on the substrate seems to play an important role in promoting in-plane nucleation and rapid coalescence. However, our experiments with bis(triethylsilyl)tellurium and antimony(III) ethoxide did not show an analogous advantage. We will further consider atomic layer epitaxy of van der Waals solids in this presentation. We thank ONR N0014-18-12511 for support and the NSF 2DCC DMR-1539916 for epitaxial substrates.

1. Eom et al., Chem. Mater. 24, 2099, 2012
2. Walter *et al.*, Appl. Surf. Sci. 480, 43, 2019
3. Mughal *et al.*, J. Vac. Sci. Technol. A 37, 010907, 2019
4. Nminibapiel *et al.*, ECS J Solid State Sci Technol 3P95, 2014
5. Mohney *et al.*, ALD2016

11:15am **NS-WeM2-3 2D Alloys of WS_2 and NbS_2 by PEALD***, **Jeff Schulpen**, C. Lam,* Eindhoven University of Technology, The Netherlands*; E. Coleman, F. Gity,* Tyndall National Institute, University College Cork, Ireland*; M. Mattinen, M. Verheijen, E. Kessels,* Eindhoven University of Technology, The Netherlands*; R. Duffy,* Tyndall National Institute, University College Cork, Ireland*; A. Bol,* Eindhoven University of Technology, The Netherlands

2D transition metal dichalcogenides (TMDs) have many unique properties such as high electronic mobilities and a large surface-to-volume ratio, making them promising materials for various applications such as nanoelectronics and electrocatalysis. In particular, *alloys* of 2D TMDs hold great potential due to their composition-controlled properties, making them more versatile than pure TMDs. Atomic layer deposition can be used to synthesize thin films of such TMD alloys with sub-monolayer growth control, making this method particularly relevant for the aforementioned applications. In this work we employ plasma-enhanced atomic layer deposition (PEALD) to synthesize alloys of the 2D TMDs NbS_2 and WS_2, i.e. $Nb_xW_{1-x}S_2$ using $W(NtBu)_2(NMe_2)_2$ and $Nb(NtBu)(NEt_2)_3$ as precursors and H_2S plasma as coreactant. We present a thorough characterization of the alloy growth, showing excellent composition control ranging from nanocrystalline WS_2 to amorphous NbS_2 based on ellipsometry, XPS, SEM, Raman spectroscopy and TEM. The morphology of the films depends strongly on the composition, as the alloy films have a significantly enhanced occurrence of out-of-plane oriented crystallites.

The suitability of $Nb_xW_{1-x}S_2$ as a channel material for transistors is evaluated by Hall measurements and FET device characterization. We find that the incorporation of only 10% Nb reduces the resistivity of the WS_2 film by 4 orders of magnitude at a mobility of 0.3 cm^2/Vs. Furthermore, improving the Nb distribution in the film through consecutive precursor dosing (ABC-type cycles) further increases the mobility by a factor of 2.5. At the same time we observe that the formation of out-of-plane oriented crystallites is strongly suppressed when using this process type, which is critical for applications in nano-electronics. Fabrication and characterization of FETs based on the alloy films are currently ongoing. Secondly, we assess the efficacy of the $Nb_xW_{1-x}S_2$ films as electrocatalysts for the hydrogen evolution reaction (HER). The alloys were found to outperform the pure NbS_2 and WS_2 films deposited by PEALD, having lower Tafel slopes and overpotentials. The alloy with a composition x = 0.84 performed best with a Tafel slope of 131 mV/dec and an overpotential of 470 mV.

Our results show that the $Nb_xW_{1-x}S_2$ alloys improve on the electrical and electrocatalytic performance of pure WS_2 and NbS_2. Furthermore, the various supercycle schemes provide a valuable platform for fundamental insight into the surface reactions and growth mechanics during the PEALD process and for further fine-tuning of the alloy functionalities.

11:30am **NS-WeM2-4 2D Molybdenum Dichalcogenides by Atomic Layer Deposition***, **Raul Zazpe**, J. Charvot, L. Hromadko, H. Sopha, J. Rodriguez Pereira , F. Bures, J. Macak,* University of Pardubice, Czechia

2D semiconductor transition metal dichalcogenides have attracted considerable attention due to their layered structure, suitable band gap, electrochemically active unsaturated edges and relatively good stability against photocorrosion. These properties result promising for different applications including, Li-ion batteries, photocatalysis and hydrogen evolution reaction (HER). Apart from the widely studied 2D MoS_2, 2D selenide and telluride equivalents, $MoSe_2$ and $MoTe_2$,have recently gained considerable interest due to their higher electrical conductivity, wider inter-layer distance and narrower bandgap as compared to MoS_2, high surface area and close to zero Gibbs free energy edges for hydrogen adsorption.

Unlike sulfide dichalcogenides, the lack of Se and Te precursors have prevented the synthesis of selenide and telluride dichalcogenides by ALD. In order to surpass such impediment, we present a set of novel in-house synthesized Se and Te compounds, which were successfully combined with commercial Mo precursor to synthesize $MoSe_2$ and $MoTe_2$ by ALD [1-5]. The as-deposited ALD $MoSe_2$ and $MoTe_2$ on substrates of different nature were extensively characterized by different techniques, which confirmed the chemical composition and revealed the growth of 2D flaky nano-crystalline $MoSe_2$ and $MoTe_2$. In parallel, $MoSe_2$ and $MoTe_2@TiO_2$ nanotube layers (TNTs) heterostructures were fabricated in a simple and fast fashion to explore and exploit the $MoSe_2$ and $MoTe_2$ photo- and electrocatalytic properties. TNTs act as excellent photoactive supporting material providing a high surface area, unique directionality for charge separation, and highly effective charge collection.

The presentation will introduce and describe the synthesis of the 2D Mo dichalcogenides, the corresponding physical and electrochemical characterization and encouraging results obtained in HER [4,5], photocatalysis [4-6] and Li-ion batteries [7].

[1] R. Zazpe et al, FlatChem (2020) 21 100166

[2] J. Charvot et al, Chempluschem (2020) 85 576

[3] J. Charvot et al, RSC Adv. (2021) 11 22140

[4] R. Zazpe et al, ACS Appl. Nano Mater. (2021) 3 12 12034

[5] R. Zazpe et al, Appl. Mater. Today (2021) 23 101017

[6] M. Motola et al, Nanoscale (2019) 11 23126

[7] H. Sopha et al FlatChem (2019) 17 100130

11:45am **NS-WeM2-5 Plasma-enhanced Atomic Layer Deposition of Crystalline MoS_2 Thin Films Using a Novel Precursor***, **Jeong-Hun Choi**, M. Ha, D. Kim, J. Ahn,* Hanyang University, Korea (Republic of)

Layered two-dimensional molybdenum sulfide (MoS_2) has attracted great interest for a promising candidate material for opto-electronics and photo sensors applications due to its unique characteristics such as tunable bandgap, high electron mobility and high current on/off ratio. In order to apply MoS_2 to the industrial field, significant efforts have been placed in obtaining a wafer-scale uniform MoS_2. Plasma-enhanced atomic layer deposition (PEALD) is a promising approach for depositing a 2D MoS_2 because of its excellent thickness control. However, the low growth temperature of PEALD makes it difficult to guarantee the quality of the MoS_2 thin films.

In the present study, to overcome this limitation, Cp based molybdenum precursor was used for the PEALD of MoS_2 thin films. This novel precursor with high thermal stability resulted in MoS_2 films with high crystallinity without post thermal treatment.The composition and crystallinity of MoS_2 thin films depends on the PEALD process conditions were investigated by X-ray photoelectron spectroscopy and transmission electron microscopy. Furthermore, through fabricating the field-effect transistors, the potential of MoS_2 for electric device component was investigated.

ALD Applications

Room Van Rysselberghe - Session AA1-WeA

ALD for Memory Applications II

Moderators: Noureddine Adjeroud, Luxembourg Institute of Science and Technology (LIST), , Christian Wenger, IHP - Leibniz Institut fuer innovative Mikroelektronik

1:30pm **AA1-WeA-1 Effects of Ultra-thin Atomic Layer Deposited MgO Buffer Layer on Structural and Electrical Properties of Beo and HfO_2 Films for Dynamic Random Access Memory Capacitors***, **Bo Wen Wang**, H. Song, S. Byun, D. Kwon, J. Lim, H. Seo, T. Kim, H. Paik, J. Shin, C. Hwang,* Seoul National University, Korea (Republic of)

In this work, magnesium oxide (MgO) thin films were grown via atomic layer deposition (ALD) as a buffer layer on titanium nitride (TiN) bottom electrode using bis(cyclopentadienyl) magnesium as the Mg precursor. Subsequently, beryllium oxide (BeO) and hafnium oxide (HfO_2) films were deposited by ALD on top of the MgO buffer layer using diethyl beryllium, tetrakis(ethylmethylamino) hafnium as the Be and Hf precursors, respectively. O_3 was used as the oxygen source for each ALD process. Such stacked films (MgO/BeO, MgO/HfO_2) were used as insulator layers for metal-insulator-metal (MIM) devices with TiN as bottom and top electrodes. The leakage current density (J) levels of the MIMs were significantly suppressed when the MgO buffer layer with a thickness of only ~1 nm was adopted. As a result, the 1 nm MgO buffer layer enabled a smaller total equivalent oxide thickness (EOT) value (defined by $J < 1\times10^{-7}$ A cm^{-2} at an applied voltage of + 0.8 V) for the application of dynamic random access memory capacitor. The electrical performance improvement might be caused by the structural change with the addition of the MgO buffer layer. Therefore, the possible templating effect of in-situ crystallization of ultra-thin (< ~ 3nm) BeO and HfO_2 films on the MgO buffer layer, which was improbable directly on TiN, was investigated through scanning/transmission electron microscopy (S/TEM). Moreover, the intermixing occurring during deposition and post-deposition annealing were discussed based on the depth profiles by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

1:45pm **AA1-WeA-2 Comparison of TiO_xN_{1-x} Layer Formation at Ferroelectric-$Hf_xZr_{1-x}O_2$/TiN Interface by H_2O and O_2 Plasma Gases During Atomic Layer Deposition***, **Takashi Onaya**,* National Institute of Advanced Industrial Science and Technology/Research fellow of Japan Society for the Promotion of Science, Japan*; T. Nabatame, T. Nagata, S. Ueda,* National Institute for Materials Science, Japan*; Y. Jung, H. Hernandez-Arriaga, J. Mohan, J. Kim,* The University of Texas at Dallas*; C. Nam, E. Tsai,* Brookhaven National Laboratory*; H. Ota, Y. Morita,* National Institute of Advanced Industrial Science and Technology, Japan

The discovery of the ferroelectricity in HfO_2-based films offered the possibility for the integration and scalability of ferroelectric memory devices because of capability of atomic layer deposition (ALD) technique. In our previous study, we have reported that the $Hf_xZr_{1-x}O_2$ (HZO) films fabricated by plasma-enhanced ALD (PE-ALD) using O_2 plasma showed a higher remanent polarization ($2P_r$) and superior fatigue properties compared to those fabricated by thermal ALD (TH-ALD) using H_2O gas. [1] To clarify the cause of these differences in ferroelectricity, we focused on the interface between the HZO film and TiN bottom-electrode (BE-TiN). In this work, we studied the TiO_xN_{1-x} interfacial layer (IL) formation between BE-TiN and HZO film deposited by TH- and PE-ALD and the ferroelectricity of TiN/HZO/TiN capacitors.

TiN/HZO/TiN capacitors were fabricated as follows: A 10-nm-thick HZO film was deposited on BE-TiN by TH- and PE-ALD at 300°Cusing H_2O and O_2 plasma as oxidants, respectively, and a $(Hf/Zr)[N(C_2H_5)CH_3]_4$ (Hf:Zr = 1:1) cocktail precursor. The Hf/Zr ratios in TH- and PE-ALD films were 0.4/0.6. Next, post-deposition annealing (PDA) was performed at 400°C for 1 min in a N_2 atmosphere. Finally, TiN top-electrode was fabricated by DC sputtering. The crystallinity was analyzed using synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) at the NSLS Ⅱ, Brookhaven National Laboratory. A TiO_xN_{1-x} IL formation was evaluated by synchrotron hard X-ray photoelectron spectroscopy (HAXPES) at the BL15XU of SPring-8.

The PE-ALD film dominantly formed ferroelectric orthorhombic phase evaluated by GIWAXS, resulting in a higher $2P_r$ of 20 µC/cm^2 than that of the TH-ALD film (13 µC/cm^2).Compared with the maximum $2P_r$ after wake-up field cycling, the PE-ALD film showed less $2P_r$ degradation (~33%) after 10^6 cycles, while the $2P_r$ of TH-ALD film decreased by ~47%. These superior fatigue properties of the PE-ALD film were attributed to the formation of TiO_xN_y IL between the HZO film and BE-TiN during the ALD process, which can prevent the formation of oxygen vacancies in the HZO film during the PDA process and field cycling, evaluated by HAXPES spectra for Ti 2p and N 1s. Based on these results, we found that the TiO_xN_y IL formation at the TiN/HZO interface using O_2 plasma during the ALD process plays an important role to stabilize the redox reaction and achieve superior fatigue properties.

This work was supported by JSPS KAKENHI (JP21J01667 and JP20H02189). The HAXPES measurements were performed under approval of the NIMS Synchrotron X-ray Station (2020A4602 and 2020A4651).

[1] T. Onaya et al., APL Mater. 9, 031111 (2021).

2:00pm **AA1-WeA-3 Atomic Layer Deposition of Ternary Germanium-Sulfur-Selenium and Its Application for Ovonic Threshold Switching***, **Seungwon Park**, M. Kim, T. Kim, S. Chung, H. Kim,* School of Electrical & Electronic Engineering, Yonsei University, Korea (Republic of)

As s steep increase of memory capacity has been required, 2-terminal storage class memory (SCM) based on three-dimesional (3D) vertical cross-point (VXP) structure is receiving a lot of attention. With this regard, selector devices are an essential part of minimizing leakage current that can make failures of memory operation. Among them, ovonic threshold switching (OTS) materials consisting of chalcogenide materials (*e.g.,* S, Se, and Te) has been regarded as a promising candidate for 3D X-point owning to its low leakage and high on current (I_{on}). Nevertheless, research on atomic layer deposition (ALD)-based OTS applications, which is crucial for sophisticated thickness control and conformality, is still in the beginning stage and especially sulfur-based ALD OTS material research is lacking despite its potential to possess superior OTS characteristics.[1]

Herein, we developed a thermal ALD $Ge_{1-x}S_x$ (Ge-S) process using $HGeCl_3$ precursor and H_2S reactant. The growth characteristics and film properties of Ge-S film were investigated in detail. Besides, by incorporating thermal ALD Ge-Se designed by W.H Kim *et al.*[2] to our Ge-S, we fabricated ALD ternary germanium-sulfur-selenium (Ge-S-Se) alloy devices spanning a broad range of compositions by adjusting the ALD super-cycle ratio. The film characteristics and electrical parameters of Ge-S/Ge-Se/Ge-S-Se were evaluated and compared to verify the effect of its composition change. We successfully presented the foundation of the thermal ALD technique of Ge-S and opened the possibility to tune threshold voltage and to apply the Ge-S-Se of various composition ratios for desired purposes suitably.

Acknowledgements

This paper was a result of the research projected supported by SK Hynix Inc.

