Live Session
Room Live - Session LI1-MoM

Plenary & ALD Innovator Award Session: Monday Live

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

10:00am **LI1-MoM-7 Plenary & ALD Innovator Award Session Welcome Introduction***, **Christophe Detavernier**, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

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10:15am **LI1-MoM-8 Meet the ALD 2020 Innovator Awardee***, **Mikko Ritala**,* University of Helsinki, Finland **INVITED**

Meet the ALD 2020 Innovator Awardee Mikko Ritala of the University of Helsinki, Finland

10:30am **LI1-MoM-9 Selective and Atomic Scale Processes to Enable Future Nano-Electronics***, **Robert Clark**,* TEL Technology Center, America, LLC **INVITED**

The economic driving force of Moore's law has enabled scaling of semiconductor devices to the point that modern feature sizes can be measured in atomic dimensions.[1,2] As shrinking the device footprint becomes increasingly difficult a new scaling paradigm making use of vertical scaling has emerged, initially by adopting non-planar devices, and now by stacking devices on top of one another to create 3D architectures as well.[3] Fabricating 3-dimensional electronic structures with atomic scale dimensions in high yields presents a number of daunting process challenges. Among these are the need to tightly control film thickness, uniformity, morphology, and composition within high aspect ratios. The need for selective deposition of functional films as well as layers used simply for patterning or alignment presents another challenge if we are to transition towards and more bottom-up style of nanomanufacturing. Selective and atomic scale processes are being developed in order to enable a number of self-aligned process schemes as well as scaling boosters required for future device nodes. Dielectric on dielectric (DoD) selective deposition is being developed to enable fully self-aligned vias to address edge placement error challenges encountered when manufacturing advanced interconnects. Selective metal on metal (MoM) depositions are useful for depositing metal capping layers as well as hardmasks. Scaling boosters such as super-vias and buried power rails could benefit from well-controlled processes with topographical selectivity. And dielectric on metal depositions (DoM) could provide relief from the growing overburdens needed to enable chemical mechanical planarization during replacement metal gate integration in the front end. Progress in these areas as well as future needs and an outlook on future device scaling pathways will be presented.

1. (a) Moore, G. E., *Electronics* **1965,***38* (8); (b) Bohr, M.,*Technical Digest of the IEEE International Electron Devices Meeting*, Washington, D.C., **2011**; pp 1-6.

2. Clark, R.D., *Materials* **2014,***7* (4), 2913-2944.

3. Clark, R., Tapily, K., Yu, K.-H., Hakamata, T., Consiglio, S., O'Meara, D., Wajda, C., Smith, J., Leusink, G. *APL Materials***2018**, 6, 050283.

11:00am **LI1-MoM-11 The First Application of ALD Technology in Display Industry***, **Hyun-Chul Choi**,* LG Display, Republic of Korea **INVITED**

TFT-LCD, which has dominated the display industry for the past 20 years, is gradually being replaced by OLED in recent years. OLED is superior to TFT-LCD in terms of image quality and design, but requires more advanced technologies and processes. OLED is vulnerable to moisture and oxygen due to the nature of organic materials, so encapsulation of OLED device plays a very important role to ensure the reliability of OLED. In small-size OLED products, thin film encapsulation (TFE) technology is used to form inorganic and organic layers on OLED device to protect OLED from moisture and oxygen. Atomic layer deposition, one of the semiconductor technologies, is successfully used to form high-quality TFE, which greatly improved the reliability of OLED. In addition, in order to enhance the performance of oxide-based large-size OLED products, MOCVD technology is steadily being researched and developed.

This plenary speech introduces the contribution of semiconductor technologies to the performance and quality of OLED. In addition, we will discuss the possibility of what semiconductor technologies can be applied for the future development of OLED technology.

11:30am **LI1-MoM-13 ALD on Powders for Catalysis***, **Frank Rosowski**,* BASF SE, Germany **INVITED**

Atomic Layer Deposition (ALD) is mainly applied in microelectronics as a thin film deposition technique. In academic research, ALD is also applied for synthesis of catalysts. The main challenge for ALD in this research field is the morphology of the substrate materials, usually small particles with high specific surface areas, e.g. up to 1000 m2/g for zeolites. In industry, catalytic reactors can hold packed beds of several tons of catalyst mass, exposing huge surface areas. But even in academia, where typical reactor loadings are on the gram scale, the surface areas to coat are in the range of hundreds of square meters, several orders of magnitude higher than for any wafer in the semiconductor industry.

At BasCat, the UniCat – BASF JointLab at Technische Universität Berlin, several projects use ALD as tool to synthesize and modify catalysts. In the field of supported metal catalysts, research is so far done along well-established lines of work, e.g. modifying supported metal catalysts with metal oxide layers, e.g. ZnO, alumina, and alucone. But the research focus lies on catalysts used for selective oxidation reactions, typically consisting of mixed metal oxides or phosphates. Catalysts are usually prepared in two batch sizes. For establishing suitable ALD process conditions, a sample size of about 1.0 cm3 is used. In a second step, catalyst amounts of 10 – 25 cm3 are prepared. It is important that process conditions established on the small scale are easily transferrable to the large scale.

For this purpose, a new and unique test facility was installed at BasCat equipped with a thermogravimetric balance as analytical small scale ALD reactor and a second reactor for catalyst synthesis on a large scale via ALD.[1] Based on our first ALD results, a fixed bed was chosen as reactor geometry for the analytical reactor and the synthesis reactor.

It was demonstrated that the fixed bed geometry is suitable for ALD yielding homogeneously covered substrates, and that scaling-up from 1.0 cm3 to 10 cm3 is possible.[2]

The combination of analytical reactor and synthesis reactor was then successfully used for modifying supported metal catalysts with layers of alumina and alucone,[3] and zinc oxide.[4] Other works included the deposition of rhenium on silver and phosphorus on vanadia.[5]

[1] Strempel, V. E., Naumann d'Alnoncourt, R., Driess, M. and Rosowski, F., Rev. Sci. Instrum., 074102. 2017

[2] Strempel, V., Knemeyer, K., Naumann d'Alnoncourt, R., Driess, M. and Rosowski, F.,Nanomaterials, 365. 2018

[3] Ingale, P., Guan, C., Kraehnert, R., Naumann d´Alnoncourt, R., Thomas, A., and Rosowski, F., Catalysis Today, submitted

12:00pm **LI1-MoM-15 The Flip Side of the Story: Atomic Layer Etching***, **Keren Kanarik**,* Lam Research Corp. **INVITED**

For the past 30 years, this conference has been largely dedicated to understanding the addition of atomically thin films. The flip side of that story is the removal of thin layers of material – Atomic Layer Etching – which only this past decade moved from "lab to fab" and into the mainstream. What took so long? What assumptions had to be revisited? In retrospect, we now understand why silicon was not the best case study system after all. More amenable materials have made it easier to find important benefits, such as the smoothing effect. A new operating regime led us to rethink the definition of an energy window. Such insights are proving vitally important for improving productivity and thus expanding the number of beneficial applications of this technology. While deposition has certainly led the way, etching offers a perspective from the flip side to understanding processes at the atomic scale. This plenary talk will share insights from the past decade, in hopes of continuing to push these complementary techniques forward in building the next generation of semiconductor devices.

12:30pm **LI1-MoM-17 JVST Best Paper Award, Closing Remarks, & Sponsor Thank You***, C Detavernier, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; **Erwin Kessels**,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

JVST Best Paper Award will be presented. You are now welcome to view all ALD/ALE On Demand Presentations

ALD Applications
Room Van Rysselberghe - Session AA1-MoA
Emerging Applications of ALD I & II

Moderators: Hyeontag Jeon, Hanyang University, Viljami Pore, ASM

1:45pm **AA1-MoA-2 Resistive Switching Maps for Films of Variable Conductivity Grown by Atomic Layer Deposition***, **Kaupo Kukli,*** University of Tartu, Estonia*; M Kemell,* University of Helsinki, Finland*; H Castán, S Dueñas,* University of Valladolid, Spain*; M Heikkilä,* University of Helsinki, Finland*; J Kozlova, M Rähn,* University of Tartu, Estonia*; M Ritala, M Leskelä,* University of Helsinki, Finland

Multilayers of oxide thin films offer an attractive basis of resistively switching media. To effectively modify the density of useful defects, properties of wide-band-gap and high-k oxides can be tailored, e.g. in Al_2O_3-TiO_2 multilayers [1]. In addition, components with high magnetic or electric polarizability may be applied as constituents, when seeking even wider functionality of switching materials. Thereby, alternate layering of more and less insulating materials can accompany with detrimental film conductivity, lowering the ratio between low and high resistivity states.

Nanolaminates with tunable composition, such as Ta_2O_5-TiO_2 [2], ZrO_2-Co_3O_4 [2], ZrO_2-Al_2O_3 [3], SiO_2-Nb_2O_5 [4], SiO_2-Fe_2O_3 [5] were grown. In such films, electrical and magnetic polarization hystereses were monitored at room temperature, together with resistive switching behavior. The latter was destabilised in structures where leaky constituents, e.g. Nb_2O_5 and Fe_2O_3, were applied. Complementarily to the common direct current resistive switching measurements with voltage pulses, we report the application of small-signal measurements. This allows memory mapping based on two-state capacitance and conductance recorded under bipolar voltages. Such hysteron-like signal-programming voltage behavior may allow reading information especially in materials which otherwise tend to remain in low resistance state in direct current measurements.

References:

[1] P. F. Siles et al., Tuning resistive switching on single-pulse doped multilayer memristors, Nanotechnology 24 (2013) 035702.

[2] S. Dueñas et al., Memory maps: Reading RRAM devices without power consumption, ECS Transact. 85 (2018) 201.

[3] H. Castán et al., Study of the influence of the dielectric composition of Al/Ti/ZrO_2:Al_2O_3/TiN/Si/Al structures on the resistive switching behavior for memory applications, ECS Transact. 85 (2018) 143.

[4] K. Kukli et al., Resistive switching in silicon oxide-niobium oxide thin films grown by atomic layer deposition from niobium pentaethoxide and hexakis(ethylamino) disilane, Nanotechnology, In press.

[5] K. Kukli et al., Atomic layer deposition and properties of mixture films and nanolaminates consisting of iron and silicon oxides, to be published.

3:00pm **AA1-MoA-7 Understanding and Controlling Release and Aerosolization of Inhaled Drug Particles Engineered by Atomic Layer Deposition***, D La Zara, F Sun, F Zhang,* Delft University of Technology, Netherlands*; M Quayle, G Petersson, S Folestad,* AstraZeneca, Sweden*;* ***Ruud van Ommen,*** Delft University of Technology, Netherlands

Inhaled drug delivery is the administration route of choice especially for respiratory diseases such as asthma and chronic obstructive pulmonary disease. However, the rapid absorption of inhaled drugs in the lungs limits their therapeutic effect, which lasts in the case of budesonide, a common drug for respiratory diseases, a couple of hours, thus requiring multiple doses per day. Moreover, an increasing number of inhaled drugs includes amorphous and sensitive drugs, which require solid-state stabilization, as well as powders with poor flowability, which necessitate improved aerosolization efficiency to meet the drug load requirements. Therefore, to improve patient compliance and enhance the therapeutic performance, it is crucial to find novel solutions to increase the lung deposited drug as well as extend the drug release in the lung.

In this work, we deposit nanoscale Al_2O_3, TiO_2 and SiO_2 films on micronized budesonide particles to tailor their dissolution and aerosolization properties. The ALD process is carried out at nearly ambient conditions in a fluidized bed reactor for a cycle range from 10 to 50, using TMA/O_3, $TiCl_4$/H_2O and $SiCl_4$/H_2O as precursors for Al_2O_3, TiO_2 and SiO_2 ALD, respectively. Transmission electron microscopy (TEM) coupled with energy dispersive X-ray mapping reveals the deposition of uniform and conformal TiO_2 and SiO_2 nanofilms, and the occurrence of Al_2O_3 subsurface growth. In fact, due to its high reactivity, TMA penetrates into the budesonide particles forming inorganic-organic shells which consist of a Al_2O_3/budesonide mixture. In-vitro dissolution tests and cell studies reveal dramatically slowed release with increasing film thickness. In particular, the in-vitro dissolution tests correlate with the cell studies which highlights the accuracy in describing the release of inhaled drug powders. The dissolution mechanism and the role of the nanofilms during drug release are investigated by ex-situ TEM of the solutions at different time points after the dissolution test. Furthermore, in-vitro aerosolization testing by fast screening impactor shows an almost 3-fold and ~2-fold increase in fine particle fraction (FPF: % <5 µm, i.e., particle size range relevant for inhalation) for the SiO_2- and TiO_2- coated particles, respectively. The higher FPF after the ALD process is attributed to the lower interparticle force which reduces the powder cohesiveness, as suggested by atomic force microscopy. Finally, the aerosolization properties are retained even after exposure at 40 °C and 75% RH for 1 month, demonstrating a good shelf performance.

3:15pm **AA1-MoA-8 In-vitro Screening of Materials and Laminates by Atomic Layer Deposition for Medical Device Coatings***, R Ritasalo,* Picosun Oy, Finland*; O Ylivaara,* VTT Technical Research Centre of Finland Ltd, Finland*; T Sillanpää, P Holmlund, A Kärkkäinen,* VTT Technical Research Centre of Finland, Finland*;* ***Tom Blomberg,*** Picosun Oy, Finland

Motivation: Chronic disease monitoring and treatment is and will continue to be the most important issue related to ever-increasing healthcare costs. Chronic diseases are linked with lifestyle problems and aging population. Therefore, new technical solutions, which would decrease the direct patient care, are actively investigated. Many different coating technologies and materials are used in medical applications depending on the desired properties of the coating. Coatings are typically used for reducing friction, providing electrical insulation, and as corrosion barriers. Atomic layer deposition (ALD) coatings are known to work excellently as hermetic barriers for water vapour, however, the barrier properties in aqueous solutions mimicking the environment of the human body are still under investigations. Potentially, ALD films could work as metal ion barriers in e.g. *orthopedics* implants and as electronic insulation for implantable electronics in cardiology and neurology segments. Irrespective of the actual use, the implantable medical device must withstand the corrosive environment inside the human body for prolonged periods of time. Hermetic sealing of the device to protect it from the corrosive environment of human body and vice versa is a key step to enable long life time for the smart medical devices.

Method: The degradation of the ALD-coated Si/SiO_2/Al interdigitated electrodes (IDEs) were investigated. The ALD films were deposited with PICOSUN® R-200 Advanced ALD reactor at different temperatures of 85, 125 and 200°C. Metal oxides such as Al_2O_3, SiO_2 and HfO_2 and their laminates were deposited in order to screen the temperature and material effect on the barrier properties. For the in-vitro study through accelerated aging tests the samples were wire-bonded and placed on phosphate buffered saline (PBS) solution and kept at 85˚C. The film degradation was on-line monitored by resistance measurements every 10 minutes until a notable rise in resistance value indicating failure of the barrier material.

Results: We will present the results from in-vitro accelerated tests and compare those to our previous excellent results with SiO_2-HfO_2 [1]. Both the studies show that the best ALD-laminates can last without failure in accelerated aging tests in PBS (85/87°C) at least 100 days corresponding over 10 years at human body (37°C). We will also present the ISO 10993-5 standard cytotoxicity test results.

The results highly support ALD as a hermetic and biocompatible corrosion resistant layer in future medical devices and implants.

[1]https://doi.org/10.1002/adfm.201806440

Acknowledgements: ULIMPIA project/PENTA under grant number PENTA-2017-Call2-16101-ULIMPIA

4:00pm **AA1-MoA-11 ALD and PE-ALD of High-Mobility Zinc-Tin-Oxide Semiconductor Layers: Towards Printable Electronic Devices***, T Cho, C Allemang, N Farjam, O Trejo, S Ravan, R Rodríguez, K Barton, R Peterson,* ***Neil Dasgupta,*** University of Michigan

Transparent amorphous oxide semiconductors (TAOS) are a valuable class of functional materials that are being explored for applications in flexible electronics. To enable next-generation devices, ranging from personal health monitoring to electronic textiles, there is a need for new material processes that enable low-temperature processing while maintaining high-quality device performance. Furthermore, the use of non-planar substrates requires deposition processes that can produce uniform, reproducible material properties without line-of-sight limitations. Therefore, there has been significant interest in ALD as an approach to engineering high-quality TAOS layers for devices such as thin-film transistors (TFTs).[1]

Among the various TAOS materials, zinc-tin-oxide (ZTO) is being explored as an alternative to indium-gallium-zinc-oxide (IGZO), as it has the potential to reduce manufacturing cost significantly by utilizing earth-abundant elements[2]. However, to date, there have been relatively few reports of TFT device performance using ALD ZTO layers, and high-temperature post-deposition anneals have been required to achieve enhancement-mode devices with high field-effect mobility (μ_{FE}). To overcome these limitations, in this study, we explore the role of oxidizers, including water and O_2 plasma. We demonstrate that through rational control of the process conditions and combining these oxidizing species in a super-cycle recipe, we can achieve μ_{FE} values of > 13 $cm^2V^{-1}s^{-1}$ in films as-deposited at 200°C. Even higher mobility values can be achieved when post-deposition anneals are performed. The process-structure-property relationships of these high-mobility ZTO films will be described, including the role of zinc:tin ratio, deposition temperature, and post-deposition treatments.

To demonstrate a pathway towards bottom-up, printable devices, area-selective ALD of ZTO is demonstrated using printed polymer inhibition layers. By using electrohydrodynamic-jet (e-jet) printing[3], we demonstrate the ability to pattern devices with < 1 µm resolution, well below the resolution of traditional ink-jet printing. Finally, printed TFTs were fabricated, demonstrating well-behaved device performance, including an on/off current ratio of almost 10^6. This research presents a pathway towards printable electronic devices based on low-temperature ALD/PE-ALD processing, which is compatible with flexible/stretchable substrates and does not require any clean-room processing.

1. J. Sheng et al. *J. Vac. Sci. Technol. A* **36**, 060801 (2018)
2. P. Schlupp et al. *Adv. Electron. Mater.***1**, 1400023 (2015)
3. J.-U. Park et al., *Nature Materials* **6**, 782 (2007)

4:15pm **AA1-MoA-12 Optimized Schottky Junctions by Atomic Layer Deposition for Piezotronic MEMS Strain Microsensors***, **Raoul Joly**, S Girod, N Adjeroud, M El Hachemi, P Grysan, T Nguyen, K Menguelti, S Klein, J Polesel,* Luxembourg Institute of Science and Technology, Luxembourg

The rapidly spreading Internet-of-Things is accelerating MEMS (Micro-ElectroMechanical Systems) industry's to deliver highly sensitive and miniaturized self-sensors with low consumption and cost effective production process. Up to now, no consistent study has emerged to propose the optimized configurations for piezotronic materials properties and electrodes interface configurations on sensors for reliable microfabrication processing for MEMS.

By the means of Atomic Layer Deposition (ALD), we developed piezotronic strain sensitive sensors integrated in polyimide cantilevers, where a zinc oxide (ZnO) thin film is deposited on top of patterned interdigitated platinum electrodes (Figure 1). Due to its high film conformality, low temperature processing, self-limiting nature and stoichiometric control at the nanoscale level, ALD technique has emerged as an ideal technique to add new functionalities in MEMS. ALD technique can coat high aspect ratio topographies, with flawless interfaces and low temperature process compatibility on organic flexible surfaces. We propose to rationalize the ALD processing to obtain wurtzite polycrystalline zinc oxide thin films with a privileged (002) orientation and to make it compatible with microfabrication processing on polymer. Hence, Schottky junctions are realized by microstructuring interdigitated micro-combs at the interface of the high work function metal and the semiconducting piezoelectric ZnO thin film. This piezotronic junction has the particularity of an exponential dependence of the flowing diode current as a function of the applied mechanical strain. The sensitivity is thus greatly improved with gauge factor higher than 100. Our associated noise analysis and signal to noise ratio measurements estimated minimal strain detection of 10^{-6}.