References

[1] S.Jia *et al*. Nature Communications **11**, 4636 (2020)

[2] W.H Kim *et al*. Nanotechnology **29**, 365202 (2018)

2:15pm **AA1-WeA-4 Scaling Down to sub-5 nm Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films with Anhydrous H_2O_2 ALD Oxidant***, **Yong Chan Jung**, J. Kim, H. Hernandez-Arriaga, D. Le, S. Hwang,* University of Texas at Dallas*; D. Alvarez, J. Spiegelman,* RASIRC*; T. Onaya,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; C. Nam, Y. Zhang,* Brookhaven National Laboratory*; S. Kim,* Kangwon National University, Korea (Republic of)*; J. Kim,* University of Texas at Dallas

The ferroelectricity of doped HfO_2 thin films have been extensively investigated in many applications such as ferroelectric field effect transistor (FeFET), ferroelectric tunneling junction (FTJ) device, and ferroelectric random-access memory (FeRAM) etc. Previous studies have demonstrated that high-quality ferroelectric doped HfO_2 thin films can be easily obtained with a thickness of 5 nm or more.[1,2] However, it is difficult to achieve good ferroelectric property as the thickness of the ferroelectric layers decreased to sub-5 nm. In addition, the crystallization temperature increases significantly with a down-scaling of the ferroelectric film thickness due to the increase of the surface-area-to-volume ratio.[2] Therefore, we intensively investigated atomic layer deposition (ALD) process and post annealing conditions to obtain stable ferroelectric property at the $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thickness of sub-5 nm.

In this study, HZO films were deposited using anhydrous H_2O_2 as an ALD oxygen source with the variation of deposition temperature at 250 °C to 350 °C. In addition, annealing temperature was varied from 400 °C to 500 °C. To confirm robust ferroelectric property, we fabricated TiN/HZO/TiN capacitors and characterized electrically (PE hysteresis, Pulse, CV and IV analysis). The crystallinity of HZO films were also analyzed using synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) at the

Brookhaven National Laboratory. In addition, the half-cycle study using *in-situ* reflection absorption infrared spectroscopy (RAIRS) has revealed that anhydrous H_2O_2 forms high surface saturation. It is suspected that this chemical densification gives the advantages of scaling and low thermal budget of ferroelectric HZO film. The detailed results will be presented.

This work was supported by the Technology Innovation Program (20010806) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea). This work was also partially supported by GRC-LMD program (#3001.001) of SRC, and the National Research Foundation of Korea (NRF) grant funded by MSIT (NRF-2019R1F1A1059972).

[1] Y. C. Jung et al., *Phys. status Solidi-RRL***15**, 2100053 (2021).

[2] S. J. Kim et al., *Appl. Phys. Lett.***112**, 172902 (2018).

2:30pm **AA1-WeA-5 Engineering the Ferroelectric Properties in Hafnium Oxide by Co-Doping during Atomic Layer Deposition***, **Kati Kühnel**, M. Lederer, A. Pourjafar, K. Mertens, F. Schöne, M. Neuber, L. Roy, T. Kämpfe, K. Seidel, M. Czernohorsky,* Fraunhofer IPMS, Center Nanoelectronic Technologies, Germany

The presence of ferroelectricity in hafnium oxide thin films can be controlled via doping. Since those layers are usually deposited via atomic layer deposition, the doping element (like Zr, Al, Si, La) is supplied via monolayers. This way, the metastable ferroelectric phase can be stabilized. However, often wake-up effects and asymmetries like imprints are present in the produced films, impairing optimal device performance in e.g. embedded non-volatile memory devices like ferroelectric field effect transistors. These imperfections will also affect the device behavior in piezo- and pyroelectric sensors and actuators.

We report on a novel method to control the phase and the switching behavior in hafnium oxide thin films by atomic layer deposition on 300 mm wafers. By utilizing two different doping elements with strong differences in their ionic properties, especially in their ionic radius and charge with respect to Hf, the here presented co-doping process enables to tune local stresses or electric fields. This is implemented by varying the doping concentration homogeneously in the layer and implementing concentration differences within the layer. For the hafnium oxide deposition two different precursors are explored, namely hafniumtetrachloride ($HfCl_4$) and tetrakis(ethylmethylamino)hafnium(IV) (TEMAHf). Water and ozone are used as oxidizers, respectively. For the electrical characterization, the ferroelectric films are implemented in MIM stacks with TiN as electrode material. These MIM stacks are annealedat different temperatures between 650 and 1050 °C to achieve the improved ferroelectric properties.

Depending on the used processing method, alternating or block wise dopant deposition, the phase stabilization of the ferroelectric orthorhombic $Pca2_1$ phase can be influenced, as indicated by the grazing incident X-ray diffraction results.

The polarization-voltage hysteresis shape can be modified by defining favored polarization axis orientations or influencing the domain wall movement. Moreover, effects like imprint can be counteracted. This is reflected in the displacement current by the current peak position, amplitude, shape and width. Consequently, this will affect the mechanical displacement and the pyroelectric properties as well, since they are dependent on the polarization behavior.

2:45pm **AA1-WeA-6 Magnetic and Electric Properties of Atomic Layer Deposited HfO_2-Fe_2O_3 Thin Films***, **Kristjan Kalam**, M. Otsus, R. Rammula,* University of Tartu, Estonia*; J. Link,* National institute of chemical physics and biophysics, Estonia*; R. Stern,* National Institute of Chemical Physics and Biophysics, Estonia*; G. Vinuesa, S. Duenas, H. Castan,* University of Valladolid, Spain*; K. Kukli, A. Tamm,* University of Tartu, Estonia

Kristjan Kalam[1], Markus Otsus[1], Raul Rammula[1], Joosep Link[2], Raivo Stern[2], Guillermo Vinuesa[3], Salvador Dueñas[3], Helena Castán[3], Kaupo Kukli[1], Aile Tamm[1]

[1] *Institute of Physics, University of Tartu, W. Ostwald 1, 50411 Tartu, Estonia.*

[2] *National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia.*

[3] *Department of Electronics, University of Valladolid. Paseo Belén, 15. 47011 Valladolid, Spain.*

E-mail of presenting author: kristjan.kalam@ut.ee

Atomic layer deposited thin films have had a role in memory technology for quite some time, mostly as high-k dielectrics [1]. In recent years, however, such thin films have become a subject of interest as having intrinsic memory properties themselves, such as ferromagnetism and resistive switching [2-3]. HfO_2 thin films have been found to exhibit resistive switching properties [2]. Fe_2O_3 thin films have exhibited ferromagnetic properties [3]. Therefore, it is of interest to investigate if HfO_2 coupled with Fe_2O_3 would exhibit both resistive switching and ferromagnetic hysteresis in the same material sample.

Precursors to the films were $FeCp_2$ and $HfCl_4$, whereby O_3 was the oxidizer. Film thickness, elemental composition and crystal structure were evaluated. Most films exhibited ferromagnetic and/or superparamagnetic properties. Even un-doped HfO_2 could be magnetized, provided that the cubic phase was stabilized and present in the sample. Some films exhibited an electrical nonvolatile memory effect, unipolar resistive switching, where the resistance of a film can be switched between two distinct values. For example, a layered structure HfO_2+ Fe_2O_3+ HfO_2+ Fe_2O_3 was found to have both ferromagnetic and resistive switching properties.

[1]Niinistö, Jaakko, et al. Atomic layer deposition of high-k oxides of the group 4 metals for memory applications. *Adv. Eng. Mater.* 11 (2009) 223-234.

[2] Lin, Kuan-Liang, et al. Electrode dependence of filament formation in HfO2 resistive-switching memory. *J. Appl. Phys.* 109 (2011) 084104.

[3] Kalam, Kristjan et al. Atomic layer deposition and properties of ZrO2/Fe2O3 thin films, *Beilstein J Nanotech.* 9 (2018) 119.

3:00pm **AA1-WeA-7 Atomic Layer Deposition of Antiferroelectric Perovskite Lead Hafnate Using O_2-Gas-Only as the Oxygen Precursor***, **Nicholas Strnad**, W. Sarney,* Army Research Laboratory*; G. Fox,* Fox Materials Consulting, LLC*; B. Hanrahan,* Army Research Laboratory*; B. Rayner,* Kurt J. Lesker Company*; R. Rudy, J. Pulskamp,* Army Research Laboratory

ALD-grown ferroelectrics have garnered much attention over the past decade due in large part to the discovery of ferroelectric doped-hafnia which has renewed interest in scalable, non-volatile, and neuromorphic memory. Nanolaminates consisting of ferroelectric, dielectric, and antiferroelectric thin films may be engineered to exhibit neuromorphic-enabling multi-state read/write capabilities, however, there are comparably few ALD processes available for archetypal antiferroelectric thin films compared to their ferroelectric and dielectric counterparts. Here, we present an ALD process to grow perovskite, antiferroelectric lead hafnate ($PbHfO_3$, PHO) using the commonly-used amide hafnium precursor tetrakis dimethylamino hafnium (TDMAH), lead bis(3-N,N-dimethyl-2-methyl-2-propanoxide) ($Pb(DMAMP)_2$) and O_2 gas as the co-precursor for both metalorganic compounds. We show that the composition may be controlled using a super-cycle consisting of *n* PbO cycles and one HfO_2 cycle. The films were deposited in an initially amorphous state with an interspersed polycrystalline PbO phase and crystallized into the perovskite state upon either furnace or rapid thermal anneal in an oxygen atmosphere. We observed dose saturation of the O_2 gas co-precursor only for extremely large exposures in excess of $3\text{x}10^9$ L. The growth per cycle (GPC) of the PHO, averaged across the supercycle, is shown to be approximately 0.5 Å. We investigate the chemical distribution and phase of the ALD PHO films before and after annealing using transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS). Quantitative electrical characterization was performed on fabricated capacitor structures using 60 nm-thick PHO on a platinized substrate, which showed double-hysteresis polarization versus voltage loops with max/min polarization values of $\pm 50\ \mu C/cm^2$ at ±16 V.

3:15pm **AA1-WeA-8 *In-situ* Half-Cycle Study of High Purity H_2O_2-based HfO_2 Atomic Layer Deposition for Hf based Ferroelectric Devices Applications***, **Jinhyun Kim**, Y. Jung, S. Hwang, D. Le, H. Hernandez-Arriaga, K. Tan,* University of Texas at Dallas*; D. Alvarez, J. Spiegelman,* RASIRC*; S. Kim,* Kangwon University*; J. Kim,* University of Texas at Dallas

Recently, we have reported the ALD characteristics and film properties of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) using high purity H_2O_2 and O_3. H_2O_2-based HZO showed higher GPC, lower wet-etch rate (WER), and higher film density than O_3-based HZO.[1] In comparison to H_2O, high purity H_2O_2 delivers 50% higher GPC, improved WER, and denser film from H_2O (SFig.1). H_2O_2 has low oxygen dissociation energy and high oxidation power comparable to O_3 as well as hydroxyl groups for ligand exchange reactions like H_2O, making it an ideal candidate for the oxide ALD process. Thus, an extensive study of H_2O_2 surface reactions is necessary to further investigate the reasons behind observed improvements. The conventional H_2O_2 precursor is commonly dissolved in a high content H_2O. Therefore, identifying the effects of H_2O_2 as an oxidant of ALD process from those of H_2O is a significant challenge.[2]

In this study, we have implemented high purity anhydrous H_2O_2 to better understand ALD growth mechanism, interface formation, and film properties attributed by H_2O_2 while prohibiting the effects of H_2O.

It is expected that different oxidants (H_2O_2, H_2O, and O_3) can significantly impact the overall film growth and interfacial growth behaviors. ALD processes of HfO_2 using various oxidants are monitored to examine the surface pathways of H_2O_2, H_2O, and O_3. Comprehensive surface studies of ALD-HfO_2, deposited using TDMA-Hf and oxidants on TiN substrate, are studied using an *in-situ* reflection absorption infrared spectroscopy (RAIRS) system.[3] Half-cycle study with differential and accumulated FTIR spectra will be investigated to identify the growth mechanism of different oxidants. This will allow us to observe the TiN and oxide interface formation and ligand exchange reaction while ALD process. Moreover, the FTIR spectra of the oxide bonding region will provide a better understanding of bonding density and oxide growth. Initial *in-situ* RAIRS study indicates that the surface absorption rate of H_2O_2 is significantly faster than H_2O, providing additional reaction sites during subsequent TDMA-Hf exposure steps. Eventually, the additional Hf–O bonds may increase film density, which can potentially provide enhanced film properties. Furthermore, interface formation is expected to be also observable using *in-situ* spectra of full ALD cycles by comparing the initial and bulk cycles (SFig.2).

This work was supported by Tech. Innovation Program (20010806) funded by MOTIE and GRC-LMD program (task#3001.001) through SRC. We thank RASIRC Inc. for providing the H_2O_2 source.

[1] J. H Kim et al., AVS, ALD 2021.

[2] D. Alvarez Jr. et al., Proc. SPIE 11326, 113260S (2020).

[3] S. M. Hwang et al., *ECS Trans.*, **92**, 265 (2019).

ALD Applications
Room Van Rysselberghe - Session AA2-WeA

Emerging Applications of ALD

Moderators: Giuseppe Alessio Verni, ASM, Adrie Mackus, Eindhoven University, Netherlands

4:00pm **AA2-WeA-11 Mechanical Properties of ALD Coatings***, **Aile Tamm,*** University of Tartu, Estonia*; H. Piirsoo,* University of Tartu,, Estonia*; J. Kozlova, T. Jõgiaas,* University of Tartu, Estonia **INVITED**

Demand in using films grown by atomic layer deposition (ALD) for the fabrication of microelectromechanical systems has significantly increased during the past decades [1]. ALD films can be used as supporting layers (seed layers, masks, etc) as well as device's functional layers. Depending on the application, the ALD film thicknesses used may vary from nanometer-level to several hundreds of nanometers, while composition can vary from pure metal or metal oxide to several metals together in one film. For the preparation of the devices, it is often required to obtain a film that combines several specific physical properties in one film.

Mechanical properties (elastic modulus and hardness) of ALD films with a thickness from 30 up to 150 nm were measured by nanoindentation using Hysitron TriboIndenter TI980 (Bruker). The properties (thickness, morphology, composition and crystallinity) of pure oxide films, like Cr_2O_3, Al_2O_3, Ta_2O_3, HfO_2 and ZrO_2 as well as layered nanostructures, like ZrO_2-SnO_2 [2], HfO_2-ZrO_2 [3], Al_2O_3-ZrO_2 [4] Al_2O_3-Ta_2O_5, HfO_2-Al_2O_3 will be discussed.

A few of the results of the layered nanostructures studies were follows:

56. the thickness and sequence of oxide layers of the two-and three-layered laminates influenced the hardness and elastic modulus of the laminates.
57. plasma ALD processes do not give advantages over thermal ALD.

This work overviews the results obtained by studying a quite wide range of materials where the mechanical and also magnetic or optical properties of the same ALD films were explored. Using alternating layers of different metal oxides allows fine-tuning of the film properties and even obtaining a film that overcomes the performance of the pure oxide film.

[1] M. Nasim, Y. Li, M. Wen, and C. Wen, “A review of high-strength nanolaminates and evaluation of their properties,” *J. Mater. Sci. Technol.*,50 (2020) 215–244.

[2] A. Tamm, H.-M. Piirsoo, T. Jõgiaas, et. al , Mechanical and Magnetic Properties of Double Layered Nanostructures of Tin and Zirconium Oxides Grown by Atomic Layer Deposition,*Nanomaterials, 11* (2021) 1633.

[3] T. Jõgiaas, M. Kull, H. Seemen, P. Ritslaid, K. Kukli, A. Tamm, Optical and mechanical properties of nanolaminates of zirconium and hafnium oxides grown by atomic layer deposition, *J. Vac. Sci. Technol.* A 38 (2020) 022406.