In the last stage of this work, we will present the strain sensors size miniaturization for integration in microcantilevers in a full polymer body, compatible with AFM (Atomic Force Microscopy) scanning probe operations (Figure 2). The influence of the ALD deposition parameters on the sensors electromechanical transducing properties will be reported as well. Thus, we propose a promising way of zinc oxide thin film processing by ALD for a reliable microfabrication processing to obtain ultrasensitive and low consumption (estimated below 50 µW) piezotronic MEMS strain microsensors.

4:45pm **AA1-MoA-14 Embedded Organics in Crystalline Fluorides: A One-Step Approach to Sensitized Luminescence***, **Per-Anders Hansen**,* University of Oslo, Norway*; T Zikmund,* Academy of Sciences of the Czech Republic, Czech Republic*; T Yu,* Utrecht University, Netherlands*; J Nitsche Kvalvik, T Aarholt, Ø Prytz,* University of Oslo, Norway*; A Meijerink,* Utrecht University, Netherlands*; O Nilsen,* University of Oslo, Norway

Photoluminescence, conversion of one type of light into another, allows turning blue LEDs into a warm white, enable molecular tagging, enhances optoelectronics and improves energy harvesting. The crucial point that decides if photoluminescence can tackle a given problem is the possibility to tune absorption, conversion and emission properties to the excitation source, required output wavelength and its efficiency. With the recent development of multi-step processes like down- and upconversion and the need to sensitize these with stronger absorption mechanisms, it is clear that optimizing all properties simultaneously is not possible within a single material class.

In this work, we have utilized the layer-by-layer approach of atomic layer deposition to combine broad absorption from an aromatic molecule with the high emission yields of crystalline multi-layer lanthanide fluorides in a single-step nanocomposite process. This approach results in complete energy transfer from the organic molecule while providing inorganic fluoride-like lanthanide luminescence. Sm^{3+} is easily quenched by organic sensitizers, but in our case we obtain strong fluoride-like Sm^{3+} emission sensitized by the strong UV absorption of terephthalic acid. This design allows combinations of otherwise incompatible species, both with respect to normally incompatible synthesis requirements and in controlling energy transfer and quenching routes.

5:00pm **AA1-MoA-15 Atomic Layer Deposition of ZnO Quantum Dots for Optoelectronics***, **Jin Li**,* Ghent University, Belgium*; Y Yu, X Bi,* Beihang University, China

In the past few years, atomic layer deposition (ALD) has been recognized as a promising way in fabricating quantum dots (QDs). In principle, ALD growth would experience an "islands" period during the initial nucleation stage before forming a continuous layer. Therefore, by intentionally freezing the ALD process in the initial stage, quantum dots can be achieved instead of continuous layers. In contrast to other common QD synthesis methods such as solution-based processes, MBE or MOCVD, ALD can easily and precisely tune the chemical composition, size and spatial distribution of QDs at a much lower cost, as well as realizing functionalized coatings on nanoscale 3-D architectures, which render it an excellent choice for implementing QDs in optoelectronic applications.

Herein, we report the study on ALD depositing metal-oxide QDs with ZnO as a model material, which is widely used in nanoscale optoelectronics.[1] The morphology evolution of as-deposited ZnO with growth condition and parameters was systematically investigated to elucidate the major influential factors for QD synthesis by ALD. Firstly, we examined the influence of the initial surface condition on the nucleation behavior of ALD, as well as the opportunity of using different plasma pre-treatment and buffer layers to improve the uniformity of nuclei distribution, which are of significance for QD deposition. Further, we demonstrated that precursor exposure time was an important factor in deciding the morphology of ALD QDs, which, in conjunction with ALD cycle number, lead to great freedom in adjusting the density and size of the QDs. In the present work, we realized monodisperse ZnO QDs with average size tunable from 8.5 to 2.1nm. The QDs exhibited highly enhanced bandgap from 3.2 eV to 5.08 eV and widely tunable defect-emissions from red/yellow to NUV band, together with good quantum yield (maximum 97.3% at 395 nm) and excellent temperature stability. In addition, the possibility of further modifying the surface state of the as-deposited QDs by coating other materials or post-treatment are explored, and the device implementation issue for ALD QDs is also discussed.

Reference

1 J. Li, Y. Yu and X. Bi, *ACS Photonics*, 2019, **6**, 1715–1727.

ALD Fundamentals
Room Auditorium - Session AF1-MoA

ALD Precursors I & II

Moderators: Seán Barry, Carleton University, Anjana Devi, Ruhr University Bochum

2:00pm **AF1-MoA-3 Atomic Layer Deposition of Ruthenium-Containing Thin Films using RuO_4 as both the Co-Reactant and the Metal Source**, ***Matthias Minjauw***, *J Feng, C Detavernier, J Dendooven,* Ghent University, Belgium

Ruthenium-containing materials often display interesting physical and chemical properties, making them relevant to a wide variety of applications. For example, a range of Ru-based ternary oxides are promising electrocatalysts with excellent chemical stability for the oxygen evolution reaction (OER).[1] In addition, their electronic properties make them interesting electrode materials, and some even show superconductivity.[2,3] Ru-based bimetallic nanomaterials are also investigated for applications in electrocatalysis.[4]

As ruthenium is a rare element, it is advisable to use such materials not in their bulk form, but as thin films or nanoparticles on high surface area substrates. Therefore, ALD would be an appropriate method of synthesis. In ALD, the most common way of making ternary oxides or binary alloys is to alternate two different metal oxide or single metal ALD processes in sequence. The metal source is typically a metalorganic precursor, in which the metallic center is in a certain oxidation state, and a co-reactant is used to achieve the desired oxidation state in the target material.[5] In this work we report a low temperature ALD route towards Ru-containing materials, in which the inorganic RuO_4-precursor is used as both the Ru-source and the oxidizing co-reactant. If the target material is a Ru-containing ternary oxide, the RuO_4-precursor can be directly combined with a metalorganic precursor in a 2-step process.

As a proof of concept, we first show that an ALD process for aluminum ruthenate can be obtained by combining $Al(CH_3)_3$ with RuO_4 in a 2-step process at sample temperatures 50°C-125°C. Similarly, Pt-doped ruthenium oxide can be obtained by reaction of the classical Pt precursor, $PtMe_3CpMe$, with RuO_4 at sample temperatures 40°C-120°C. Both processes display good ALD-behavior, as is evident from the saturation of the half-reactions and the linearity of growth (shown in Figure 1 and 2 for the TMA/RuO_4 process). As a general reaction mechanism for the 2-step process, we propose that the RuO_4-precursor combusts the organic ligands of the chemisorbed metalorganic precursors, while simultaneously binding RuO_2 to the surface. Both films are amorphous as-deposited, and the elemental composition is shown in Table 1. Finally, we show that a crystalline Ru-rich Pt-Ru alloy can be obtained by introducing an additional reduction step after the RuO_4 exposure, making it a 3-step process (Table 1).

[1] Kim et al. *J. Am. Chem. Soc.,* **2017**, 139, 12076.

[2] Koster et al. *Rev. Mod. Phys.,* **2012**, 84, 253.

[3] Maeno et al. *Nature,* **1994**, 372, 532.

[4] Li et al. *Energy Environ. Sci.*, **2018**, 11, 1232.

[5] Han et al., *Chem. Mater.,* **2012**, 24, 4686.

2:30pm **AF1-MoA-5 Visual Screening of Precursors for ALD/MLD**, ***Ola Nilsen***, *P Hansen,* University of Oslo, Norway

When evaluating possible new precursors for ALD/MLD, properties like sublimability, melting point and thermal decomposition is required. There are already well-established tools to provide such information, such as TGA-MS, DSC, DTA, and many more. However, these techniques typically involve routines that does not easily allow for handling of air sensitive materials, or easy access of compounds you fear are going to leave a mess. In addition, most techniques do not reveal what your compounds are doing in the dark.

We have filmed our compounds during thermal treatments and used image analysis to extract the equivalent of the properties above, being able to differentiate between decomposition, degassing and sublimation. While doing so, we discover compounds that jump, dance, pop and otherwise misbehave when heated. Such behavior will lead to misinterpretation by the techniques mentioned above, but when revealed by our visual approach, we are better suited at screening for suitable precursors for ALD and MLD processes. Examples from well-known ALD precursors to possible new types of suitable compounds will be given, in addition to a couple of surprises.

3:00pm **AF1-MoA-7 β-Silyl-Diamides and β-Silyl-Amidoamines Lead to Unusual Co(II & IV) Precursors**, ***David Zanders,*** Ruhr University Bochum, Germany*; M Griffiths, G Bacic,* Carleton University, Canada*; J Masuda,* Saint Mary's University, Canada*; A Devi,* Ruhr University Bochum, Germany*; S Barry,* Carleton University, Canada

Cobalt-containing thin films and nanomaterials such as elemental Co or $CoSi_2$ have recently garnered significant interest as potential next-generation interconnects to replace Cu in future microelectronic devices. ALD is favorable for the deposition of these materials owing to low processing temperatures, precise control of thickness and conformal coverage over complex device geometries considering modern, demanding processing criteria. A review of the current Co-containing precursors remain scarce, and mechanistic deposition studies are rare.[1] Throughout the periodic table, silylamines where the Si is in β position to a bound metal center are excellent ligands (e.g. $-N(SiMe_3)_2$) to enhance thermal stability and volatility).[2] Yet the thermal budget (*e.g.* thermal stability, shelf life) is poor in the case of the known Co(II) congener $Co[N(SiMe_3)_2]_2$ $_2$ and a recent CoO ALD process demonstrated that the monomeric THF adduct shows higher thermal stability and evaporation characteristics but contains an oxygen in the ligand environment.[3] This presentation will discuss new oxygen-free, cyclic silyl-diamido and -amidoamino Co ALD precursors and the deposition of Co-containing films (Figure 1).

Our initial study[4] unearthed an unprecedentedly highly stable and volatile Co(IV) bis-β-silyldiamide (**1**), which was characterized by TGA and DSC, with a thermal range of 47 °C between the 1 Torr vapor pressure temperature ((150.4 ± 0.1) °C) and the onset of decomposition (197 °C) (Figure 1). Compound **1** has a facile synthesis and showed saturated adsorption by QCM studies. Additionally, we report a promising Co(II) bis-β-silylamidoamine (**2**), a complex with multi-gram scalable synthesis, and a thermal range of 50 °C , with a low melting point (62 °C) and a significantly lower 1 Torr vapor pressure temperature ((112.2 ± 0.1) °C) than **1** (Figure 2). Both precursors were subjected to ALD process development for Co-containing thin films. Typical ALD growth characteristics in terms of saturation, ALD window and linearity as well as film composition will be discussed using methods ranging from XRR, AFM, RBS/NRA and XPS.

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

[2] M. F. Lappert et al.,*Metal amide chemistry*, Wiley, **2009**.

[3] T. Iivonen et al.,*Journal of Vacuum Science & Technology A***2019**, *37*, 10908.

[4] D. Zanders et al., *Chemrxiv***2020**, DOI: 10.26434/chemrxiv.11691825.v1

3:15pm **AF1-MoA-8 A Low Cost, High Efficiency TMA-Replacement for the Deposition of Pure Aluminum Nitride Films by ALD**, ***Sydney Buttera,*** Carleton University, Canada*; P Rouf, H Pedersen,* Linköping University, Sweden*; S Barry,* Carleton University, Canada

Since its inception, the field of ALD has demonstrated its reliance on the importance of main group chemistry. The most fundamental process of the deposition of aluminum oxide from trimethylaluminum (TMA) and water has been extensively studied and used in labs and in industry internationally; it is extremely well understood, and by extension, can now be evaluated for improvement. By rationally designing and synthesizing precursors based on a TMA framework, we aim to develop ALD processes in which we can regulate surface chemistry, limit decomposition pathways, and deposit low-impurity thin films. In this research, we have implemented straightforward reactivity between precursors and surface sites to enable the deposition of high quality AlN films using a novel ALD precursor.

This presentation will describe the synthesis, characterization, and use of a heteroleptic bis(hydride)mono(dimethylamide)aluminum(III) precursor ($AlH_2(NMe_2)_2$) for the deposition of aluminum nitride films by ALD. This precursor and its predecessors are based on a TMA framework where methyl ligands are replaced using ligands with only Al-N and Al-H bonds in order to reduce carbon impurities in deposited films. This result was preceded by work on other novel ALD precursors, including tris(dimethylamido)aluminum(III), mono(hydride)bis(dimethylamide)aluminum(III), and a series of $Al(^{Me}NacNac)_x(NMe_2)_{3-x}$ (x = 1, 3) compounds, which will also be discussed.

Bis(hydride)mono(dimethylamide)aluminum(III) has been chosen as the optimal AlN precursor due to its thermal stability, volatility with a 1 Torr temperature of 55 °C, and its presence of only hydrogen and nitrogen bonded to the metal centre. Using this precursor, AlN films have been deposited by ALD using NH_3 plasma as the coreagent between 100 and 250 °C. The films produced were uniform and stoichiometric with an Al:N ratio of 1.04. It was also demonstrated that film crystallinity increased with increased number of ALD cycles and increased deposition temperature. Importantly, impurity levels were extremely low with less than 2% oxygen and less than 1% carbon in AlN films. Electrical measurements were also carried out on AlN films.

By using a simple precursor such as $AlH_2(Nme_2)_2$ instead of TMA for the deposition of aluminum oxides and nitrides, we can improve film quality and reduce material cost by up to 2 orders of magnitude. This precursor is extremely simple to synthesize, has minimal safety concerns, and its replacement of TMA in depositions could lead to a multitude of benefits for both researchers and final films alike.

4:15pm **AF1-MoA-12 Polymeric Tin Trifluoroacetate Precursors for Atomic Layer Deposition of Fluorine-Doped Tin(IV) Oxide***, **Goran Bacic,** E Goodwin,* Carleton University, Canada*; J Gagnon, R Boyd,* University of Ottawa, Canada*; S McGarry, S Barry,* Carleton University, Canada

Transparent conducting materials are critical components in many optoelectronic devices, and ALD has been particularly important in their continued development. Fluorine-doped tin(IV) oxide (FTO) has certain advantages over alternatives like tin-doped indium(III) oxide (ITO) or aluminum-doped zinc(II) oxide (AZO), namely resistance to chemical attack, UV photobleaching, high temperature degradation, and mechanical abrasion. FTO is also ubiquitous and cheap, readily available and comprised of only earth-abundant elements. Despite this, ALD of FTO has never been reported. This may be due to the extreme hazards associated with hydrogen fluoride and organotin precursors used in CVD, or the high cost of other known fluorination pathways in CVD and ALD (e.g., fluorinated metals and *β*-diketonates).

Tin trifluoroacetates ($Sn(tfa)_x$) have been reported as FTO CVD precursors that react with air to make FTO films second only to those made by CVD from tetramethyl tin (Me_4Sn) with CF_3Br and ozone. We took interest in $Sn(tfa)_x$ as environmentally-friendly and safe precursors to deposit FTO with ALD, with the hope to enable the use of nanostructured and flexible substrates.

We have found two tin trifluoroacetates with potential to be ALD precursors: hexatin(II)-di-μ₃-oxyoctakis(μ-trifluoroacetate) [$Sn_6O_2(tfa)_8$, Figure 1a] and tin(IV) tetrakis(μ-trifluoroacetate) ($[Sn(tfa)_4]_n$, Figure 1b). Both are polymers that reversibly depolymerize upon heating and volatilize without decomposition into their constituent subunits (Figure 1d-f). They are also complementary: $Sn_6O_2(tfa)_8$ can be prepared using green chemistry but is less volatile; while $Sn(tfa)_4$ is highly volatile and more reactive but is difficult to prepare. Weighing these options, we determined that $Sn_6O_2(tfa)_8$ was the precursor of choice due to its excellent properties, low cost, thermal stability, and previously reported success for CVD.

We deposited high quality FTO on oxide surfaces with $Sn_6O_2(tfa)_8$, air and water over a wide temperature range (250-400 °C). Uniform, dense, and smooth films were formed on Al_2O_3 and glass with self-limiting behaviour (Figure 1c). They were highly conductive (2.4 mΩ cm), transparent (88%), and stable to ambient conditions. However, we found saturation with air to be too sluggish. Using N_2O as an oxidant greatly enhanced the rate of deposition at 400 °C, and this process represents the first use of N_2O in ALD of SnO_2. Interestingly, no growth occurred using either O_2 nor N_2O without a water pulse before or during oxidation. This presentation will discuss the deposition chemistry of FTO films, and focus on possible mechanisms using synthetic, deposition, and computational strategies.

4:45pm **AF1-MoA-14 Highly Volatile In(III) Triazenide Precursors for Atomic Layer Deposition of Indium Nitride***, **Nathan O'Brien,** P Rouf, R Samii, K Rönnby,* Linköping University, Sweden*; S Buttera,* Carleton University, Canada*; V Kessler,* Swedish University of Agricultural Sciences, Sweden*; L Ojamäe, H Pedersen,* Linköping University, Sweden

Indium nitride (InN) is interesting for high frequency electronics due to its high electron mobility, small effective electron mass and high electron saturation velocity. However, the problematic deposition of InN films by conventional methods, such as CVD, has prevented its full exploration in electronics. This is due to the low temperature tolerated by the InN crystal as it decomposes to In metal and N_2 gas at 500 °C. ALD is a promising alternative to CVD for low temperature deposition of InN. We recently used hexacoordinted guanidinates[1] and amidinates[2,3] (In[*i*Pr–N=C(R)–N–*i*Pr]₃; where R = NMe_2, Me and H) precursors with NH_3 plasma for ALD of InN.[4] It was revealed that smaller and less electron donating substituents on the endocyclic carbon of the ligand backbone led to improved precursor surface chemistry. An alternative ligand to amidinates is the triazenide (R–N=N–N–R), which differs by the nitrogen atom in the endocyclic position. Development of this ligand could produce a new family of precursors with enhanced surface chemistry for ALD of InN. In this presentation, the synthesis, structure and thermal properties for six In(III) triazenide complexes, depicted as $In[R^1N_3R^2]_3$, will be shown and discussed. Reaction of alkyl azide ($R^1–N_3$; where R^1 = *i*Pr, *s*Bu and *t*Bu) with an alkyllithium ($R^2–Li$; where R^2 = *i*Pr, *s*Bu and *t*Bu) formed the lithium intermediate ($[R^1N_3R^2]Li$), which was reacted with $InCl_3$ to give complexes **1**-**6** in good yields. The crystal structure of **1** (In[*i*PrN₃*i*Pr]₃) showed the In atom in a distorted-octahedral geometry with In–N bond lengths of 2.21(5) Å. Compound **1** sublimed at 80 ºC, whilst the bulkier symmetrical complexes **4** (In[*s*BuN₃*s*Bu]₃) and **6** (In[*t*BuN₃*t*Bu]₃) sublimed at higher temperatures of 95 and 120 ºC, respectively. Unsymmetrical complexes **2** (In[*i*PrN₃*s*Bu]₃), **3** (In[*i*PrN₃*t*Bu]₃) and **5** (In[*s*BuN₃*t*Bu]₃) showed sublimation temperatures between 100-110 ºC, but decreased in thermal stability. Thermogravimetric analysis of **1** showed single step evaporation between 145-215 ºC. ALD of InN using **1** and NH3 plasma afforded epitaxial InN on 4H-SiC that was stoichiometric with low amount of impurities. Two temperature growth intervals were observed when depositing InN films. In the high temperature interval, **1** underwent a gas phase thermal decomposition to produce a more reactive In(III) compound whilst retaining self-limiting growth behavior. DFT calculations detailing the decomposition pathways will be shown and discussed.