[4] T Jõgiaas, R. Zabels, A. Tarre, A. Tamm, Hardness and modulus of elasticity of atomic layer deposited Al2O3-ZrO2 nanolaminates and mixtures, *Mat Chem Phys.*240 (2020) 122270.

4:30pm **AA2-WeA-13 Superconducting Tantalum Nitride Prepared by Plasma ALD With RF Biasing for Quantum Applications***, **Silke Peeters,*** Eindhoven University of Technology, Netherlands*; C. Lennon, R. Hadfield,* University of Glasgow, UK*; E. Kessels, H. Knoops,* Eindhoven University of Technology, Netherlands

This contribution reports the first critical temperatures (T_c) for tantalum nitride prepared by plasma ALD and outlines the promising electrical and structural properties of this material for application as a low-loss superconducting material in quantum devices. The motivation is to further improve quantum device performance for which a reduction of material-related decoherence sources is critical. The recent demonstration of Ta superconducting transmon qubit coherence times above 0.3 milliseconds[1] calls for further exploration of Ta-based materials for quantum applications.

This work focuses on TaN, as reported T_c values for superconductivity exceed those of Ta[2]. Moreover, nitridation of superconductors has been shown to better protect against loss due to surface oxidation[3]. To our knowledge, no superconducting transition has been reported for TaN prepared by ALD. Literature on TaN prepared by techniques such as dc magnetron sputtering and pulsed laser deposition reveals that, together with resistivity, stoichiometry and crystal structure are critical film properties in achieving superconducting TaN films.

Thin TaN layers are prepared by plasma-enhanced ALD using TBTDMT and Ar-H_2 plasma at 250 °C with RF substrate biasing. A low room temperature resistivity of 221 μΩ cm of a 35 nm film is measured for a 20 W RF bias, which is a hundredfold improvement compared to films prepared without biasing. XPS measurements confirm that applying a substrate bias counteracts O incorporation during deposition. In addition, XPS reveals a significant increase in C content. Strikingly, these films are of $(N+C):Ta \approx 1$ stoichiometry, and it is verified that C is present in Ta-C bonds. As tantalum carbonitrides display similar superconducting properties, this may provide additional opportunities of tuning layer properties. Moreover, XRD measurements show a (111) and (200) fcc crystal structure, where the cubic structure yields the highest T_c for TaN according to literature[4]. TEM analysis reveals an increase in crystal size due to substrate biasing. Preliminary liquid He four-point probe measurements on these samples indicate a T_c above 6 K.

Through substrate biasing stoichiometric fcc $Ta(C_x)N_y$ thin films of enhanced conductivity were obtained. The control of film properties and the relation with the superconducting transition will be discussed in this contribution.

References

1. Place *et al. Nat. Commun.***12**, 1779 (2021)

2. Thorwarth *et al. Solid State Commun.***20**, 870 (1976)

3. Wang *et al. Jpn. J. Appl. Phys.* **42**, 1843 (2003)

4. Reichelt *et al. J. Appl. Phys.* **49**, 5284 (1978)

4:45pm **AA2-WeA-14 Membrane Design by ALD for Hydrogen Purification***, L. Badouric, M. Drobek, A. Julbe, **Mikhael Bechelany,*** European Institute of Membranes, France

Hydrogen (H_2) is one of the energy vectors essential for the success of the energy transition. In less than twenty-five years, hydrogen is expected to represent 18% of the total energy consumed on the planet thus leading to possible CO_2 emissions decrease by 6 gigatonnes compared to current levels. At the same time, hydrogen energy technologies involve major environmental, research and industrial challenges. In this presentation, we will show our efforts in designing membranes by Atomic Layer Deposition (ALD) for hydrogen purification.

In view of the increasing use of hydrogen as "green energy carrier", the various aspects of its production must be considered and optimized. Indeed, the continuous separation/purification of H_2 is a key step in the production chain. When polymer (low selectivity and temperature resistance) or palladium-based membranes (more expensive and highly sensitive to sulfur compounds) cannot be used for H_2 purification, the application of inorganic or hybrid ultra-microporous membranes is a relevant option. In this context, we will present a preparation of highly selective ultra-thin prototype membranes deposited on the surface or inner porosity of commercial porous supports by Atomic Layer Deposition (ALD). The design and synthesis conditions of these membranes are optimized according to the constraints of the targeted application, in order to maximize the thermochemical stability, the abrasion resistance as well as the membranes performance (H_2 selectivity and permeability). Several examples including the development of Metal Organic Frameworks (MOFs) [1] and Palladium - based membranes [2] as well as their composites prepared by Atomic Layer Deposition (ALD) [3] will be highlighted in this presentation.

[1] Journal of Membrane Science, 2015, 475, 39–46

[2] Journal of membrane Science, 2020, 596, 117701

[3] Chemistry of Materials 2018, 30, 7368-7390

Area Selective ALD
Room Baekeland - Session AS1-WeA

Area Selective Deposition I

Moderators: Amy Brummer, Georgia Institute of Technology, Il-Kwon Oh, Ajou University

1:30pm **AS1-WeA-1 Polystyrene Brush Deactivation Layers for Area Selective Atomic Layer Deposition**, ***Caitlin McFeely***, *M. Snelgrove , K. Shiel, G. Hughes,* School of Physical Sciences, Dublin City University , Ireland*; P. Yadav, M. Morris,* AMBER Research Centre and School of Chemistry, Trinity College Dublin, Ireland*; E. McGlynn, R. O'Connor,* School of Physical Sciences, Dublin City University, Ireland

Research into the field of area-selective atomic layer deposition (AS-ALD) is key for the development of new methods for the fabrication of modern microelectronics, as current technologies are reaching their limits. Typically, the selectivity originates from modifications that either activate or deactivate the substrate surface. Polymer brushes have been previously shown to act both as an activation or deactivation layer within the field of area selective deposition (ASD) [1,2]. These brushes have been widely researched due to their capacity to enable rapid fabrication, making them an industrial relevant route for processing semiconductor devices [3]. Here we focus of the use of polystyrene (PS), which is a polymer known for its ability to act as a deactivation layer for the use in ASD.

This work studies the effect that the thickness of a PS brush has on its ability to act as an effective deactivation layer against a thermal HfO_2 atomic layer deposition (ALD) process using $HfCl_4$ and H_2O as the precursor and co-reactant, respectively. Using X-ray photoelectron spectroscopy as the primary characterisation technique, our results show an increasing blocking efficacy with an increase in the PS brush thickness. The thickest PS brush, of approximately 11 nm, effectively blocked a 300 cycle ALD process which resulted in 19 nm of HfO_2 on native oxide covered Si. Due to the significantly faster fabrication times of PS brushes, this process is deemed a highly competitive alternative to the more widely used AS-ALD methodologies such as self-assembled monolayers.

(1) Snelgrove, M.; McFeely, C.; Mani-Gonzalez, P. G.; Lahtonen, K.; Lundy, R.; Hughes, G.; Valden, M.; McGlynn, E.; Yadav, P.; Saari, J.; Morris, M. A.; O'Connor, R. Aluminium Oxide Formation via Atomic Layer Deposition Using a Polymer Brush Mediated Selective Infiltration Approach. *Appl. Surf. Sci.*2020, *515*.

(2) Snelgrove, M.; McFeely, C.; Shiel, K.; Hughes, G.; Yadav, P.; Weiland, C.; Woicik, J. C.; Mani-Gonzalez, P. G.; Lundy, R.; Morris, M. A.; McGlynn, E.; O'Connor, R. Analysing Trimethylaluminum Infiltration into Polymer Brushes Using a Scalable Area Selective Vapor Phase Process. *Mater. Adv.*2021, *2* (2), 769–781.

(3) Lundy, R.; Yadav, P.; Selkirk, A.; Mullen, E.; Ghoshal, T.; Cummins, C.; Morris, M. A. Optimizing Polymer Brush Coverage To Develop Highly Coherent Sub-5 Nm Oxide Films by Ion Inclusion. *Chem. Mater.*2019, *31* (22), 9338–9345.

1:45pm **AS1-WeA-2 Area Selective Deposition of Ruthenium using a W Precursor Inhibitor**, ***Chi Thang Nguyen***, *N. Trinh, M. Lee, H. Lee,* Department of Materials Science and Engineering, Incheon National University, Korea (Republic of)

Atomic layer deposition (ALD) enables the precise control of Angstrom-scale film thickness with excellent conformality due to its self-saturated surface reactions. By maximizing the surface-dependent growth, ALD could be extended to one of the patterning technologies, area selective atomic layer deposition (AS-ASD), over thin film deposition. For AS-ALD, inhibitors, such as self-assembled monolayers (SAMs), have been commonly used to deactivate surface chemical reactivity. In our group, we have proposed another opportunity of precursors, which are originally developed for thin film deposition by ALD, as an inhibitor for AS-ALD. Precursor inhibitors could have several advantages over conventional SAM inhibitors, such as high compatibility, capability for vapor phase delivery, bifunctionality, and relatively small size. In this work, we investigated a Ru ASD process usinga W precursor inhibitor which was developed for W ALD. Interestingly, it was observed that surface energy measured by water contact angle analysis was deceased with increasing exposure time which is an opposite trend to the results in ASD research. To understand the change, the adsorption energy and behavior of the W precursor inhibitor were studied by using density functional theory (DFT) calculation. A single exposure of the W precursor inhibitor layer could block the growth of Ru ALD up to 200 cycles with selectivity over 90 %.The absorption density of the W inhibitor was improved by using multi-exposure instead of continuous exposure. The results from the physical interaction simulation of the W inhibitor by Monte Carlo (MC) simulation show that the packing density of the inhibitor could be further increased by minimizing steric hindrance effects during adsorption. As a result, the blocking property of the W precursor inhibitor was improved, blocking up to 300 Ru ALD cycles.

2:00pm **AS1-WeA-3 Electron-beam Functional Group Pattering on HOPG for Area-Selective Atomic Layer Deposition**, ***Matthias Young***, *G. Koerner, Q. Wyatt,* University of Missouri*; B. Bateman,* Berea College*; C. Boyle, M. Maschmann,* University of Missouri

In this work we report on a new area selective atomic layer deposition (AS-ALD) approach enabled by a spatially controlled hydroxylation process. The processing occurs within a low-pressure water vapor ambient established within an environmental scanning electron microscope (ESEM). The ESEM electron beam interacts with the water vapor and generates a local region of reactive species (e.g. hydroxyl radicals) in the vicinity of the focused electron beam. Here, we functionalize exfoliated highly ordered pyrolytic graphite (HOPG) substrates which are natively nonreactive to the ALD precursors. The electron-beam patterning process introduces reactive hydroxyls on the graphene substrate. The hydroxylated region is sufficiently stable to withstand ALD deposition temperature of 150 ^{o}C, and the pattern fidelity is enabling for dense selective ALD growth in the patterned area.

In the current study, hydroxyl functionalization and ALD deposition occurs along line scans and square regions of up to 2 x 2 micron in area. We show that the hydroxyl functionalization, and thus ALD deposition efficacy, is highly dependent on ambient water vapor pressure and electron beam dwell time. The hydroxyl functionalization and resulting ALD coating is characterized using atomic force microscopy and energy dispersive spectroscopy (EDS) mapping. Line widths as small as 40 nm and growth/no growth selectivity in excess of 99% are demonstrated.

2:15pm **AS1-WeA-4 Inhibitor Adsorption During Area-Selective ALD: Do Mixtures of Adsorption Configurations Lead to a Loss of Selectivity?**, ***Marc Merkx***, *I. Tezsevin, P. Yu, J. Li, R. Lengers, E. Kessels,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Técnica Federico Santa Mariá, Chile*; A. Mackus,* Eindhoven University of Technology, Netherlands

Small molecule inhibitors (SMIs) are attracting interest in the field of area-selective atomic layer deposition (ALD) because of their straightforward integration into industrial process flows. However, one of the challenges is that SMIs typically adsorb in a mixture of adsorption configurations, which often are not all suited for precursor blocking. In this work, we compare two inhibitors, aniline and acetylacetone (Hacac), and study whether the different adsorption configurations can be a curse or a blessing for obtaining a high selectivity.

Aniline provides metal/dielectric selectivity (e.g. Ru versus SiO_2)[1] for area-selective ALD. Density functional theory (DFT) calculations show that aniline adsorbs either with the amine group to the surface through a δbond or with the phenyl ring through a π-bond. Although the δ-configuration is less strongly bonded to the Ru than the π-configuration, both are bonded sufficiently strong, resulting in a stable inhibition layer that is inert toward incoming precursor molecules. Random sequential adsorption (RSA) simulations were used to predict the coverage and packing of SMIs in saturation.[2] These simulations show that a significant fraction (~30%) of the aniline adsorbs in the δ-configuration, thereby enhancing the inhibitor coverage. In addition, the simulations predict that there are no gaps that are large enough to act as nucleation sites for precursor adsorption.

Hacac can be employed to achieve selectivity between different oxide surfaces (e.g. Al_2O_3 and SiO_2).[3] Infrared (IR) spectroscopy and DFT calculations show that Hacac adsorbs either in chelate or monodentate configuration, where both or only one of the O atoms bonds to the surface, respectively. The monodentate configuration was found to desorb due to its lower binding energy to the surface. In addition, interactions with the precursor through its unreacted C-OH/C=O group lead to displacement of the Hacac inhibitor molecules from the surface and therefore loss of selectivity. IR spectroscopy and RSA simulations show that this configuration makes up ~20% of the adsorbed Hacac in saturation, while it does not contribute to precursor blocking.

In summary, having a mixture of inhibitor adsorption configurations leads to a loss of selectivity for Hacac, while it improves precursor blocking for aniline. A mixture of configurations can therefore be beneficial or detrimental for the selectivity depending on the binding energy and orientation of each bonding configuration involved.

[1] Merkx *et al., Chem. Matter***32**, 7788 (2020).

[2] Evans, *Rev. Mod. Phys.***65**, 1281 (1993)

[3] Merkx *et al., Chem. Matter*. **32**, 3335 (2020).

2:30pm **AS1-WeA-5 Area Selective Deposition for ZnO Hard Mask by 2D-like Carbon fabricated by Molecular Layer Deposition***, **Seunghwan Lee**, G. Baek, H. Yang,* Hanyang University, Korea*; T. Van, B. Shong,* Hongik University, Korea (Republic of)*; J. Park,* Hanyang University, Korea

Area selective deposition (ASD) is a promising technique as a bottom-up process for creating improved overlay or self-alignment, attaining errorless alignment, increasing yield, and reducing cost of manufacturing. The selectively grown metal or metal oxide can be employed as a robust hard mask. For bottom-up process, area selective atomic layer deposition has been researched vigorous using surface chemistry. In this research, a strategy for ASD using molecular layer deposition (MLD) is introduced, which is useful for conformal deposition of organic layer that delays film growth.

An indicone layer, which has alkoxide sturcutre, was fabricated by MLD process using INCA-1 (bis(trimethysily)-amidodiethylindium) and HQ (hydroquinone), and was thermally annealed. The atomic structures of as-dep and annealed indicone films were analyzed by XPS and Raman spectra. The indium was almost completely removed with annealing process, and carbon structure was transformed to graphitic carbon above 450 °C annealing temperature. The thermally annealed indicone was used as an inhibitor, which can delay 60 cycles of ZnO (equivalent to a thickness of about 11nm). In addition, to prove chemical mechanism of precursor adsorption on graphitic carbon, density functional theory calculations were utilized. Finally, ALD ZnO was selectively deposited on Al_2O_3/SiO_2 line pattern for interconnecting SiO_2 line pattern by transferring hard mask using RIE.

2:45pm **AS1-WeA-6 Bifunctionality of Si Precursors to Enable Area Selective Deposition of Ru and Atomic Layer Deposition of SiO_2***, **Sumaira Yasmeen**, B. Gu, Y. Kang, H. Lee,* Incheon National University, Korea (Republic of)

Area selective deposition (ASD) has enabled the growth of materials on the target areas of patterned substrates to address the existing roadblocks in the semiconductor industry. ASD is very crucial in the current era as it has shown many possible ways to enable the down-scaling of electronic devices with process simplification. Several different approaches have been used for ASD including the use of self-assembled monolayers (SAMs) and small molecule inhibitors (SMIs). However, due to the associated disadvantages like the long-chain size of SAMs, poor selectivity, and thermal degradability of SMIs, researchers have diverted their attention to the use of precursors as inhibitors. The main advantage of using precursor inhibitors is to cultivate their bifunctionality as an inhibitor for ASD and a precursor for atomic layer deposition (ALD). In other words, they can be used as precursors for specific ALDs when used with a proper counter reactant, as well as can be used as inhibitors as they do not react with the mild counter reactants. In this work, we investigated two different Si precursor inhibitors which can form SiO_2 ALD using ozone counter reactant, and also due to their chemoselectivity, they inhibit the surface towards several ALDs which require H_2O or O_2 as a counter reactant. The Si precursor inhibitors selectively adsorb on the SiO_2 surface but not on Cu, so in this way, Ru can be selectively deposited on the Cu surface. Furthermore, when used ozone as a counter reactant, it forms ALD SiO_2. Experimental analysis and electrical measurements confirmed the formation of high-quality SiO_2 film using both Si precursor inhibitors. Dielectric constant, leakage current, and O/Si stoichiometric ratio of ALD SiO_2 from both Si precursor inhibitors were found to be consistent with conventional SiO_2 ALD film. The adsorption chemistry of the Si precursor inhibitors and Ru blocking were investigated using theoretical density functional theory calculation, Monte Carlo simulations, and experimental approaches. Understanding the precursors' chemistry and physical and chemical interactions can open doors for many other precursor molecules to be used as inhibitors for the next generation nanofabrication.

3:00pm **AS1-WeA-7 TiO_2 Area-Selective Deposition: Using Selectivity Loss Mechanisms to Advance Applications in Nanopatterns and EUV Resist Materials***, **Rachel Nye**,* North Carolina State University*; K. Van Dongen,* KU Leuven, Belgium*; D. De Simone, J. de Marneffe, H. Oka,* IMEC, Belgium*; G. Parsons,* North Carolina State University*; A. Delabie,* IMEC, Belgium **INVITED**

Area-selective deposition (ASD) is rapidly gaining interest as a bottom-up nanopatterning technique in semiconductor manufacturing to facilitate shrinking device sizes that traditionally rely on expensive and complex lithography steps. One key feature of ASD that has not been well established in literature is the amenability of processes to feature scales relevant to electronic devices (i.e. sub-50 nm patterns).[1] Additionally, there is growing industrial interest to expand ASD applications to new fields such as EUV lithography, where ASD of etch resistant layers could improve pattern resolution and reduce line-edge roughness (LER).[2]

In this work, we present a study of TiO_2 ASD that addresses both challenges: demonstrating successful ASD on 45 nm half-pitch patterns and on EUV resist materials. First, the selectivity loss mechanism of TiO_2 ALD ($TiCl_4/H_2O$ at 150 °C) on dimethylamino-trimethylsilane (DMA-TMS) passivated SiO_2 is investigated. Scanning electron microscopy, Rutherford backscattering spectrometry (RBS), and kinetic modeling results demonstrate nucleation site generation during TiO_2 as the primary contributor towards selectivity loss on the TMS non-growth surface. These undesired nucleation sites are effectively mitigated with periodic etching and subsequent re-passivation of the surface, resulting in significant selectivity improvement on the growth surface (TiN) with minimal defectivity on the non-growth surface (passivated SiO_2), according to transmission electron microscopy (TEM) images (Fig. 1). The DMA-TMS inhibitor is perfectly suited for this cyclical ASD process as it passivates SiO_2 without affecting TiO_2. Furthermore, we discuss the feature size-dependence of selectivity. As a next step, we explore TiO_2 ASD on methacrylate-based EUV resist materials on the basis of EUV exposure and protecting group using RBS measurements (Fig. 2). We provide insight into selectivity loss mechanisms on the EUV resist materials and utilize this information to tune the polymer structure to induce selectivity to TiO_2 ALD for use in resist hardening or tone inversion applications.

In summary, we take a considerable step in the advancement of TiO_2 ASD using mechanistic insights to improve selectivity in both nanopatterns and EUV resists. The impact of these results may be used to advance progress of feature-scale ASD research as well as catalyze ASD applications to improve pattern resolution and LER on ultra-small EUV lithography patterns.

(1) Parsons, G. N.; Clark, R. D. *Chem. Mater.* **2020**, *32* (12), 4920–4953.

(2) Wu, B.; Kumar, A. *J. Vac. Sci. Technol. B.* **2007**, *25* (6), 1743.

Area Selective ALD
Room Baekeland - Session AS2-WeA

Area Selective Deposition II

Moderators: Stacey Bent, Stanford University, Rachel Nye, North Carolina State University

4:00pm **AS2-WeA-11 Intrinsic Area-Selective Atomic Layer Deposition of Aluminium Nitride***, **Bernhard van der Wel**, T. Aarnink, A. Kovalgin,* University of Twente, the Netherlands

Group III-V nitrides (in short III-N such as AlN, GaN, InN and their alloys) are thermally and chemically stable semiconductors suitable for use in optical and high-power electronics as their bandgaps cover a spectral range from deep ultraviolet to near infrared [1]. Fabrication of mono-crystalline III-N substrates is expensive, as well as their realization on silicon wafers, typically involving high-temperatures and thick buffer layers. Fabrication of poly-crystalline variants are a viable route to reduce fabrication costs and deposit with a low thermal budget (≤ 400 °C).

Atomic layer deposition (ALD) is well-known to offer high conformality, large area uniformity and film thickness control at sub-nm scale. Self-limiting surface reactions in ALD, requiring presence of certain chemical groups on the surface for enabling such reactions, can be beneficially utilized to achieve area-selective deposition. The latter is required to overcome critical alignment requirements during film patterning and reduce the amount of lithography steps [2].

In this work, we demonstrate inherent area-selective atomic layer deposition (ASALD) of Aluminium Nitride (AlN) films in purely thermal mode (350 °C) and at a low reactor pressure (1.5e-3 mbar), from trimethylaluminium (TMA) and ammonia (NH_3). AlN is selectively grown on patterned substrates, consisting of areas of sputtered AlN and thermal SiO_2 ranging from 2×2 μm^2 to 10×10 mm^2. Proper pre-treatment facilitates growth on the sputtered AlN. Film growth is monitored in-situ by spectroscopic ellipsometry (SE) and verified by ex-situ SE and atomic-force microscopy. After 350 cycles the film thickness on sputtered AlN is approximately 12.5 nm, whereas on the SiO2 area the thickness is less than 1 nm. The interfaces, confirming selective deposition, are examined by transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS, sputter profiling) confirmed the selectivity and showed a stoichiometric Al to N ratio with oxygen and carbon contaminations as low as 8% and 3%, respectively.

[1] D. A. Neumayer and J. G. Ekerdt, "Growth of Group III Nitrides. A Review of Precursors and Techniques," Chem. Mater., vol. 8, no. 1, pp. 9–25, Jan. 1996.
[2] A. J. M. Mackus, M. J. M. Merkx, and W. M. M. Kessels, "From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity," Chem. Mater., vol. 31, no. 1, pp. 2–12, 2019.

4:15pm **AS2-WeA-12 Surface-Diffusion Control Enables Tailored-Aspect-Ratio Nanostructures in Area-Selective Atomic Layer Deposition***, **Philip Klement**, D. Anders, L. Gümbel, M. Bastianello, F. Michel, J. Schörmann, M. Elm,* Institute of Experimental Physics I & Center for Materials Research (ZfM), Justus Liebig University Giessen, Giessen, Germany*; C. Heiliger,* Institute of Theoretical Physics & Center for Materials Research (ZfM), Justus Liebig University Giessen, Giessen, Germany*; S. Chatterjee,* Institute of Experimental Physics I & Center for Materials Research (ZfM), Justus Liebig University Giessen, Giessen, Germany

Area-selective atomic layer deposition is a key technology for modern microelectronics as it eliminates alignment errors inherent to conventional approaches by enabling material deposition only in specific areas. Typically, the selectivity originates from surface modifications of the substrate that allow or block precursor adsorption. The control of the deposition process currently remains a major challenge as the selectivity of the no-growth areas is lost quickly.

Here, we show that surface modifications of the substrate strongly manipulate the surface diffusion. The selective deposition of TiO_2 on poly (methyl methacrylate) and SiO_2 yields localized nanostructures with tailored aspect ratios. Controlling the surface diffusion allows to tune such nanostructures as it boosts the growth rate at the interface of the growth and no-growth areas. Kinetic Monte-Carlo calculations reveal that species move from high to low diffusion areas. Further, we identify the catalytic activity of $TiCl_4$ during the formation of carboxylic acid on poly (methyl methacrylate) as the reaction mechanism responsible for the loss of selectivity, and show that process optimization leads to higher selectivity. Our work enables the precise control of area-selective atomic layer deposition on the nanoscale, and offers new strategies in area-selective deposition processes by exploiting surface diffusion effects.

4:30pm **AS2-WeA-13 Study on Area-Selective Atomic Layer Deposition of Al_2O_3 with a Series of Al Precursors***, **Il-Kwon Oh**,* Ajou University, Korea (Republic of) **INVITED**

Area-selective atomic layer deposition (AS-ALD) offers the advantage of exploiting surface chemistry to deposit a material in a targeted area. Therefore, it may allow a reduction in the number of lithography and etch steps, resulting in lowering of errors in the patterning process as well as a decrease in manufacturing costs. For example, a self-aligned hard mask fabricated by AS-ALD can guide etching of via holes and deposition of metal wires in the metallization process to avoid shorts between metal layers.

Several metal oxide systems, such as Al_2O_3, TiO_2, ZnO, and HfO_2, have been explored for AS-ALD processes. For a hard mask, Al_2O_3 possesses advantages over other metal oxides due to its high hardness as well as chemical inertness for etching selectivity. However, despite extensive studies on ALD Al_2O_3, there are few studies on AS-ALD of Al_2O_3. Furthermore, literature suggests that Al_2O_3 may be comparatively difficult to block; for example, the blocking selectivity of Al_2O_3 is limited to only ~6 nm whereas ZnO can be blocked for over ~30 nm. The difference in blocking highlights the importance of precursor chemistry for AS-ALD, which motivates the current study to elucidate the mechanism of Al_2O_3 AS-ALD based on a comparative study of Al precursors.

In this work, the recent development of AS-ALD is introduced. Furthermore, as an example, fundamental study on AS-ALD Al_2O_3 is presented. Four Al precursors; trichloroaluminum ($AlCl_3$), dimethylaluminum chloride ($Al(CH_3)_2Cl$), trimethylaluminum ($Al(CH_3)_3$), and triethylaluminum ($Al(C_2H_5)_3$) are used for comparison, offering a comparative study of precursor ligand properties (reactivity, polarity, and geometric factors) by changing both the number of methyl (Me) and chloride (Cl) group in $AlMe_xCl_{3-x}$ (x=0, 1, and 3) and the chain length of alkyl ligands in AlC_nH_{2n+1} (n=1 and 2). Results of quantum chemical calculations of the reaction pathways show product energetics that are strongly correlated with experimental observations. The blocking properties of the four Al precursors will be compared and the results discussed based on the growth mechanism. Finally, Al_2O_3 selective pattern is successfully fabricated, which would be useful for back-end-of-line (BEOL) semiconductor process. By pursuing first principles design of selective ALD processes, this work may enable new methods for additive nanoscale.

5:00pm **AS2-WeA-15 Selective Hydration of TiO_2 and In_2O_3: A Strategy for Site-Selective Atomic Layer Deposition at Surface Defects***, A. Martinson, E. Kamphaus, J. Jones, N. Shan,* Argonne National Laboratory, USA*; C. Luo, A. Hock,* Illinois Institute of Technology*; L. Cheng,* Argonne National Laboratory, USA*; **Ashley R. Bielinski**,* Argonne National Laboratory

While ALD is most commonly employed in uniform conformal growth, more selective precursors and processes may allow for more precise synthetic strategies including targeted reaction at subtly unique surface sites including those that lead to electronic defects. We outline a selective hydration strategy to target reaction at the step edges of rutile TiO2 and In_2O_3. We computationally and experimentally investigate the feasibility of facet- and site-selective ALD through accurate asymmetric slab models from which the free energy of adsorption at unique surface sites is leveraged to predict step selectivity. Computational evaluation of ALD precursor adsorption free energies on multiple dehydrated facets further refine the feasibility of a temperature-dependent selective hydration strategy. Initial experiments of Ga_2O_3 ALD nucleation on TiO_2 single crystals and MgO ALD on In_2O_3 broadly support the computational predictions and strategy. The strategies outlined here provide one possible route to selectively target growth at structural defects of oxide surfaces.

5:15pm **AS2-WeA-16 Self-Assembled Monolayer and "Click" Chemistry Deposition Treatments for Area-Specific Processing***, **Chad Brick**, R. Liberatore,* Gelest, Inc*; B. Arkles,* Department of Chemistry, Temple University*; J. Goff,* Gelest, Inc

Self-assembled monolayers (SAMs) formed or modified by rapid "click" chemical reactions are receiving significant attention due to their demonstrated ability to promote or facilitate area-specific or area-selective deposition utilizing processes that occur on time scales compatible with high-throughput manufacture and cyclic deposition schemes. By precision tailoring of the chemical structure of the SAM layer, the selectivity and speed of the reactions with both the underlying substrate and subsequent deposition cycles can be enhanced in order to provide rapid, selective processes with few or no chemical byproducts. In this work we demonstrate that cyclic azasilanes and cyclic thiasilanes can rapidly bond to the surface of hydroxyl-covered substrates in the vapor phase, with saturated coverage being reached in several seconds in a manufacturing-worthy atomic layer deposition tool. The effects of processing parameters, including pulse time, temperature, substrate type, and pre-treatment on the deposition profile, as well as the subsequent reactivity of cyclic azasilanes to further modify the chemical nature of the surface are discussed, with an emphasis on rapid "click" chemical processes compatible with high throughput. It was observed that on hydroxyl (OH)-terminated surfaces such as silicon native or thermal oxide the cyclic silanes reach a saturation point in approximately five seconds under typical ALD conditions over the temperature range of 30 °C to 300 °C, as determined by water contact angle and ellipsometry. The reactivity and selectivity of cyclic azasilanes to other oxide surfaces as well as non-oxides such as copper, silicon nitride, and HF-etched silicon will be discussed, as will process to remove azasilane monolayers after deposition.

Emerging Materials
Room Auditorium - Session EM1-WeA
Emerging Materials

Moderators: Nathanaelle Schneider, CNRS-IPVF, Charles H. Winter, Wayne State University

1:30pm **EM1-WeA-1 Self-Limiting Growth of Monocrystalline GaN Films via Sequential Triethylgallium and Forming Gas Plasma Cycles in Hollow-Cathode Plasma-ALD Reactor**, *D. Shukla, S. Ilhom, A. Mohammad, B. Willis,* University of Connecticut; *A. Okyay,* Stanford University; ***Necmi Biyikli,*** University of Connecticut

Low-temperature synthesis efforts for high-quality GaN thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early GaN growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, shifting to stainless-steel based hollow-cathode plasma source revealed polycrystalline GaN films with preferred (002) orientation. Upon further modification of plasma source and reactor chamber design, eventually we achieved single-crystal GaN film growth on sapphire substrates. In this presentation we share our experimental findings on the epitaxial growth of GaN films using hollow-cathode plasma-assisted ALD (HCPA-ALD).