[1] S. T. Barry et al. *Dalton Trans.* **2011,** *40*, 9425-9430. [2] A. Devi et al. *Dalton Trans.* **2017**, *46*, 10220-10231. [3] R. G. Gordon et al. *Chem. Eur. J.* **2018**, *24*, 9525-9529. [4] Rouf et al. *J. Phys. Chem. C*, 123, 25691-25700.

ALD Fundamentals
Room Jan & Hubert Van Eyck - Session AF2-MoA
Plasma Enhanced ALD

Moderators: Sumit Agarwal, Colorado School of Mines, Seung Wook Ryu, SK Hynix

1:45pm **AF2-MoA-2 Ion Energy Distribution and Fluxes for a Newly-Designed Remote Plasma Source for ALD for GaN Devices***, **Harm C.M. Knoops,*** Oxford Instruments Plasma Technology, Netherlands*; K Arts, J Buiter, L Martini,* Eindhoven University of Technology, Netherlands*; T Hemakumara,* Oxford Instruments Plasma Technology, Netherlands*; M Powell,* Oxford Instruments Plasma Technology, UK*; A Kurek, Y Shu,* Oxford Instruments Plasma Technology, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; C Hodson, A O'Mahony,* Oxford Instruments Plasma Technology, Netherlands

Gallium nitride devices have been found to benefit from low-damage remote plasma ALD processing to not exceed energy and flux levels leading to device damage. At the same time plasma species concentrations and impact energies in these processes must be sufficient to allow for high throughput and high-quality film deposition. This contribution will outline ion energy distribution functions and flux levels for a remote plasma ALD reactor, Oxford Instruments Atomfab™. This tool includes a new, RF-driven, remote plasma source. The source design is optimized for ALD on GaN High Electron Mobility Transistors (HEMTs) for substrates up to 200 mm in diameter and allows for Al_2O_3 cycles of less than one second.

The plasma source has been evaluated using a retarding field energy analyzer (RFEA). As expected from a remote plasma, a strong reduction of the ion flux was observed when increasing the pressure. A roughly exponential decrease in ion flux as a function of pressure was observed for plasmas generated in Ar and also in O_2/Ar mixtures. The average ion energy also generally decreases with pressure, although the effect is less obvious. For example, the plasma source of Atomfab at 100 W plasma power and ~375 mTorr pressure gives modest ion energies (<50 eV) and very low ion flux ($<10^{13}$ cm^{-2} s^{-1}). Furthermore, the short plasma exposure time required for Atomfab to reach saturation (0.25 s plasma), means that the ion energy dose per ALD cycle is relatively low. By increasing plasma power and decreasing pressure, the ion flux can be increased to the 10^{14} cm^{-2} s^{-1} range if desired.

To validate that these conditions were suitable for GaN HEMT devices, ALD depositions were carried out using a standard Atomfab configuration. Al_2O_3 layers were grown on GaN HEMTs at 300 °C where the best electrical device performance was obtained by including an NH_3 plasma pre-treatment (100 mV hysteresis and 125 mV dispersion). Interestingly, this was achieved using a <1 s cycle time, while maintaining a refractive index >1.63 and a film thickness non-uniformity <±1.0% over the wafer. General characteristics and plasma aspects of this new remote plasma source will be discussed together with their impact on ALD processing.

2:00pm **AF2-MoA-3 Plasma-Enhanced Atomic Layer Deposition of Cobalt and Cobalt Nitride: What Controls the Incorporation of Nitrogen?***, **Gerben van Straaten**, R Deckers, M Vos, E Kessels, A Creatore,* Eindhoven University of Technology, Netherlands

Cobalt is a transition metal with a wide range of applications, including as a catalyst for the Fischer-Tropsch reaction, as a contact material in spintronic devices and as a potential replacement for copper in IC interconnects. In many of these applications, precise control over the thickness of the Co film is required and this can be obtained via Atomic Layer Deposition (ALD). ALD of Co thin films and nanoparticles can be achieved using a variety of Co precursors together with NH_{3-} plasma[1]. However, nitrogen has been identified earlier in literature, as a species that can be incorporated into Co films from the NH_3 plasma during ALD[2]. Here we demonstrate that nitrogen incorporation is a major factor affecting the resistivity of Co thin films and thus their performance for interconnect applications. At the same time, incorporation of nitrogen in the film also leads to the formation of cobalt nitrides, which are materials with interesting magnetic and catalytic properties.

Analysis of the N content in ALD-deposited Co shows that the nitrogen incorporation process is strongly temperature-dependent. In particular, we find a critical temperature of 290° C: below this temperature CoN_x is deposited, while above it we obtain metallic Co with traces of N. This opens up possibilities for the controlled deposition of both Co and CoN_x using the same process. To gain more insight into the formation of CoN_x during ALD, we analyzed the effect of NH_3 plasma exposure on cobalt and show that an inductively coupled NH_3 plasma can incorporate nitrogen into the top 4 nm of a Co thin film. By combining Temperature Programmed Desorption (TPD) with in-situ Spectroscopic Ellipsometry (SE) we show that the cobalt nitride is metastable and that it decomposes in two stages: surface-bound nitrogen starts to leave at 170° C, while nitrogen present deeper in the film starts to leave around 260° C and leads to the complete removal of all nitrogen from the film.

Detailed analysis of the film surface after NH_3 plasma exposure reveals that it is initially passivated by nitrogen atoms but that free adsorption sites are generated by N_2 desorption at elevated temperatures. This yields further insight into the mechanism by which the Co precursors adsorb on the Co and CoN_x surfaces. Based on these insights we formulate a reaction mechanism for Co ALD which includes a competition between nitrogen incorporation and desorption and the effect on Co precursor adsorption.

[1] M. F. J. Vos, G. van Straaten, W. M. M. Kessels, and A. J. M. Mackus, *J. Phys. Chem. C*, p. acs.jpcc.8b06342, Sep 2018

[2] H.-B.-R. Lee and H. Kim, *Electrochem. Solid-State Lett.*, vol. 9, no. 11, p. G323, Nov 2006

2:15pm **AF2-MoA-4 Recent Advances in Hollow Cathode Technology for Plasma Assisted ALD***, **K. Scott Butcher**, V Georgiev, D Georgieva,* Meaglow Ltd, Canada

In the past, hollow cathode plasma sources were primarily used in the Semiconductor Industry as sputter sources, however we have developed a range of gas-based sources that have been widely adopted for plasma assisted atomic layer deposition. This has largely been because of reduced oxygen contamination evident with these plasma sources when depositing non-oxide films (eg. [1]) though other advantages include high radical flux and relatively low ion damage. There have now been over forty journal papers published in relation to our hollow cathode sources. In this presentation we talk about some of the recent advances in their design, in particular the introduction of aluminum cathodes, which, like our titanium cathodes, are compatible with deposition on silicon. Aluminum is a relatively soft metal, and its resistance to sputtering might be questioned, however Langmuir probe measurements and other observations reveal that for operation below a certain power density, compatible with our third-generation designs, a protective dielectric coating is produced in the first few moments of operation with either nitrogen or oxygen plasmas. These hard coatings help to protect the underlying aluminum while providing an added advantage of decreased electron recombination at the cathode walls.

Finally, we have been able to demonstrate scalability to 12” diameter with our newest designs, and lower pressure operation than was available with our second-generation sources.

[1] J. Mater. Chem. C. 2 (2014) 2123.

2:30pm **AF2-MoA-5 Detection of Oxygen Vacancies in H_2-Plasma Enhanced Atomic Layer Deposited (PEALD) Ferroelectric Hafnia Zirconia Thin Films***, **H. Alex Hsain**,* NC State University*; G Walters,* University of Florida*; Y Lee, J Jones,* NC State University*; T Nishida,* University of Florida

Oxygen vacancies are suggested to be one of the main driving factors in stabilizing the unexpected polar orthorhombic phase ($Pca2_1$) in ferroelectric hafnia.[1] They also play a key role in the so called “wake-up” effect in which the remnant polarization of a ferroelectric device increases with repetitive electric field cycling.[2] Studies have suggested that the wake-up effect is caused by a redistribution of oxygen vacancies.[3] As a result, devices must be preconditioned with a set number of wake-up cycles in order to achieve the desired properties which comes at the expense of the device lifetime. There is an urgent need to detect – and control – the oxygen vacancy concentration in hafnia-based devices. For the first time, we report a direct method of detecting oxygen vacancies in ferroelectric hafnia-zirconia ($Hf_{0.5}Zr_{0.5}O_2$) thin films using depth profiling X-Ray Photoelectron Spectroscopy (XPS).

Recently, Walters et al. found that inclusion of an H_2-plasma step after oxidation can significantly decrease the wake-up effect.[4] We fabricate films via Plasma-Enhanced Atomic Layer Deposition and study the effect of H_2-plasma time duration on ferroelectric properties. We find that increasing H_2-plasma exposure time from 0 to 5 seconds increases the switched polarization from 0 to 27 $\mu C/cm^2$. Upon further exposure to H_2 plasma, the films display a distinct “pinched” hysteresis loop showing that the films become anti-ferroelectric. To reveal the mechanism by which H_2 plasma dramatically changes the ferroelectric properties, we use XPS to characterize the chemical and stoichiometric nature of HZO films.

Elemental quantification indicates a significant reduction in oxygen content in the HZO/TiN layer with higher exposure of H_2-plasma suggesting that H_2-plasma can directly reduce HZO into sub-oxides and form oxygen vacancies. The deconvolution of the O 1s peak in plasma-treated films suggests a shift toward lower binding energy which would occur in the presence of oxygen vacancy formation in the films.[5] Inspection of the Hf 4d and Zr 3d spectra also reveal a shift toward lower binding energy for films exposed to the highest plasma time. Grazing Incidence X-Ray Diffraction (GIXRD) corroborates these findings by a peak shift from 30.5° toward lower 2θ which supports the stabilization of the polar orthorhombic phase in intermediate H_2 plasma exposure times. Our study suggests that H_2-plasma enhanced ALD in conjunction with XPS could be a promising route for designing a wide array of HZO functional devices using defect engineering.

1 DOI: 10.1039/C7NR06342C 2 DOI: 10.1063/1.4829064. 3 DOI: 10.1063/1.4940370 4 DOI: 10.1063/1.5135709 5 DOI: 10.1016/j.apsusc.2017.11.016

3:00pm **AF2-MoA-7 Effect of an Electric Field on the Material Properties of Hafnium Oxide Thin Films Deposited by Plasma Enhanced Atomic Layer Deposition***, **Vivek Beladiya**, A Szeghalmi,* Friedrich Schiller University, Germany

HfO_2 is widely used metal-oxide in semiconductors and optics due to high dielectric constant and high refractive index. The HfO_2 thin films were deposited using plasma enhanced atomic layer deposition at 100 °C using tetrakis(dimethylamino)hafnium and oxygen plasma. Additionally, substrate biasing up to -100 V was applied during the oxygen reaction step. The HfO_2 thin films of various thickness from 30 nm to 100 nm were deposited. The mechanical, optical, structural and chemical properties of hafnium oxide were investigated.

The mechanical stress in the ~30 and ~100 nm HfO_2 film changed from tensile to compressive when an average-bias voltage of -50 V was applied. The increase in the refractive index was observed with an increase in average-bias voltage. The high refractive index of 2.03 were observed when ~30 nm and ~100 nm HfO_2 thin films were deposited using an average-bias voltage of -50 V. The XRD measurement showed an increase in crystallization of ~100 nm HfO_2 thin films when average bias voltage was increased to -50 V. Thus crystallization can be the reason for induced stress in the HfO_2 thin films. The AFM and XRR measurements showed an increase in surface roughness with the increase in average-bias voltage. Nano-crystalline hillocks were observed in AFM images of HfO_2 thin film deposited with average-bias voltage of -50 V. The density of the films increased and reached a maximum value of 9.07 g/cm^3, when average-bias voltage was increased to -50 V. The FTIR measurement showed a decrease in OH impurity into the film with an increase in average-bias voltage.

It is shown that substrate biasing can be an effective technique to modify properties of HfO_2 thin films and good quality films can be realized at low temperature.

3:15pm **AF2-MoA-8 Study of the Surface Species During Thermal and Plasma-Enhanced Atomic Layer Deposition of Titanium Oxide Films using In-situ IR-Spectroscopy and Iin Vacuo X-ray Photoelectron Spectroscopy**, ***Sofie Vandenbroucke,*** Ghent University - IMEC, Belgium; *E Levrau, M Minjauw, M Van Daele,* Ghent University, Belgium; *E Solano,* Ghent University, Belgium, Spain; *R Vos,* IMEC, Belgium; *J Dendooven, C Detavernier,* Ghent University, Belgium

Understanding ALD reaction mechanisms is key to optimize the quality of thin metal oxide films for various applications. One class of precursors that are of particular interest for the deposition of metal oxide films are the alkylamine precursors. They are liquid at room temperature, have a relatively high vapor pressure, are easily oxidized and do not contain halogen atoms. However, they can leave C, N and H impurities in the film due to the low thermal stability of the ligands.

In situ Fourier Transform Infrared Spectroscopy (FTIR) is often used to study the surface species present during each ALD half-cycle. However, peak identification can be inconclusive and no quantification based on relative peak intensities is possible. The use of a complementary technique such as in vacuo X-ray Photoelectron Sprectroscopy (XPS) might tackle this problem. Peak identification by XPS is more unambiguous and the technique is known for the quantification of chemical groups, but compared to FTIR the detection limit is higher and the sensitivity to low abundant surface groups thus lower. This unique combination of surface techniques is very powerful and relevant for studying surface reactions and surface treatments in general.

In this work, in situ FTIR and in vacuo XPS are used as complementary techniques to gain more insight in the ALD growth of TiO_2 from the alkylamine precursor tetrakis(dimethylamino)titanium (TDMAT) in combination with water vapor, water plasma or oxygen plasma. For the thermal process using water vapor, a typical ligand exchange reaction mechanism was observed. For the plasma enhanced ALD processes a decomposition and combustion reaction could be detected as a secondary reaction mechanism. Surface species such as imines (N=C) and isocyanate (N=C=O) were observed by in situ FTIR for both plasma processes (Figure 1). In addition, nitrites (NOx) could be distinguished during the oxygen plasma process using in vacuo XPS (Figure 2). A schematic overview of all surface species present during ALD growth can be seen in Figure 3.

The resulting films of the thermal process were found to contain a higher amount of C and N impurities compared to the plasma enhanced processes, despite the presence of a secondary decomposition and combustion reaction for the latter. For the water vapor process 2 % of N and 7 % of C impurities were observed with in vacuo XPS, while the films produced with the water plasma process showed only 2 % of N and 3 % of C impurities. Remarkably, only 1% of N and no C impurities were found for the oxygen plasma process.

ALD Fundamentals
Room Jan & Hubert Van Eyck - Session AF3-MoA
ALD Growth and Surface Chemistry

Moderators: Christian Dussarat, Air Liquide Laboratories, Simon D. Elliott, Schrödinger

4:00pm **AF3-MoA-11 As Deposited Epitaxial Functional Complex Oxides - Enabling Novel Technology**, ***Henrik H. Sønsteby,*** University of Oslo, Norway **INVITED**

Low temperature direct epitaxy of functional complex oxides is attracting increased attention in novel device integration. Traditional techniques for depositing epitaxial films of complex oxides with sharp interfaces and high structural integrity, such as MBE and PLD, require high vacuum and high temperature. In addition, upscaling for device manufacturing is not straightforward due to limitations in deposition area. Techniques like CVD and sputtering are also employed, but the resulting films are often in need of post-deposition annealing to facilitate solid phase epitaxy.

This has usually also been considered true for ALD, however recent development has led to ALD emerging as a viable technique for epitaxy of a range of complex oxides at low temperatures. Careful selection of precursors, deposition conditions, substrates and pulsing recipes are key to enabling direct epitaxy.

In this talk, I will use complex nickelates and ferrites as examples to emphasize how ALD can solve key issues in complex oxide device fabrication. I will discuss strategies for direct epitaxy via ALD, and show how the resulting films have functionality that can compete with films deposited by more traditional physical techniques. Some surprising features related to epitaxial quality with respect to pulsing recipes will be discussed. I will show results on possibilities of doping such materials to enhance functionality, and how this affects epitaxy. Examples of extremely sharp as deposited interfaces will be used as highlights on what ALD can achieve in the world of complex oxides.

Finally, I will propose architectures for all-ALD complex oxide electronic devices that may offer fundamentally different behavior as compared to traditional silicon technology (that is currently close to reaching inherent physical limitations). This will highlight how ALD can enable new technology under deposition conditions that are viable for monolithic device integration.

4:45pm **AF3-MoA-14 RT Atomic Layer Deposition of Aluminum Silicate and its Application to Ion Sorption Surfaces**, *Y Mori, T Saito, K Saito, K Yoshida, M Miura, K Kanomata, B Ahmmad, S Kubota,* ***Fumihiko Hirose,*** Yamagata University, Japan

Aluminum-silicate is a main material of zeolite minerals, used as an ion sorption surface in the field of water purification. In the zeolite minerals, Al atoms are negatively charged in the aluminum-silicate framework, which causes the ion sorption in the mineral in an aqueous solution. In our laboratory, we have been developing the RT atomic layer deposition of aluminum silicate to offer the ion sensing function in flexible electronics. Conventionally, the plasm enhanced aluminum silicate ALD was reported where the minimum growth temperature was 150˚C. In this study, we designed the RT ALD with a successive adsorption process of tris [dimethylamino] silane (TDMAS) and trimethylaluminum (TMA) using an oxidizer of plasma excited humidified Ar.

N-type Si (100) samples and PEN films were used as substrates. Before the ALD process, all the samples were treated with plasma excited humidified argon for a prolonged time to remove the surface contaminants from the air. In the precursor adsorption step, TDMAS was first introduced to the sample surface with an exposure of 2×10^5 L Then TMA was introduced to the TDMAS saturated oxide surface with exposures ranging from 4×10^3 to 1×10^5 L. After the TMA exposure, the chamber was evacuated for 70 s to remove the residual gas there. In the oxidizing step, the plasma excited humidified argon was introduced to the chamber for 300 s. After the oxidizing step, the chamber was evacuated for 30 s.

Fig. 1 shows the XPS narrow scan spectra of Al 2p and Si 2p obtained from the RT deposited aluminum silicate on Si substrate. The Si to Al atomic ratio in the deposited film was estimated as 1.01. Fig.2 indicates that the aluminum silicate dipped in a NaCl solution absorb Na ion from the solution and the adsorbed Na is exchanged with K in a KCl solution. This suggests that the RT deposited aluminum silicate works like the conventional zeolite mineral. In the conference, we shall discuss the growth mechanism of aluminum silicate and ion sorption mechanisms.