The films were deposited using triethylgallium (TEG) and forming gas (95/5% N_2/H_2) plasma as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed at 240 °C substrate temperature and 150 W rf-power. Both in-situ and ex-situ ellipsometry were employed to monitor the surface reactions, measure the thickness variation, and optical properties of the films. When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained for GaN films on sapphire substrates showed a notable increase. Grazing-incidence XRD measurements revealed polycrystalline films on Si substrates while GaN/sapphire samples showed no crystal peak. When theta-2theta scans were done, we observed a strong single peak at (002) orientation, confirming the monocrystalline character of these GaN films. High-resolution transmission electron microscopy (HR-TEM) revealed the epitaxial relationship of the GaN layers grown on sapphire substrates. We attribute this significant improvement in crystal quality to the synergistic impact of customized HCPA-ALD reactor, large-diameter third-generation hollow-cathode plasma source, and optimized growth conditions with low-hydrogen forming gas plasma chemistry. With further improvement, we aim to achieve device quality electrical properties that can be used for prototype device fabrication.

1:45pm **EM1-WeA-2 ALD of $In_{1-x}Ga_xN$**, ***Henrik Pedersen***, *P. Rouf, C. Hsu,* Linköping University, IFM, Sweden

Alloying group 13-nitrides to ternary phases allows tuning of the bandgap from 6.2 eV for pure AlN down to 0.7 eV for pure InN. The bandgap of $In_{1-x}Ga_xN$ can theoretically span from UV to IR (3.4–0.7 eV), including the whole visible light range by varying x, making it promising material for optoelectronic applications. However, the ability to vary the composition of $In_{1-x}Ga_xN$ is limited by the theoretically predicted metastability of $In_{1-x}Ga_xN$ for 0.05 < x < 0.95, which leads to phase separation into their binary materials. The deposition of $In_{1-x}Ga_xN$ is also hindered by the low thermal stability of InN, which decomposes into In metal and N_2 at around 500 °C, making traditional CVD approaches ill-suited. We have recently shown that ALD is a promising technique to deposit InN thin films with excellent structural quality,[1] ALD is therefore a promising alternative to CVD for $In_{1-x}Ga_xN$ with x close to 0.5. In our efforts to deposit $In_{0.5}Ga_{0.5}N$ we have explored two ALD approaches:

By using a short period superlattice, with alternating monolayers of GaN and InN, $In_{0.5}Ga_{0.5}N$ deposition was attempted from repeated *n* InN and *m* GaN monolayers (*n*=*m*= 1, 2, 3…) using triethyl gallium (TEG), trimethyl indium (TMI) and ammonia plasma at 320 °C. This approach afforded single-crystalline $In_{1-x}Ga_xN$ with tunable x between 0.3 and 0.7 by varying the ratio between *n* and *m*. The crystalline quality of $In_{1-x}Ga_xN$ prepared by this multilayer approach ALD is remarkably better than that prepared by conventional continuous CVD and earlier reported ALD work using a multilayer approach with thicker layers of InN and GaN in the multilayer.

By mixing solid Ga(III) and In(III) triazenides in the same evaporator and co-subliming the two metal precursors $In_{1-x}Ga_xN$ was deposited using a single, mixed metal pulse and NH_3 plasma at 350 °C.[2] $In_{1-x}Ga_xN$ was successfully deposited using this approach and the value of x could be tuned by changing the sublimation- and deposition temperatures, and the ratio of the two metal precursors. An $In_{1-x}Ga_xN$ film with x = 0.5 was deposited and found to have a band gap of 1.94 eV. The $In_{1-x}Ga_xN$ film grew epitaxially on 4H–SiC(0001) without need for a buffer layer and without phase segregation or decomposition of the $In_{1-x}Ga_xN$ into the binary materials or In droplets.

Our results reveal a promising potential of ALD over conventional growth techniques to prepare ternary group 13-nitrides with tunable composition at low temperature, which provides the possibility to grow heterostructures with metastable alloys for device application.

Refs.

58. Hsu et al. *Appl. Phys. Lett.* **2020**, *117*, 093101.
59. Rouf et al. *J. Mater. Chem. C***2021**, *9*, 13077.

2:00pm **EM1-WeA-3 Atomic Layer Doped Epitaxial β-Ga_2O_3 Films Grown via Supercycle and Co-dosing Approaches at 240 ℃**, ***Saidjafarzoda Ilhom,*** *A. Mohammad, D. Shukla, B. Willis,* University of Connecticut; *A. Okyay,* Stanford University; *N. Biyikli,* University of Connecticut

Wide and ultrawide bandgap (WBG/UWBG) semiconductors make the backbone of high-power high-frequency electronics, used in electric vehicles, 5G and beyond wireless communication systems, and smart power grids. However, the relatively complex growth reactors and typical growth temperatures around 1000 °C lead to increased production costs. Gallium oxide (Ga_2O_3) is an emerging UWBG semiconductor showing superior material properties particularly ideal for harsh environment (high temperature, high-energy radiation, corrosion) applications. Reducing the growth and doping process temperatures for Ga_2O_3 would potentially enable a wider integration platform towards post-CMOS integration and flexible electronics.

Hence, we report on the low-temperature as-grown crystalline β-Ga_2O_3 films on Si, glass, and sapphire via hollow-cathode plasma-enhanced atomic layer deposition (HCPA-ALD). The films were deposited using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Additionally, we have employed in situ atomic layer doping to n-type dope β-Ga_2O_3 films where tris-dimethylaminosilane (TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. Growth experiments have been performed at 240 °C under 50 W rf-power. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Additionally, eachunit ALD-cycle was followed by an in-situ Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both in-situ and ex-situ ellipsometry were employed to measure the thickness and optical properties of the films. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial β-Ga_2O_3 films with monoclinic β-phase. On the other hand, GIXRD of the samples grown on Si and glass displayed polycrystalline β-Ga_2O_3 films. Further outcomes from our ongoing optical and electrical characterizations will provide additional insight to overcome the challenges in achieving device quality undoped and doped β-Ga_2O_3 layers at low growth temperatures. A significant effort will be devoted for the comparison of Si and Sn-doping strategies, and if needed, ex-situ thermal annealing studies will be carried out for doping activation.

2:15pm **EM1-WeA-4 Closing in on Room-Temperature Metal-Insulator-Transitions for Next Generation Electronics by Epitaxial Nickelate ALD***, **Linn Rykkje**, H. Sønsteby, O. Nilsen,* University of Oslo, Norway

Complex oxides exhibiting metal-insulator transitions (MITs) are exemplar materials systems with strong correlation and emergent functional phenomena. Particularly the rare-earth nickelates (*RE*NiO$_3$, with trivalent rare-earth *RE* = La, Pr, Nd, …, Lu) are of interest as their MITs occur concomitantly with a structural transition. Underlying their rich phase diagram and the MIT's physical origin is a complex interplay of interactions; though it remains an unsolved puzzle in fundamental research, the exotic properties rooted in it have great potential for electronics applications.

Among the *RE*NiO$_3$s, the MIT temperature of NdNiO$_3$ (T_{MI} = 200 K) is the closest to room temperature. Tuning the T_{MI} can be carried out using strain or by partial substitution of Nd with larger RE cations (see phase diagram). A more significant challenge, however, has been to develop a synthesis route that stabilizes Ni^{3+} and provides sufficient control under industrially relevant conditions. For instance, high temperatures and ultrahigh vacuum (UHV) typically facilitate epitaxy, but are incompatible with monolithic device integration.

In this talk we show that with ALD – since long embraced by the electronics industry – we can grow high-quality epitaxial NdNiO$_3$ thin films with excellent control of thickness, uniformity, and chemical composition. This is achieved at low temperatures (225 ^{o}C) without constraints to the substrate geometry or need for UHV. Thin films of stoichiometric composition show low resistivities at room temperature and a sharp MIT, which are desired properties of a functional electronic switch in future neuromorphic architectures. Quaternary oxide thin films of the form (*RE*,Nd)NiO$_3$ have been successfully deposited using ALD with the aim of tuning the T_{MI} close to 273 K. Further chemical and electrical characterizations are needed, however, to establish and control the effect of partial *RE* substitution on the T_{MI}.

Although much of the fundamental behavior of the *RE*NiO$_3$s remains contested, their potential for applications is undisputed; in fact, many members are already found in various device concepts. The success in using low-temperature ALD to grow high-quality NdNiO$_3$ (stoichiometric and cation substituted) thin films with a sharp MIT could promote the implementation of such switching-materials in next-generation electronics. A complex oxide field-effect transistor may thus be more within reach than previously anticipated, offering a viable alternative and/or complement to Si-based circuitry. Based on fundamentally different mechanisms, this could pave the path for a greener and more sustainable integrated circuit technology in the future.

2:30pm **EM1-WeA-5 Plasma-Enhanced Atomic Layer Deposition of Spinel Ferrite CoFe$_2$O$_4$ and NiFe$_2$O$_4$ Thin Films***, **Mari Napari**,* University of Southampton, UK*; M. Heikkila,* University of Helsinki, Finland*; S. Kinnunen, J. Julin,* University of Jyvaskyla, Finland*; T. Prodromakis,* University of Southampton, UK

Thin films of insulating ferro- and ferrimagnetic complex oxides with high Curie temperatures, such as spinel ferrites, are essential for many emerging applications utilising room temperature spin-polarisation and magneto-optical effects, e. g. spintronics and sensors [1]. There is a need for a synthesis method for high quality magnetic oxides with large scale processing compatibility. Here, we have developed PEALD processes for two spinel ferrite materials, CoFe$_2$O$_4$ (CFO) and NiFe$_{2.5}$O$_4$ (NFO) using ferrocene and cobalt(III)- or nickel(II) acetylacetonate as precursors in direct plasma PEALD at 250°C. The CFO films were deposited with 1:2 Co:Fe ratio, while the NFO films were grown iron-rich to ensure that the ferrimagnetic property is not hampered by a parasitic antiferromagnetic nickel oxide component [2]. Stoichiometry of the grown ternary oxide films was confirmed with time-of-flight elastic recoil detection analysis measurements, which also showed that the low light element impurity content of the films (H < 2.0 at. -%, C < 0.3 at. -%,) originates mainly from the acetylacetonate sources. According to the X-ray diffraction measurements of 40 nm thick films, the PEALD CFO and NFO have the desired (inverse) spinel structure, and the films grown on sapphire substrates are strongly (111) oriented already as-deposited. Helium ion microscopy and atomic force microscopy both showed that the films are continuous and free of aggregations. The oriented CFO films on sapphire have a very smooth surface (r_{rms} < 0.3 nm) but the NFO with a same thickness has a higher surface roughness (r_{rms} > 1.5 nm), which is in accordance with the previous observations of the ALD-grown iron-rich NFO [3]. In addition to the growth and structural characteristics we will present the results of the magnetic property measurements of the films.

[1] Hirohata et al. IEEE Trans. Magnetics 5 (2015) 0800511

[2] Napari et al. InfoMat 2 (2020) 769

[3] Bratvold et al. J. Vac. Sci. Technol. A 37 (2019) 021502

2:45pm **EM1-WeA-6 Engineering Maxwell-Wagner Polarization in Al$_2$O$_3$/TiO$_2$/Al$_2$O$_3$ Nanolaminates Grown by Atomic Layer Deposition***, **Partha Sarathi Padhi**,* Raja Ramanna Centre for Advanced Technology, India*; R. Ajimsha, S. Rai, P. Misra,* Raja Ramanna Centre for Advanced Technology, India

Recently multilayered nanolaminates (NLs) of two dielectrics with conductivity contrast exhibiting giant dielectric constant owing to interface induced Maxwell–Wagner (M-W) relaxation have emerged as potential candidate for high density storage capacitors. The M-W polarization can be engineered precisely by controlling the thicknesses of sublayers and number of interfaces. We report growth of Al$_2$O$_3$/TiO$_2$ (ATA) NLs on Si and Au/Si substrates using atomic layer deposition, wherein M-W relaxation induced high dielectric constant was realized and engineered by tuning sublayer thicknesses. Trimethylaluminum (Al (CH$_3$)$_3$) and Titanium tetrachloride (TiCl$_4$) were used as source for Al and Ti respectively, while deionized water (H$_2$O) was used as source for oxygen. Depositions were carried out at 200 °C and the average growth per cycle for TiO$_2$ and Al$_2$O$_3$ was ~ 0.4 and 1.6 Å respectively. The thickness of Al$_2$O$_3$ and TiO$_2$ layers were kept same in a given NL and was reduced from ~ 2.4 to 0.17 nm in different NLs keeping the total stack thickness fixed at ~ 60 nm. X-ray reflectivity curves from these NLs with intense Bragg peaks and clean Kiessig fringes, as shown in Fig. 1, confirmed the multilayer structures with uniform thickness along with distinct interfaces. The dielectric properties of ATA NLs were studied in Au/ATA/Au device configuration using impedance spectroscopy in frequency range of 10–10^6 Hz. The dielectric constant of ATA NLs at 10 Hz was found to increase from ~ 23 to 290 with decreasing sublayer thicknesses from ~ 2.4 to 0.17 nm (Fig. 2(a)), while the dielectric loss was initially found to reduce from ~ 0.8 to 0.06 with reduction in sublayer thicknesses down to ~ 0.48 nm and then increased up to ~ 0.24 with further reduction in sublayer thicknesses down to ~ 0.17 nm (Fig. 2(b)). The dielectric constant of ~ 290 obtained for the ATA NL with ~ 0.17 nm sublayer thickness is significantly larger than that of both Al$_2$O$_3$ (K ~10) and TiO$_2$ (K ~ 20) and is proposed to be due to M-W type dielectric relaxation caused by space charge polarization across the interfaces of Al$_2$O$_3$/TiO$_2$. Temperature dependent dispersion in dielectric constant and loss of ~ 0.48 nm ATA NL clearly revealed two sets of thermally activated relaxations, confirming existence of interfacial M-W relaxation (Fig. 3). The ATA NLs of sublayer thickness ~ 0.17 nm showed high capacitance density of ~ 43.1 fF/μm^2, low loss of ~ 0.24 at 10 Hz, low EOT of ~ 0.8 nm, high breakdown field of ~ 0.265 MV/cm, low leakage current density of ~ 8.5 x 10 $^{-4}$ A/cm^2 at 1V and cut-off frequency of ~ 12KHz which are promising for development of next generation high density storage capacitors.

3:00pm **EM1-WeA-7 Plasma Enhanced Spatial ALD of Silver and Copper Thin Films at Atmospheric Pressure using B$_2$O$_3$ Seed Layers***, **Tim Hasselmann**, B. Misimi,* University of Wuppertal, Germany*; N. Boysen,* Ruhr University Bochum, Germany*; D. Rogalla,* RUBION, Ruhr University Bochum, Germany*; D. Theirich,* University of Wuppertal, Germany*; A. Devi,* Ruhr University Bochum, Germany*; T. Riedl,* University of Wuppertal, Germany

Due to their excellent electrical and optical properties^{1,2} silver and copper thin films are used in various (opto-)electronic devices, e.g. as semi-transparent electrodes^{3,4}. Both of these metals have already been deposited using PE-ALD which provides a precise thickness control and homogeneous film growth at low temperatures $^{5–9}$. However, since metals have a relatively high surface energy and thus tend to grow according to the Volmer-Weber-Mode^{10}, most of the films consist of isolated islands instead of a percolated and conductive layer. Two possibilities to overcome these issue are the increase of the growth rate, since a correlation between growth rate and nucleation and thus percolation was observed, where a higher growth rate leads to earlier percolation^{6,8} and the use of seed layers to enhance the wetting of the deposited metal on the surface^{11}.