5:00pm **AF3-MoA-15 Nucleation and Growth of Thermal ALD Au Films - Towards Coalescence of Ultrathin Films**, ***Virginia Wheeler,*** *B Greenberg, N Nepal, J Avila, B Feigelson,* U.S. Naval Research Laboratory

Gold (Au) is the metal of choice in many electronic and optoelectronic applications due the beneficial combination of high electrical and thermal conductivity with excellent resistance to corrosion. For this reason, significant efforts have been made to develop ALD Au precursors, resulting in two possible options - $Me_3Au(PMe_3)$ and $Me_2Au(S_2CNEt_2)$[1,2]. The latter is particularly interesting due to its ability to thermally deposit films with near bulk resistivities[2]. However, to obtain fully coalesced films required relatively thick (>20nm) and thus limits their use as transparent metal films in applications such as neutral beam splitters, transparent electrodes, and thermal insulating and solar control coatings. In this work, we focus on understanding the nucleation and growth mechanisms of thermal ALD Au films and the influence of substrate and deposition parameters on the ability to reduce the thickness at which fully coalesced films can be attained.

ALD Au films were deposited in a Veeco Savannah 200 reactor using $Me_2Au(S_2CNEt_2)$ and ozone at temperatures (T_g) from 125-200° C. The Au precursor was held at 110° C and delivered using a vapor boosted process. Initial films were deposited on a variety of substrates with different chemical inertness, wettability, and roughness including sapphire, Si, ALD TiN, Au, and others. SEM images reveal that growth proceeds similar to other CVD Au processes on all substrates with nucleation and growth of individual islands, which then form elongated structures that lead to percolation and eventual coalesced films. This type of growth makes it difficult to define thickness with traditional methods such as ellipsometry. Thus, we use a combination of XRR, ellipsometry, and XPS to evaluate the films and define ALD windows. For instance, at 200 cycles, film thickness constant at ~24 nm from 150-200° C but the density and total coverage increases with temperature.

Initial results at 150° C also show that the percolation threshold (t_c) is dependent on substrate with t_c on Au < sapphire < Si < ALD TiN, suggesting that thinner films can be obtained on more inert surfaces. Thick films (50-60nm) show resistivities of 3-4.8 μΩ cm depending on substrate and pinhole density. At low T_g here, the kinetic freezing model can be used to describe the crossover from island growth to coalescence[3]. This suggests that t_c is influenced by growth temperature, surface diffusion constant, and surface energy. We will discuss our approach to decouple these aspects and their resulting effect on reducing t_c.

[1] Griffiths, et al. *Chem. Mat.* 2016, 28, 44-46

[2] Makela, et al. *Chem Mat.* 2017, 29, 6130-6136

[3] Jeffers, et al. *JAP* 1994, 75, 5016-5020

5:15pm **AF3-MoA-16 ABC-Type Pulsing for Improved ALD of Group 13 Nitrides using Trialkyl Metal Precursors***, **Henrik Pedersen**, P Rouf, P Deminskyi,* Linköping University, Sweden*; T Törndahl,* Uppsala University, Sweden*; L Ojamäe,* Linköping University, Sweden

The group 13 nitrides (13-Ns) are essential electronic device materials for present and future technologies. Deposition of AlN and GaN are well explored by CVD at high temperatures (800-1000 °C). This aids epitaxial growth and ligand removal, rendering high crystalline quality films with low impurity levels. As 13-N CVD almost exclusively uses the trimethyl complexes of the group 13 metals, carbon is the major unwanted impurity with concentrations in the 10^{17} cm^{-3} range by SIMS.

ALD is less explored for the 13-Ns but could potentially open routes to low deposition temperatures and allow topographically more advanced 13-N structures. However, the low deposition temperatures used in ALD compared to CVD hampers the removal of ligands from the surface leading to an increase in impurity levels, mainly carbon, to the several atomic percentage levels.

We explore the possibility to improve ALD of 13-Ns with the standard trialkyl metal precursors by developing the time-resolved precursor supply further by adding an additional pulse between the metal and nitrogen precursor pulses to an ABC-type pulsing ALD. The role of the additional B-pulse is to aid the ligand removal from the surface and thereby reduce the impurity levels in the film that additionally allows higher degree of 13-N atoms rearrangement leading to higher film crystallinity.

ABC-type pulsing allowed thermal ALD of AlN from $AlMe_3$ and NH_3 at 480 °C, which is 150 °C above the decomposition temperature for $AlMe_3$. A B-pulse of H_2, N_2 or Ar between the $AlMe_3$ and NH_3 pulses was shown by XPS measurements to reduce the carbon content in AlN from about 3 at. % to below the 1 at. % detection limit of C by XPS. We show by mass spectrometry combined with kinetic- and quantum chemical modeling that the B-pulse lowers the carbon content by enhancing desorption and preventing re-adsorption of methyl ligands from the surface. The surface methyl groups desorb as CH_3, CH_4 and C_2H_x. Addition of a B-pulse also increases the crystallinity of the AlN, as seen from the GIXRD peak intensity.

ABC-type pulsing also aided to improve the deposition of GaN with plasma ALD from $GaEt_3$ and NH_3 plasma. B-pulses of H_2 gas, Ar plasma and H_2 plasma where explored and all found to increase the growth per cycle compared to AB-pulsing ALD. The highest increase was found for H_2 plasma. We speculate that the growth per cycle increase can be explained by enhanced surface chemical mechanisms for removal of the relatively bulky ethyl groups from the surface where Ar-plasma enhanced the β-elimination of ethyl groups, H_2 allows for elimination as ethane and H_2 plasma allows both mechanisms.

5:30pm **AF3-MoA-17 Atomic Layer Deposition of Metal Thin Film using Discrete Feeding Method (DFM) and Electric Field/Potential Assisted-Atomic Layer Deposition (EA-ALD)***, **Ji Won Han**, T Park,* Hanyang University, Republic of Korea*; H Jin,* SK Hynix Inc, Republic of Korea*; Y Kim,* Hanyang University, Republic of Korea

Ruthenium (Ru) has been considered as a promising electrode material for next generation semiconductor devices due to its low resistivity (~ 7 μΩ·cm), high oxidation resistance, and its conductive oxide phase, RuO2 (~ 30 μΩ·cm). As a complicated 3-dimensional integration scheme has been developed recently to improve the degree of device integration, ultrathin (< 5 nm) and uniform Ru metal electrode is required. Even though atomic layer deposition (ALD) of Ru film was employed, it is difficult to achieve ultrathin and continuous film due to island growth at the initial stage of growth. Therefore, we proposed advanced ALD processes, discrete feeding method (DFM) and electric field/potential assisted ALD (EA-ALD).

DFM is composed of subdivided precursor feeding and purge which enables instant removal of physisorbed precursor molecules screening functional group on substrate, hence chemical adsorption efficiency and surface coverage can be improved. EA-ALD also improves chemical adsorption and surface coverage by applying bias voltage on substrate during precursor/reactant injection. Electric field formed across ALD reactor increases impingement of precursor and modulated surface potential changes activation energy of ALD reaction on surface. Nucleation at initial stage of deposition improved by advanced ALD method and thus critical thickness for coalescence of Ru islands is reduced. Microstructure, density and resistivity of Ru film are improved consequently. While physical properties are improved, chemical composition and binding state of Ru were also changed, resulting change in effective work function of Ru film.

Atomic Layer Etching
Room Baekeland - Session ALE1-MoA

ALE of Metals and Alloys

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), Alfredo Mameli, TNO/Holst Center

1:30pm **ALE1-MoA-1 Mechanistic Insights into Thermal Dry Atomic Layer Etching of Metals and Alloys***, **Andrew Teplyakov**,* University of Delaware **INVITED**

The mechanisms of thermally induced reactions of atomic layer deposition (ALD) and atomic layer etching (ALE) can be in sometimes viewed as proceeding in opposite directions. However, for atomic layer processing of metals, that would mean that the best designed and most efficient reaction pathways leading to metal deposition would produce insurmountable energy barriers for a reverse process to occur spontaneously. If ligand detachment, exchange, and decomposition could be desirable for ALD, the etching of the same metals would require careful consideration of the etching mechanisms at the atomic and molecular level. Given that the mechanisms of ALE can be very complex, the key concepts and approaches will be described here for thermal dry etching processing and for distinguishing thermodynamic and kinetic regimes of etching. The mechanistic investigation of thermal dry etching of cobalt, iron, and CoFeB alloy will be the primary target of this work. The effects of surface oxidation and chlorination will be explored as a means to kinetically control the process, and preferential etching of one of the components of the alloy will be considered. Finally, a number of potential effects of the mechanisms of dry etching on the morphology of the surfaces produced and, specifically, on the “smoothing” effect of dry etching will be discussed.

2:00pm **ALE1-MoA-3 Thermal Atomic Layer Etching of Nickel Using SO_2Cl_2 and $P(CH_3)_3$***, **Jessica Murdzek**, S George,* University of Colorado - Boulder

Thermal atomic layer etching (ALE) is defined by sequential surface modification and volatile release reactions. Thermal metal ALE 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 ALE is developed by first changing the Ni oxidation state by chlorination using SO_2Cl_2. Subsequently, the Ni is etched by the binding of $P(CH_3)_3$ (PMe_3) ligands that can volatilize the nickel chloride.

The logic of this approach is based on the Covalent Bond Classification (CBC) method. The key is forming metal complexes that obey the “18 electron rule” or “16 electron rule”. X ligands are one-electron donors like Cl. L ligands are two-electron donors like PMe_3. According to the CBC method, Ni has 10 d-electrons and Ni complexes typically have NiX_2L_3 or NiX_2L_2 configurations to obey the “18 electron rule” or “16 electron rule”. The goal for Ni ALE is then to create volatile nickel compounds that are either NiX_2L_3 or NiX_2L_2 formed by sequential SO_2Cl_2 and PMe_3 surface reactions. The proposed surface chemistry for Ni ALE (Figure 1) assumes SO_2Cl_2 exposure leads to $NiCl_2$ on the Ni substrate. Then the $NiCl_2$ is volatilized by binding with PMe_3 to form either $NiCl_2(PMe_3)_3$ or $NiCl_2(PMe_3)_2$.