In this work, we provide detailed growth studies of Ag and Cu thin films grown from [Ag(NHC)(hmds)], [Ag(fod)(PEt$_3$)] and [Cu(NHC)(hmds)] precursors by spatial PE-ALD at atmospheric pressure. Interestingly, we find a significant effect of B$_2$O$_3$ seed layers on the growth of both metal films, compared to neat Si substrates. Specifically, for Cu films a substantially increased growth per cycle (GPC) of $2.1\text{x}10^{14}$ Cu atoms cm^{-2} is found with a 10 nm thick B_2O_3 seed layer compared to a GPC of $3.3\text{x}10^{13}$ Cu atoms cm^{-2} on neat Si substrates. At the same time the B_2O_3 seed layer strongly affects the percolation threshold and continuity of the grown metal layers. A comparison of Ag layers with a similar areal density of Ag atoms (~ $3\text{x}10^{17}$ Ag atoms cm^{-2}) shows that on top of a B_2O_3 seed layer the Ag film is percolated with a high electrical conductivity, whereas its analogue on neat Si consists of separate islands and is found electrically insulating.

Detailed studies on the growth mechanism in dependence of the B_2O_3 seed layer will be presented and its potential use in area-selective ALD of metals will be discussed.

60. Matula, R. A. *J. Phys. Chem. Ref. Data* 8, 1147–1298 (1979).
61. Barnes, W. L. et al. *Nature* 424, 824–830 (2003).
62. Bellchambers, P. et al. *ChemNanoMat* 5, 619–624 (2019).
63. *Chem. A* 4, 14481–14508 (2016).
64. Kariniemi, M. *et al.Chem. Mater.* 23, 2901–2907 (2011).
65. *J. Vac. Sci. Technol. A.* 33, 01A131 (2015).
66. Boysen, N. *et al.Angew. Chemie - Int. Ed.* 57, 16224–16227 (2018).
67. *Adv. Mater. Interfaces* 4, 1–6 (2017).
68. Boysen, N. *et al.Chem. Commun.* 56, 13752–13755 (2020).
69. Venables, J. A. et al. *Reports Prog. Phys.* 47, 399–459 (1984).
70. Amusan, A. A. *et al.J. Vac. Sci. Technol. A.* 34, 01A126 (2016).

3:15pm **EM1-WeA-8 Silicon-Based Polymer-Derived Ceramic Coatings by Post-Processing of Pre-Ceramic MLD Thin Films*, Kristina Ashurbekova,* *M. Knez,* CIC nanoGUNE, Spain

Si-based polymer-derived ceramics (PDCs) belong to an emerging class of advanced materials that provide high strength, hardness, corrosion protection and heat dissipation, even upon use in extreme environments like high temperatures or chemically reactive plasma conditions. For example, wet-chemically synthesized aluminum doped SiOC PDCs retained their mechanical properties up to 1900°C in addition to an increased creep and corrosion resistance [1].

In the present work, MLD-deposited siloxane-alumina (SiAlCHO) thin films have been used as pre-ceramic polymers for a polymer-derived amorphous silicoaluminum oxycarbide (SiAlCO) synthesis by high-temperature post-processing. Pre-ceramic SiAlCHO films were grown by applying sequential surface reactions between 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V4D4) and trimethylaluminum [2]. To increase the mass yield during the polymer-to-ceramic transformation, cross-linking of the growing chains is desired. For this purpose, we introduced di-tert-butyl peroxide into the MLD process to cross-link the chains through their vinyl groups. The resulting film exhibited improved properties, such as 12% higher film density and enhanced thermal stability, if compared to the non-cross-linked film [3].

The fabrication of the final SiAlCO PDCs coatings was carried out by pyrolyzing the SiAlCHO MLD films in an Ar atmosphere and in vacuum at 900^{o}C. The Raman spectra showed D and G peaks at 1350 cm^{-1} and 1590 cm^{-1}, respectively, thereby indicating the formation of free sp2-hybridized carbon in the resulting PDCs film. The in situ sp2-carbon, formed by decomposition of Me and Vi groups in the SiO2MeVi moieties within the SiAlCO PDC film was identified by X-ray photoelectron spectroscopy (XPS). The spectra showed presence of C=C sp2 bonds and C-H bonds at the interface of free carbon nanoclusters. The elimination of a part of the organic groups is confirmed with the XPS survey scan data, where the Si:C ratio in the film after pyrolysis was reduced from 1:3 to 1.5:1. Transmission electron microscopy confirmed that the PDC film remained amorphous and defect-free after pyrolysis. Interestingly, annealing a 5 nm thick SiAlCO PDC film in vacuum at 900°C showed the formation of a conformal graphene shell on the surface of the amorphous SiAlCO PDC (Supplementary Fig. 1). This MLD-derived conformal SiAlCO PDC thin film showed exceptional uniformity, linear shrinkage, and thermal stability up to 1100°C.

[1] Wen Q., et al., Prog. in Mater. Science, 2020, 109, 100623.

[2] Ashurbekova Kr., et al., Chem. Mater., 2021, 33, 3, 1022–1030.

[3] Ashurbekova Kr., et al., Chem. Commun., 2021,57, 2160-2163.

Emerging Materials
Room Van Eyck - Session EM2-WeA

Vapor Phase Infiltration

Moderators: Anjana Devi, Ruhr University Bochum, Maarit Karppinen, Aalto University

1:30pm **EM2-WeA-1 Vapor Phase Infiltration of Polymers for the Synthesis of Organic-Inorganic Hybrid Materials: Process Kinetics, Chemical Pathways, and Final Hybrid Structure*, Mark Losego,*** Georgia Institute of Technology **INVITED**

Vapor phase infiltration (VPI) infuses polymers with inorganic atomic clusters to create unique organic-inorganic hybrid materials with novel chemical, electrical, optical, and mechanical properties. These new materials have been used in applications ranging from energy harvesting to filtration media to photolithographic hard masks. This talk will discuss our efforts to develop an appropriate phenomenological model to describe the VPI processing kinetics and our use of *in situ* gravimetry to validate this model. The talk will also explore our current understanding of the final hybrid structure and our use of electron microscopy, spectroscopy, and density functional theory (DFT) to understand the inorganic's chemical state and its bonding structure to the polymer. Finally, several example applications will be discussed, and it will be shown how an understanding of the processing kinetics and chemical structure can be used to scale the VPI process to treat macroscale objects – including plastic components and textiles – as well as the additional complications and/or opportunities that avail themselves from process scale-up.

2:00pm **EM2-WeA-3 Atomic Layer Deposition on Polymer Thin Films: On the Role of Precursor Infiltration and Reactivity*, Robin Petit,*** *J. Li, B. Van de Voorde, S. Van Vlierberghe, P. Smet, C. Detavernier,* Ghent University, Belgium

Polymers play a role in a variety of applications owing to their flexibility, low toxicity and ease of processing. In many cases (e.g., lighting, photovoltaics, displays), they are incorporated into devices as host materials for electro-optical components (e.g., quantum dots), which are sensitive to the environment, i.e., moisture, oxygen and temperature. Polymers do not provide adequate protection, apparent from their high water vapor and oxygen transmission rates. To improve the stability, they are coated with barrier layers. We report on the use of Al_2O_3 ALD, with TMA and H_2O, to coat polymer thin films: polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate glycol) (PET-G) [1].

Polymers being complex molecular networks encompassing a free volume, this free volume causes a growth delay during Al_2O_3 ALD on polymers, calling for an understanding of the nucleation, precursor infiltration and polymer relaxation effects that impact this growth delay. Here, the reactivity of the polymers towards TMA is investigated with FTIR and XPS, while the extent of TMA infiltration as a function of deposition temperature is probed with in situ ellipsometry (SE).

Our results show that the temperature and presence, location and amount of polymer functional groups (C-O, C=O) influence the growth delay. While PS showed no infiltration, TMA-induced swelling was observed for PMMA and PET-G, with a change in reversibility as a function of temperature (Fig. 1). At low temperatures, TMA mainly physisorbs, while a pericyclic reaction drives the interaction with TMA for PMMA and PET-G at elevated temperatures (Fig. 2). For PET-G, this reaction can result in chain scission, accounting for the significant TMA infiltration. Furthermore, SE is used to determine the moment of closed layer formation, halting the infiltration and indicating the onset of linear growth (Fig. 3). The better understanding of the influence of the ALD deposition conditions and polymer properties on the barrier growth enables faster, more effective barrier creation for other ALD-polymer combinations.

[1] Petit, R. R.; Li, J.; Van de Voorde, B.; Van Vlierberghe, S.; Smet, P. F.; Detavernier, C. Atomic Layer Deposition on Polymer Thin Films: On the Role of Precursor Infiltration and Reactivity. ACS Appl. Mater. Interfaces 2021, 13, 38, 46151–46163.

2:15pm **EM2-WeA-4 Obtaining Robust Hydrophilic Surface on Soft Polymer Through Atmospheric Pressure ALD*, Albert Santoso,*** *B. van der Berg, V. van Steijn, R. van Ommen,* Delft University of Technology, Netherlands

In the recent times, the use of modified soft polymer is increasing in a range of applications, such as biotechnology and medicine. Due to their flexible nature, good optical transparency, and high fidelity, soft polymers such as PDMS (polydimethoxysilane) are known to be a good coating and microfluidics material. As a result, fields such as optical sensor, membrane separation, and bio-assays benefit tremendously. However, this polymer suffers from the lack of a hydrophilic group, limiting its application to several commercial potentials, especially in proper fluidic handling. Furthermore, research in obtaining robust hydrophilicity often involves changing the bulk material and/or extremely complicated processes. Therefore, there is a need for precise surface manipulation with relatively simple processes. Among many surface modification techniques, atomic layer deposition (ALD) is known for its atom-level control. Furthermore, its deposition on a polymer involves both surface reaction and infiltration, leading to formation of buffer layer without changing much of its bulk properties. This study focuses on the use of atmospheric pressure atomic layer deposition (APALD). Opposed to the conventional vacuum ALD, it makes the use of vacuum technology superfluous and at the same time allows convective transport to challenge the limitation in aspect ratio coverage. The results shows that deposition of 100 cycles form a 46nm layer of titanium oxide, of which the surface contact angle stays 74° over a period of 8 weeks. This is much more hydrophilic than bare PDMS (110°) and vacuum ALD (recovering back to 90°). Both scanning electron microscopy and x-ray photoelectron spectroscopy depth profiling show that uniform deposition of surface and formation of mixed layer in the range of few microns are vital for preventing diffusion of uncured monomers to the surface, leading to more stable hydrophilic surface. Furthermore, this result is confirmed by washing some PDMS in organic solvent to reduce the amount of uncured monomer, resulting in a contact angle of 65° after 8 weeks. There are also little to no changes observed in the transparency and mechanical property. This study not only provides a novel and easy method to modify soft polymer such as PDMS, but also opens up various potential in the field of microfluidic coating and commercial layer deposition.

2:30pm **EM2-WeA-5 Modified 3D Printed Architectures: Effects of Infiltration by Alumina on ABS***, **Atilla Varga**, S. Barry,* Carleton University, Canada

In recent years 3D printing has gained enormous popularity thanks to its affordability, accessibility, ease of use, and the ability to easily employ a variety of polymer materials. These potential polymer substrates are highly tunable in flexibility and strength which make them the ideal for printing filaments, they can incorporate metal powders, wood fibers, carbon fibers, and other composites.[1] The integration of 3D printing and industrial nanoscale processes such as ALD will have a significant impact in the development of advanced 3D printed architectures leading to a wide array of applications as currently being investigated.

Our group has previously shown improvement of solvent stability for 3D-printed acrylonitrile-butadiene-styrene (ABS) architectures using an alumina thin film.[2] We demonstrated a 30-50% increase in solvent exposure resistance with a ~200 nm thin film. In addition we observed infiltration in the ABS polymer when no thermal pretreatment was performed on the ABS architecture, with deposition carried out above the glass transition temperature.

Infiltration requires inherently different conditions than film deposition, specifically a longer exposure to the precursors, which ideally improves infiltration depth.[3] By infiltrating ABS rather than overcoating it with alumina, we will be improving the material's glass transition temperature (Tg). Various deposition parameters such as pulse length, soak time, and temperature have varying effects on the glass transition temperature and will be discussed.

The Tg of ABS could be improved by 10° C after the infiltration of alumina. Interestingly, this improvement was effective for only one heat-cool cycle. After cooling , the plastic reverted to its normal Tg. We speculate that this is caused by the plastic flowing together, out of the infiltrated alumina matrix. Scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDX) will be used to examine the modified polymer structures (Figure 1). Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and conductivity probe measurements will be used to observe the physical property changes (focusing on Tg of the treated compared to the untreated polymer).

[1] T. Abudula et al., *Front. Bioeng. Biotechnol.*, **2020**, 8, 586186

[2] Varga A. C., Barry, S. T., *J. Vac. Sci. Technol. A.***2022**, accepted

[3] Robin R. P. et al., *ACS Appl. Mater. Interfaces***2021**, 13, *38*, 46151–46163

2:45pm **EM2-WeA-6 Polymer-Inorganic Hybrids for Inducing Self-Healing Functionality in Metal Oxides***, **Oksana Yurkevich**, E. Modin,* CIC nanoGUNE, Spain*; I. Šarić, M. Petravić,* University of Rijeka, Croatia*; M. Knez,* CIC nanoGUNE, Spain

A rapid surge of research works is the commitment to the sustainability of mankind. However, the vast majority of these works are devoted to the self-healing of organic materials. At the same time, there is a growing demand for implementing this functionality to the inorganic materials due to the rapid development in the area of flexible electronics. The few existent examples for inorganic materials rely on liquid healing agents, such as liquid metals or liquid precursors. The progress in this field remains very challenging, mainly because of a lack of feasible healing agents and suitable ways to supply them to the damaged site. In this work, we propose an approach to form self-healing metal oxides (MeO) by applying the vapor phase infiltration (VPI) method.

We used VPI as a tool to induce self-healing properties into hybrid organic-inorganic materials. This was achieved by infiltration of metal organics into the polymers which do not possess reactive oxygen-containing functional groups. Application of a typical VPI process to a functional polymeric substrate will result in the formation of dispersed metal oxide clusters and nanoparticles (NPs) inside the polymer along with an inorganic thin film of the same MeO on the surface. This hybrid polymer matrix with dispersed NPs can serve as a reservoir with healing agents for a repair of a cracked MeO film. Self-healing of inorganic materials and structures was realized also without liquid agents by making use of the mobility of inorganic NPs within polymers, as the spatial distribution of NPs can be tuned by means of harnessing both enthalpy and entropy.

After the infiltration process, samples were transferred into the microscope chamber and cut in a controllable way by a Focused Ion Beam (FIB). Usage of FIB and SEM allowed inspecting the ruptured area of the hybrid structure prior to and after its exposure to the ambient atmosphere. X-ray photoelectron spectroscopy (XPS), energy-dispersive x-ray spectroscopy (EDX), and transmission electron microscopy (TEM) were used to analyze the chemical structure and composition of the obtained hybrids. The self-healing effect after exposure of the FIB-cut sample to air was observed for zinc and indium metal oxides (Fig.1). Hereby, we introduce an alternative materials architecture and construction framework for designing inorganic materials capable to self-heal.

3:00pm **EM2-WeA-7 Tailoring the Interfacial Interactions of Porous Polymer Membranes to Accelerate Atomic Layer Deposition: The Latent Path to Antifouling Membranes***, **Rahul Shevate**, V. Rozyyev, R. Pathak, A. Mane, S. Darling, J. Elam,* Argonne National Laboratory, USA

Atomic layer deposition (ALD) is a powerful strategy to engineer hybrid organic-inorganic membranes with emergent functionalities. The combination of atomic-level thickness control, wide materials palette, and unprecedented conformality allow the physiochemical properties (e.g., hydrophilicity) of mesoporous polymer membranes to be precisely tuned. The nucleation of ALD materials growth on polymer surfaces relies on chemical interactions between the ALD metalorganic precursor and functional groups in the polymer structure and these interactions dictate the number of ALD cycles required to achieve a continuous coating.Strategies to enhance these interactions could enable desirable properties such as anti-fouling behavior to be imparted on inert polymer surfaces that lack the necessary functional groups for ALD nucleation.In this study, we demonstrate that the reactivity of polyacrylonitrile (PAN) membranes towards ALD metal oxide (MO) precursors with Lewis acid characteristics is enhanced by introducing Lewis base functional groups (amidoxime: Am) on the PAN backbone. The resulting Lewis acid-base interactions accelerates the MO nucleation in Am-PAN and reduce the number of deposition cycles required to achieve hydrophilicity compared to the untreated PAN membrane. Unveiling the reaction mechanism, the in-situ FTIR intensity changes established enhanced interaction dynamics between the ALD MO precursors and the Am-PAN membrane, unlike the PAN membrane. For similar MO cycles, through both spectroscopic and thermogravimetric analysis, we observe enhanced MO loading in the Am-PAN membrane compared to the PAN membrane. Here we have verified that strong Lewis acid-base interactions led to enhanced loading for a range of ALD MO materials including Al_2O_3, TiO_2, SnO_2, and ZnO. Most importantly, the Al_2O_3-Am-PAN hybrid membrane showed 23.3% higher antifouling capability compared to the pristine PAN membrane. Our approach expands the scope of design options for fouling-resistant porous hybrid inorganic-organic membranes and may reduce manufacturing costs of water treatment membranes.

Keywords: ALD, membranes, metal-binding functionalities, water treatment, filtration, nanoporous structures

3:15pm **EM2-WeA-8 Ruthenium Nanostructures via Sequential Infiltration Synthesis in Self-Assembled Diblock Copolymer Thin Films***, **Nithin Poonkottil**,* Ghent University, Belgium*; E. Solano,* ALBA Synchrotron, Spain*; A. Muriqi, M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; C. Detavernier, J. Dendooven,* Ghent University, Belgium

Vapor phase infiltration or sequential infiltration synthesis (SIS) is an ALD-derived technique for creating organic-inorganic hybrid materials, by allowing ALD precursors and reactants to react within the free volume of soft materials like polymers. SIS on diblock copolymer (di-BCP) films is critical in lithography, where material growth is typically achieved selectively in one block while the other remains inert. A plasma treatment can be used to remove the organic components, resulting in nanopatterns that resemble the reacted block. However, metal nanopatterns derived from SIS are still in its infancy, as most reports focus on metal oxides, mainly Al_2O_3.[1]

We present SIS of Ru[2] without any pre-treatment, using alternating infiltration of RuO_4 and H_2 in polystyrene-block-polymethylmethacrylate (PS-b-PMMA) templates, followed by plasma treatment to create patterns of Ru nanostructures (Fig.1A).Experiments on blanket PS and PMMA films show that RuO_4 infiltration is selective (Fig.1B) into PS, with no significant out-diffusion of RuO_4 from PS, and thus a strong interaction between RuO_4 and PS. Density functional theory calculations corroborate that PS-RuO_4 interaction is energetically favorable, whereas the PMMA-RuO_4 interaction is not. The inertness of PMMA is attributed to its compact structure with no sufficient space between units to accommodate RuO_4 molecules. *In situ* FTIR shows that aromatic CH and C=C bondsin PS are consumed during theRuO_4 infiltration. XPS depth profiles confirm the infiltration of Ru throughout the polymer. An enhanced morphology and density contrast between the PS and PMMA domains in the di-BCP films after infiltration is evident from scanning electron and atomic force microscopy (Fig.2), elucidating that a single SIS cycle can already considerably change the nature of the PS domains. In grazing incidence wide angle X-ray scattering images, the diffraction signals of Ru become more pronounced with increasing number of SIS cycles, confirming the crystalline nature of the infiltrated Ru nanostructures. A significant increase in crystallinity of Ru is observed after the polymer is removed by plasma, with clear diffraction peaks present even after a single SIS cycle. Finally, the formation of Ru nanolines resembling the di-BCP nanostructure after the plasma treatment is confirmed in AFM images (Fig.2).

1.Waldman et al.,*J. Chem. Phys.**2019**,151,190901*

*2.Minjauw et al.,J. Mater. Chem C **2015**,3,132-137*

This work is funded by the EU's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No.765378. We thank M. Baryshnikova, P.Vanelderen, H. S.Suh from imec for providing the di-BCP films.

Emerging Materials
Room Van Eyck - Session EM3-WeA

Hybrid Coatings

Moderators: Christophe Detavernier, Ghent University, Belgium, Mark Losego, Georgia Institute of Technology

4:00pm **EM3-WeA-11 Photoactive Hybrid Materials by MLD***, **Ola Nilsen**, P. Hansen,* University of Oslo, Norway **INVITED**

The sequential methodology of ALD/MLD allows for combinations of a remarkable wide range materials. This can be exploited in construction of photoactive materials, particularly for those based on multi-step processes like down and upconversion. Such materials relies on efficient processes for both absorbers, emitters and transfer of excited states while limiting non-radiative decay. It is clear that optimizing all properties simultaneously is not possible within a single material class.

With the ALD/MLD approach, we can combine highly absorbing organic molecules with fluorides and oxides and many more. By such manner, we have achieved complete energy transfer from the organic molecule terephthalic acid to Sm3+ without quenching. We also show drastic suppression of concentration quenching of multilayered structures of lanthanides as compared to solid solutions by confining energy migration in 2D planes. The flexibility of the MLD approach allows for exploration combinations of absorbers and emitters with a large variation in chemistry. Although one may be limited in the size of accessible molecules via the gas phase, the range may be quite large. This way of design allows combinations of otherwise incompatible species, both with respect to normally incompatible synthesis requirements and in controlling energy transfer and quenching routes.

4:30pm **EM3-WeA-13 Cerium (III) based Hybrid Inorganic-Organic Thin Films by ALD/MLD***, **Parmish Kaur**,* Ruhr University Bochum, Germany*; A. Muriqi,* Tyndall National Institute, University College Cork, Ireland*; J. Wree,* Ruhr University Bochum, Germany*; R. Ghiyasi, M. Safdar,* Aalto University, Finland*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; M. Karppinen,* Aalto University, Finland*; A. Devi,* Ruhr University Bochum, Germany

Ce-based hybrid materials are projected to be promising for applications such as catalysis, sensors, information storage, luminescent materials to name a few. However, they have been mainly developed by classical routes such as solvothermal and hydrothermal synthesis and thus suffer a major disadvantage of unwanted solvent molecules being trapped in the hybrid materials. Atomic/molecular layer deposition (ALD/MLD) is a solvent-free, gas-phase deposition technique for the deposition of hybrid organic-inorganic thin films which gives precise control over thickness, composition, and uniformity over large area substrates. Although one of the key factors of a well-functioning ALD/MLD process is the compatibility of the employed organic and inorganic precursors in terms of volatility, thermal stability, and reactivity and this aspect hasn't been thoroughly investigated.

We have performed a systematic study to find compatible Ce and organic precursors for the growth of Ce-based hybrid thin films. This was realized by in-depth characterization of precursors, processes and supporting the findings by theoretical investigations using density functional theory (DFT). Thermal analysis studies showed that the precursors [Ce(dpdmg)$_3$], terephthalic acid (TPA), and hydroquinone (HQ) are sufficiently volatile and thermally stable to be deposited at 200 °C. Additionally, the reactivity of the precursors was modelled by DFT, which revealed the favourable reaction between inorganic and organic precursors. Thus, the combination of the chosen precursors was found to be compatible in terms of their matching physicochemical properties. The Ce-based hybrid thin films were deposited using [Ce(dpdmg)$_3$] as a source for Ce, while two different organic precursors, namely TPA and HQ, were tested as organic precursors yielding Ce-TPA and Ce-HQ hybrid thin films. The growth rate for Ce-TPA hybrid films was 5.4 Å cycle^{-1} and for Ce-HQ hybrid films it was 4.8 Å cycle^{-1} on Si(100) at a deposition temperature of 200 °C. FTIR studies confirmed the successful deprotonation of the organic precursors, the presence of metal-oxygen bonding, and the benzene ring vibrations in the hybrid films. Additionally, the Bader charge calculations predicted the oxidation state of the cerium in the films to be +3 which was further confirmed experimentally by XPS studies. Furthermore, XPS analysis confirmed the successful formation of Ce-O bonds. UV-Vis spectroscopy showed the π-π^* transitions and LMCT transition present in the films, while the films are also UV absorbing. Hence, Ce-based hybrid thin films can be promising as redox-active or UV-absorbing materials.

4:45pm **EM3-WeA-14 Modifying the Physico-Chemical Properties of Polymer Nanofiltration Membranes with Metal Oxide ALD***, **Kirti Sankhala**, T. Segal-Peretz ,* Technion, Israel

Atomic layer deposition (ALD) is an emerging technology to tune the surface chemistry of membranes by providing conformal, smooth, and ultrathin coatings of various materials, such as metal oxides.[1,2,3] The addition of an ultra-thin layer of metal oxides on a negatively charged polymer membrane surface offers enhanced surface energy and hydrophilicity with a possibility to fine-tune the pore size and reduce surface roughness.[4]

In this work, we enhance the chemical and physical properties of commercially available NF270 nanofiltration membranesby tin dioxide (SnO_2) coating via ALD. SnO_2 ALD was selected due to the high hydrophilicity and positive surface charge of SnO_2 among various metal oxides.[5] In nanofiltration, the separations at the atomic or molecular scale are strongly influenced by electrostatic interactions and play a critical role in membrane performance. As ALD provides a conformal and nonporous coating layer, applying a large number of ALD cycles inevitably leads to pore blocking. However, a small number of ALD cycles (< 20) enables tuning of both the pore size and the pore chemistry.[6]Several cycles of SnO_2 ALD, providing ca. 1-3 nm thick coating,increases the membrane's hydrophilicity, decreases its roughness, and reduces negative surface charges. This coating leads to higher salt rejection and salt selectivity with a slight decrease in membrane permeability. The morphological details of the hybrid inorganic-organic membranes obtained using scanning and transmission electron microscopies shed light on the conformal growth of SnO_2 ALD on the nanofiltration membranes.

References

(1) Wang, C.-M.; Kong, D.-L.; Chen, Q.; Xue, J.-M. *Front Mater Sci***2013**, *7*, 335.

(2) Itzhak, T.; Segev-Mark, N.; Simon, A.; Abetz, V.; Ramon, G. Z.; Segal-Peretz, T. *ACS Appl. Mater. Interfaces***2021**, *13* (13), 15591–15600. https://doi.org/10.1021/acsami.0c23084.

(3) Zhang, Z.; Simon, A.; Abetz, C.; Held, M.; Höhme, A.-L.; Schneider, E. S.; Segal-Peretz, T.; Abetz, V. *Adv. Mater.***2021**, *33* (48), 2105251. https://doi.org/10.1002/adma.202105251.

(4) Wu, F.; Misra, M.; Mohanty, A. K. *Prog. Polym. Sci.***2021**, *117*, 101395. https://doi.org/10.1016/j.progpolymsci.2021.101395.

(5) Xia, Z.; Rozyyev, V.; Mane, A. U.; Elam, J. W.; Darling, S. B. *Langmuir***2021**, *37* (39), 11618–11624. https://doi.org/10.1021/acs.langmuir.1c02028.

(6) Zhou, X.; Zhao, Y.-Y.; Kim, S.-R.; Elimelech, M.; Hu, S.; Kim, J.-H. *Environ. Sci. Technol.***2018**, *52* (24), 14311–14320. https://doi.org/10.1021/acs.est.8b03967.

5:00pm **EM3-WeA-15 Modelling of the Growth of Al_2O_3-Based Hybrid Films: Role of Terminal Groups in Aromatic Molecules***, **Arbresha Muriqi,*** Tyndall National Institute, University College Cork, Ireland*; M. Karppinen,* Aalto University, Finland*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Hybrid organic-inorganic materials fabricated using Molecular Layer Deposition (MLD) display unique properties and hold great promise for many technological applications. Much has been done in developing different MLD processes but much less is known about the growth mechanism in MLD films.

In this study we use first principles density functional theory (DFT) to investigate in detail the growth mechanism of hybrid films of aluminium oxide and aromatic molecules with different terminal groups deposited by MLD. We explore the reactions between the post-$Al(CH_3)_3$ (TMA) pulse methyl-terminated Al_2O_3 surface and homo- or hetero-bifunctional aromatic molecules with hydroxy (OH) and/or amino (NH_2) terminal groups: hydroquinone (HQ), p-phenylenediamine (PD) and 4-aminophenol (AP). DFT calculations show that the aromatic molecules bind favorably to TMA fragments via formation of Al-O, Al-N bonds and loss of CH_4. Importantly it is most favorable for the aromatic molecules to orient in an upright configuration, by avoiding the unwanted double reactions found for aliphaic diols, which will lead to thicker and more flexible hybrid films. We calculated a higher reactivity of the OH group with TMA compared to NH_2, However, aromatic molecules terminated with NH_2 groups are still an option to promote the film growth. We also explore the MLD chemistry with functionalised aromatic molecules to examine the influence of phenyl functionalization on the MLD chemistry. We found that we can modify the core of the aromatic molecules to target particular properties using specific chemical groups which promote the deposition of thicker and more stable hybrid films. Finally, we examine the reactions between the methyl terminated Al_2O_3 surface with new possible MLD aromatic precursors as hydroquinone bis(2-hydroxyethyl)ether and 1,1'-biphenyl-4,4'- diamine where DFT shows that the selected aromatic molecules react favorably with TMA fragments on the Al_2O_3 surface and are worthy of further experimental investigation.

[1] Arbresha Muriqi, Maarit Karppinen, Michael Nolan, Role of terminal groups in aromatic molecules on the growth of Al_2O_3-based hybrid materials, *Dalton Transactions*, 2021, 50, 17583-17593.

5:15pm **EM3-WeA-16 Engineering Biomimetic Biocompatible and Selectively Antibacterial Ultrathin Films by Vapor Phase Chemistry***, **Karina Ashurbekova,** K. Ashurbekova,* CIC nanoGUNE, Spain*; A. Muriqi,* Tyndall National Institute, University College Cork, Ireland*; L. Barandiaran, B. Alonso-Lerma ,* CIC nanoGUNE, Spain*; I. Šarić ,* University of Rijeka , Croatia*; E. Modin, R. Perez-Jimenez ,* CIC nanoGUNE, Spain*; M. Petravić,* University of Rijeka, Croatia*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; M. Knez,* CIC nanoGUNE, Spain

This work describes a strategy for growing conformal ultrathin films of chitin and hybrid chitin-based biomaterials from the gas phase by Molecular Layer Deposition (MLD). We present a new class of organic–inorganic hybrid polymers, which we coin "metallosaccharides", based on sugar monomers as precursors. For a controlled growth, we couple the monosaccharide N-Acetyl-D-mannosamine (ManNAc) with trimethylaluminum (TMA) or Titanium tetraisopropoxide (TTIP) from the vapor phase in repetitive cycles to obtain the respective biomimetic alumochitin or titanochitin thin films. The analysis of the resulting films was done by applying ATR-FTIR, X-ray photoelectron spectroscopy (XPS), Solid-state NMR (ssNMR), High resolution TEM (HRTEM) and Energy dispersive X-Ray spectroscopy (EDXS).

The evaluation of the antimicrobial activity of the alumochitin and titanochitin MLD films against Gram-positive (Staphylococcus aureus, S. aureus) and Gram-negative (Escherichia coli, E.Coli) bacteria was assessed. The attachment of the bacteria and their proliferation on metallochitin-covered glass substrates, were analyzed by confocal microscopy. The results show a great antimicrobial activity of both alumochitin and titanochitin MLD films against gram-positive and gram-negative bacteria, making the films highly interesting for the fabrication of bioactive surfaces.

The biocompatibility of both alumochitin and titanochitin hybrid MLD films was characterized by testing the *in vitro*proliferative behaviors of HEK (Human Embryonic Kidney) 93 human cells cultured on the substrates. We mainly focused on the cell attachment and proliferation. All MLD-coated substrates showed higher cell proliferation than the reference samples, namely uncoated coverslips.

The chemical interactions between the precursors ManNAc and TMA or TTIP, and the probability of the hybrid alumochitin or titanochitin film formation were modeled by density functional theory (DFT) and showed energetically favorablereaction mechanisms.

This project has received funding from the European Union´s Horizon 2020 research and innovation programme under the Marie Sklodowska -Curie grant agreement No 765378.

Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS-WeA2

2D Materials II

Moderators: Suzanne Mohney, Penn State University, Riikka Puurunen, Aalto University, Finland

4:00pm **NS-WeA2-11 Controlled Encapsulation of Monolayer MoS_2 with Ultrathin Aluminum Oxide for Low Resistance Tunnel Contact Formation***, **Alex Henning**, S. Levashov, J. Primbs, M. Bissolo, T. Grünleitner, C. Qian, J. Finley, I. Sharp,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany

Seamless integration of two-dimensional (2D) semiconductors with bulk materials is essential for preserving and exploiting their outstanding optoelectronic properties within functional devices. In this respect, ALD has proven to be a critical tool for the dielectric integration of 2D materials by tailoring substrates and interfaces.[1] A major challenge that prevents harnessing the full potential of 2D materials is to contact mono- and few-layer systems with metals without introducing defects or otherwise impeding interfacial charge transport. Here, we demonstrate the encapsulation and doping of monolayer MoS_2 with van der Waals (vdW) bonded aluminum oxide (AlO_x) and aluminum oxynitride (AlO_xN_y) by ALD. This is accomplished at low substrate temperature (40 °C) *via* sequential exposure to TMA and ozone or TMA and N_2 plasma, respectively. Unique to the field of 2D materials, we utilize *in situ* spectroscopic ellipsometry to assess the effects of adsorbed reactants and film formation on the dielectric function and excitonic properties of a vdW material during ALD, thus allowing optimization of film growth *and* adlayer modulation doping in real-time.

Current-voltage measurements of monolayer MoS_2 field-effect transistors (FETs) reveal that the nanometer-thin AlO_x coating increases the carrier concentration (from 1×10^{12} cm^{-2} to 2×10^{13} cm^{-2}), while it also protects MoS_2 from defect creation during metallization and processing. Complementary Raman spectroscopy and atomic force microscopy characterization reveal the reversibility of modulation doping induced by the AlO_x adlayer. Encapsulated monolayer MoS_2 FETs exhibit a lower contact resistance and an order of magnitude larger maximum drive current, I_{ON}. By alleviating the effects from the contact interfaces, we were able to reliably determine a field-effect room-temperature mobility of ~10 cm^2/Vs for the applied monolayer MoS_2, synthesized by chemical vapor deposition on a large scale (6Carbon Techn.).

Overall, this work demonstrates the scalable and damage-free encapsulation and doping of 2D materials with weakly bonded and ultrathin AlO_x and AlO_xN_y by ALD near room temperature, as well as the fabrication of tunnel contacts, readily compatible with polymer and lift-off processing. Beyond the demonstrated application as a contact interfacial layer, the nanometer-thin conformal coatings are potentially relevant for surface functionalization in chemical sensors and modulation doping of 2D and organic materials implemented in optoelectronic devices.

[1] Grünleitner, T.; Henning*, A.; Bissolo, M.; Kleibert, A.; Vaz, C.A.F.; Stier, A.; Finley, J.J..; Sharp*, I.D.: *Adv. Funct. Mater.* 2022, 2111341.

4:15pm **NS-WeA2-12 Synthesis of Crystalline Tungsten Disulfide Using Atomic Layer Deposition and Post-Deposition Sulfur Annealing***, **Kamesh Mullapudi**, R. Addou,* Oregon State University*; C. Dezelah, D. Moser, J. Woodruff, R. Kanjolia,* EMD Performance Materials*; J. Conley Jr.,* Oregon State University

2D transition metal dichalcogenides have attracted interest in recent years for their unique optical and electrical properties. Tungsten disulfide (WS-₂)in particular, has gained attention for its applications as channel material for next generation FETs[1] and catalysis.[2] Popular methods such as mechanical exfoliation and chemical vapor deposition have been demonstrated to synthesize crystalline films with grain sizes of up to a few microns and show good electrical properties, but lack scalability and precise layer thickness control, respectively.[3] Atomic layer deposition (ALD) is an ideal technique for achieving highly conformal and uniform films with the layer by layer thickness control needed for these applications, but faces challenges in achieving high crystallinity. Recent work on ALD WS_2 has achieved films with superior electrical properties by improving film crystallinity, either by inducing substrate inhibited growth[4]or by post-deposition annealing.[5] However, growing crystallites of the order of a few microns remains a challenge and new processes are needed.

In this work, we report ALD of WS_2 using bis(t-butylimido)bis(trimethylsilylmethyl)tungsten (WSN-4) and H_2S. 200 cycles of a 1/5/10/0.1/5/10 s WSN-4/soak/N_2/H_2S/soak/$N\text{-}_2$ pulse sequence shows film growth at temperatures above 290 °C. Grazing incidence x-ray diffractograms of as-deposited films show a strong peak at 13.9° near the dominant 14.32° (002) peak of 2H polytype of WS_2. While no characteristic Raman signal is seen for as-deposited films, x-ray photoelectron spectroscopy reveals the presence of sulfur-deficient WS_2 at 290 °C with improved film quality at a deposition temperature of 350 °C. Post-deposition elevated temperature anneals in elemental sulfur produce a significant improvement in crystallinity at temperatures as low as 600 ºC, with SEM images revealing multi-layered WS_2 pyramids with sizes of up to ~ 1 µm. The presence of WS_2 in sulfur-annealed films is further confirmed by the signature Raman 2LA(M), $E\text{-}^1_{2g}$ and $A\text{-}_{1g}$ peaks.

Further details on the ALD process, sulfur annealing, and electrical properties will be presented at the meeting.

71. D. Lin *et al.,* in *2020 IEEE International Electron Devices Meeting (IEDM)* (2020), p. 3.6.1
72. D. Voiry, *et al.,* Nat Mater **12**, 850 (2013).
73. M. Mattinen *et al.,* Adv. Mater. Interfaces **8**, 2001677 (2021).
74. B. Groven, *et al.,* Chem. Mater. **30**, 7648 (2018).
75. H. Yang *et al.,* Research **2021**, (2021).

4:30pm **NS-WeA2-13 In-Situ-Prepared Protective Seed Layer by Plasma ALD on Graphene***, S. Riazimehr,* Oxford Instruments Plasma Technology, Germany*; A. Esteki,* RWTH Aachen University, Germany*; M. Powell,* Oxford Instruments Plasma Technology, UK*; M. Otto, G. Rinke, Z. Wang,* AMO GmbH, Germany*; A. Omahony,* Oxford Instruments Plasma Technology, UK*; M. Lemme,* RWTH Aachen University, Germany and AMO GmbH, Germany*; R. Sundaram,* Oxford Instruments Plasma Technology, UK*; **Harm Knoops**,* Oxford Instruments Plasma Technology, Netherlands

In this work, we describe a novel method to deposit high-κ dielectrics on graphene through an in-situ-prepared protective aluminum nitride (AlN) seed-layer. The process is performed in an Oxford Instruments Atomfab^{TM} plasma ALD system.[1] Short and low power remote plasma conditions were used to directly grow a thin layer of AlN on graphene, followed by deposition of high-quality aluminum oxide (Al_2O_3) by remote plasma ALD.

For the development of graphene-based devices, such as transistors, photodetectors, or optical modulators, a deposition of a high-quality dielectric film on graphene is required. However, this deposition is challenging because nucleation on pristine graphene is difficult. While defect-induced nucleation, for example through plasma exposure, improves nucleation, it also decreases the quality of the graphene layer. Recently we reported dielectric deposition using remote plasma ALD, without observable damage, by protecting the graphene by hexagonal boron nitride (hBN).[2] However, using hBN involves additional transfer processes, which may complicate the fabrication and introduce contamination, defects, and wrinkles.

Inspired by this process, we developed a new process using an in-situ deposited AlN seed-layer to protect the graphene effectively, which enables plasma-assisted deposition of Al_2O_3 without damaging the graphene. Raman measurements demonstrate that the wafer encapsulated by PEALD without AlN shows damage to the graphene, while the wafer protected by the AlN seed layer shows negligible damage. This result confirms that a thin layer of AlN provides sufficient protection for the graphene against the O_2 plasma in the subsequent Al_2O_3 deposition step. The N_2 based plasma conditions for the AlN layer were such to allow AlN growth but not lead to observable damage to the graphene. In this contribution, we will furthermore discuss electrical and device properties for this scalable wafer-level production method.

Acknowledgment: This project has received funding from the European Union's Horizon 2020 research and innovation program 2D-EPL (952792) and German BMBF project GIMMIK (03XP0210).

References:

76. Knoops et al., JVST A 39 (6), 2021
77. Canto et al., Adv. Mater. Technol. 6 (11), 2021

4:45pm **NS-WeA2-14 Polycrystalline MoS_2 Thin Films at 100 °C by Plasma-Enhanced Atomic Layer Deposition***, **Miika Mattinen**, M. Verheijen,* Eindhoven University of Technology, The Netherlands*; F. Gity, E. Coleman, R. Duffy,* Tyndall National Institute, University College Cork, Ireland*; E. Kessels,* Eindhoven University of Technology, The Netherlands*; A. Bol,* University of Michigan, Ann Arbor and Eindhoven University of Technology

Transition metal dichalcogenides (TMDCs), such as MoS_2, are 2-dimensional materials that exhibit vast potential in a variety of applications due to their unique and favorable electronic, optical, and mechanical properties. However, synthesis of uniform, high-quality TMDC films under application-relevant conditions remains a challenge. The most commonly used CVD processes operate at high temperatures that are incompatible with many substrates and applications. For example, typical plastic substrates used for flexible electronics can only withstand temperatures up to about 150 °C.[1] As a result, using ALD to prepare TMDC films is being pursued actively.[2,3]In this contribution, we show deposition of polycrystalline MoS_2 (c-MoS_2) thin films at temperatures down to 100 °C using plasma-enhanced ALD (PEALD). To date, this is the lowest temperature process reported for c-MoS_2 films using any chemical gas-phase method. Building on an existing PEALD process using $Mo(N^tBu)_2(NMe_2)_2$ and mixed $H_2S/H_2/Ar$ plasma as precursors,[4] we have identified H_2 content in the plasma feed gas as a crucial parameter in controlling the composition and properties of MoS_x films. Based on thorough film characterization, we find that adding H_2 in the plasma helps avoid excess S incorporation at low temperatures. The correct stoichiometry, in turn, enables crystallization of MoS_2. By increasing the plasma feed gas H_2 content to 80%, we are able to deposit polycrystalline MoS_2 films at temperatures as low as 100 °C, compared to a minimum temperature of 300 °C without any H_2.We have further demonstrated the generality of the approach by depositing TiS_2 and WS_2 films at lower temperatures than those achieved previously without added H_2.Besides crystallinity, the feed gas H_2 content is found to control growth rate, film morphology, and electrical properties. For example, electrical conductivity can be varied by at least four orders of magnitude. Thus, the PEALD process enables tailoring MoS_x films to meet the requirements of different applications, such as flexible electronics (low-temperature c-MoS_2) and electrocatalysis (a-MoS_x).

1 Yao and Gang, *J. Appl. Phys.* **2020**, 127, 030902
2 Mattinen et al., *Adv. Mater. Interfaces* **2021**, 8, 2001677
3 Kim et al., *Adv. Mater.*, **2021**, 20059074 Sharma et al., *Nanoscale*, **2018**, 10, 8615

5:00pm **NS-WeA2-15 Selectively Decorated Pt Nanoparticle on WS_2 by Atomic Layer Deposition for High-Performance Gas Sensor***, **Dain Shin,*** School of Electrical and Electronic Engineering, Yonsei University, Korea (Republic of)*; T. Nakazawa,* TANAKA Kikinzoku Kogyo K.K., Isehara Technical Center, Japan*; I. Sohn, S. Chung, H. Kim,* School of Electrical and Electronic Engineering, Yonsei University, Korea (Republic of)

Two-dimensional transition metal dichalcogenides (2D TMDCs) have attracted much attention in many research fields owing to their remarkable electrical, chemical, and optical properties. In addition, 2D TMDC-based gas sensor indicates significant gas detection characteristics at room temperature, opposed to the oxide-based sensor which requires external heating for gas detection.[1] Therefore, various 2D TMDC gas sensor studies have been conducted, and as the use of gas sensor expands, performance improvement becomes the challenge of TMDC gas sensors.

Sensing characteristics of 2D TMDC can be enhanced via functionalizing with a noble metal such as Pt, Au, Pd. Among them, Pt is known as a highly effective oxidation catalyst, and Pt nanoparticles (Pt NPs) can make sensing surface more sensitive to gas molecules owing to electronic sensitization and spillover effects.[2] In contrast, as the Pt NPs are difficult to form, atomic layer deposition (ALD) is used to precisely control atomic-scale deposits.

In this study, ALD Pt decorated tungsten disulfide (WS_2) was used as a sensing channel to maximize the response of the gas sensor. Pt NPs preferentially grew at higher surface energy point such as dangling bonds and grain boundaries of WS_2. Then, sensing characteristics of selectively decorated on WS_2 gas sensor was evaluated by various gases. It showed that the NO_2 response extremely increased with the number of ALD cycles. However, when the Pt film was formed at the increased number of cycles, the response decreased due to the loss of the semiconducting property of WS_2. Thus, we could investigate the proper number of cycles for maximizing the sensing response. In addition, it showed that the selectivity of the gas sensor could also be improved by the ALD Pt process.

References

[1] K.Y. Ko, J.G. Song, Y. Kim, T. Choi, S. Shin, C.W. Lee, K. Lee, J. Koo, H. Lee, J. Kim, T. Lee, J. Park, and H. Kim, ACS Nano 10, 9287 (2016).

[2] C. Wang, L. Yin, L. Zhang, D. Xiang, and R. Gao, Sensors 10, 2088 (2010).

Author Index

Bold page numbers indicate presenter

Author Index

Author Index

Author Index

Author Index

Author Index

Author Index