To demonstrate this approach, Ni ALE was studied using in situ quartz crystal microbalance (QCM) and ex situ X-ray reflectivity (XRR) measurements. The in situ QCM measurements at 200 °C revealed pronounced mass increases during chlorination with SO_2Cl_2 exposures and mass decreases during volatilization with PMe_3 exposures. The ex situ XRR measurements monitored the linear reduction in Ni thickness versus number of Ni ALE cycles. Ni etch rates were temperature dependent and varied from 0.39 Å/cycle at 125 °C to 2.16 Å/cycle at 200 °C (Figure 2). The nickel substrate was also examined versus number of Ni ALE cycles using scanning electron microscopy (SEM). The SEM images were homogeneous during the initial etching. However, there was evidence for surface pitting after 60-100 Ni ALE cycles at 150 °C.

2:30pm **ALE1-MoA-5 Thermal-Plasma ALE on Selected Metals for EUV and Integration Processes***, **Xia (Gary) Sang**, E Chen, J Chang,* University of California Los Angeles

Nanometer-level metal patterning is receiving increasing amount of attention as they find application in back-end of line (BOEL) integration and as mask materials in Extreme Ultra-Violet (EUV) lithography. These metals are often etch-resistant, thus an effective chemical etching process needs to be developed with atomic-scale level of controllability, including uniformity and selectivity. In this talk, atomic layer etching (ALE) of Cu and Ni, for their intended application in BOEL and EUV are presented.

The unique aspect of this ALE process is the combined effect of directional chemical ions and isotropic reactive neutrals. Specifically, ALE of Ni and Cu thin film is realized using sequential surface modification by directional plasma oxidation and removal of the modified surface layer by isotropic gas phase formic acid exposure. Both blanket and patterned samples were studied using this reaction scheme. A etch rate of 3 to 5 nm/cycle is determined from the blanket samples, and final features with sidewall angle of 87 is obtained on patterned samples. The effectiveness of the approach is chemically confirmed by the measuring the increase and decrease of the signals of metal oxide peaks using XPS. Etched thickness and final feature geometry are determined by SEM and TEM.

With proper chemistries and experimental conditions, this thermal-plasma ALE is capable of delivering highly selective and anisotropic patterning of metals by creating the chemical contrast and its directionality by a reactive ion while removing the modified layer entirely with an isotropic chemical processes. Applications such as next-generation logic and spintronic memory devices could benefit greatly from this patterning approach. It is expected that the approach is generalizable to a broader selection of metals.

2:45pm **ALE1-MoA-6 Thermal-Cyclic Atomic Layer Etching of Cobalt via Organometallic Complex***, **Sumiko Fujisaki**, Y Yamaguchi, H Kobayashi, K Shinoda, M Yamada, H Hamamura,* Hitachi, Japan*; M Izawa,* Hitachi High-Technologies, Japan **INVITED**

Isotropic atomic-layer etching (ALE), which produces atomically precise removal, will have an important role in semiconductor manufacturing. This is because highly selective ALE has become necessary to deal with processing of new materials in minitualized 3D devices. In the past several years, isotropic ALE of various materials has been reported which includes thermal ALE for metal oxides and thermal-cyclic ALE for nitride films [1]. To meet the requirements concertning the variety of materials to be etched, isotropic ALE of cobalt must be developed. Thermal ALE of cobalt has been reported by using treatment with formic acid and ligands to produce volatile cobalt complexes [2]. Also, the authors have successfully demonstrated isotropic ALE of cobalt film with smooth etched surfaces, which is important issue in the development of ALE of cobalt [3].

Experimental apparatus used in this study is 300-mm ALE tool equipped with inductively-coupled plasma source and infrared (IR) lamps. One cycle of this thermal-cyclic ALE process is roughly divided into two steps: oxidation and organometallization. In the first step, surface of cobalt film is oxidized by oxygen plasma at low temperature. In the second step, the cobalt oxide is converted into organo-cobalt complex by diketone at high temperature. The organo-cobalt complex then desorbs from the film surface because of its higher volatility. Processing condition is optimized so that the cobalt oxide layer formed in the first step is completely removed in the second step. Thus, etched amount can be controlled by oxidation thickness of cobalt and number of cyclic repetitions. Temperature cycle is important to obtain smooth etched surface. Our ALE tool produces short processing time because it is equipped with IR lamps for rapid heating. The mechanism of the surface reaction of the cobalt ALE was examined by x-ray photoelectron spectroscopy (XPS). Several oxygen 1s peaks were detected in the range from 525 to 535 eV after the first oxidation step. A peak at 530 eV decreased after the sample was exposed to diketone. This result implies that the peak at 530 eV, which is ascribed to a certain oxidation state of cobalt, dominantly contributes to formation and desorption of diketone-cobalt complex.

[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-TuM8 (2019).

Atomic Layer Etching
Room Baekeland - Session ALE2-MoA
ALE of Metal Oxides

Moderators: Venkateswara Pallem, AirLiquide, Ishii Yohei, Hitachi High Technologies

4:15pm **ALE2-MoA-12 Ab Initio Study on the Surface Reactions of Thermal Atomic Layer Etching of Al_2O_3***, **Xiao Hu**,* Chemnitz University of Technology, Germany*; J Schuster, S Schulz,* Fraunhofer Institute for Electronic Nano Systems, Germany

Thermal ALE is a novel approach for the isotropic etching of materials with atomic-level precision [1]. This technology will be important for the fabrication of advanced semiconductor devices, such as GAAFET and 3D NAND-Flash. The goal of this work was to understand the chemical mechanisms of thermal ALE using ab initio calculations. We chose Al_2O_3 ALE using HF and $Al(CH_3)_3$ as the case study. In the first half-cycle of Al_2O_3 ALE, it has been known that the fluorine precursor HF reacts with the Al_2O_3 surface to form an intermediate AlF_3 layer and H_2O molecules [1, 2]. The present work specifically focused on the second half-cycle reaction, where the metal precursor $Al(CH_3)_3$ etches the intermediate AlF_3 layer releasing volatile by-products.

Ab initio thermodynamic calculations were performed to predict the preferred etch products. Several possible Al-monomers and -dimers have been considered as the gaseous products. The calculation results show that the Al-dimers are more stable than their corresponding monomers. The most favorable etch product is the $Al_2F_2(CH_3)_4$ dimer, where two F atoms bridge the adjacent Al centers.

The surface reactions between the AlF_3 surface and $Al(CH_3)_3$ were investigated using dispersion-corrected density functional theory (DFT-D). The etch of the pristine surface by $Al(CH_3)_3$ is unfavorable due to a large reaction barrier (> 3 eV). Stability of the AlF_3 surface can be reduced by surface modification where some surface F atoms are replaced by the CH_3 groups of $Al(CH_3)_3$. This step is accomplished by a ligand-exchange reaction, as shown in Fig.1. The transition state calculated by DFT agrees well with that proposed by George et al [1].

The subsequent etch of the modified surface proceeds via two possible pathways: (1) direct etching by $Al(CH_3)_3$ with formation of Al-dimers; and (2) desorption of etch products caused by surface reconstruction. In both cases, the etch kinetics is mainly determined by the number of surface CH_3 groups. The surface CH_3 has two positive roles in etch reactions. First, the strength of the $Al-CH_3$ bond is much weaker than that of the $Al-F$ bond. Second, the F atom in AlF_3 has a coordination number of two, whereas the CH_3 group typically favors a coordination number of one. Therefore, some chemical bonds of AlF_3 have been broken after surface modification.

Lastly, based on a detailed understanding of the reaction mechanisms, we have discussed the strategies for the design and screening of reactive precursors for thermal ALE.

[1] George, S.M. and Lee, Y. ACS Nano, 2016, 10(5), 4889-4894. [2] Natarajan, S.K. and Elliott, S.D. Chem. Mater., 2018, 30(17), 5912-5922.

4:30pm **ALE2-MoA-13 Volatile Products from Thermal Atomic Layer Etching Observed using Mass Spectrometer with Line-of-Sight Detection***, **Andrew Cavanagh**, A Lii-Rosales, S George,* University of Colorado - Boulder

Identification of gas products from thermal atomic layer etching (ALE) is critical to understand the underlying surface chemistry. Previous quadrupole mass spectrometry (QMS) experiments identified the etch products from Al_2O_3 ALE using HF and trimethylaluminum (TMA) as the reactants [1]. These experiments sampled gas products with no line-of-sight between the substrate surface and the QMS ionizer. These QMS experiments observed dimers of the etch product, dimethylaluminum fluoride (DMAF), with itself (DMAF + DMAF) or with TMA (DMAF + TMA) [1].

For higher sensitivity and no wall-effects, a new apparatus (Figure 1) was built to provide line-of-sight between the substrate and the QMS ionizer. In this apparatus, a small reactor containing a powder sample is positioned in a larger vacuum chamber. The etch products emerge from an aperture in the reactor and are supersonically expanded into a lower vacuum region. The etch products then pass through a skimmer into the even lower pressure region containing the QMS ionizer. With this arrangement, the reactor can be maintained at ~1 Torr. The etch products can also have line-of-sight to the QMS ionizer with the ionization region at ~10^{-8} Torr.

Using this new apparatus, the ligand-exchange reaction of DMAC with AlF_3 was examined to study thermal Al_2O_3 ALE using HF and DMAC as the reactants [2]. Various monomer and dimer species were observed versus temperature (Figure 2). DMAC dimers and DMAC dimers that have undergone Cl/F exchange with AlF_3 are detected at lower temperatures. The main etch product, $AlCl_2(CH_3)$, is observed with increasing intensity at higher temperatures >230 °C. The ligand-exchange reaction of $SiCl_4$ with ZrF_4 was also examined to study thermal ZrO_2 ALE using HF and $SiCl_4$ as the reactants [3]. SiF_xCl_y species are observed from the halogen ligand-exchange reaction at >240 °C (Figure 3). $ZrCl_4$ is observed as the main Zr-containing etch product at >240 °C. $ZrFCl_3$ is detected as an additional product at higher temperatures >320 °C.

[1] J.W. Clancey, A.S. Cavanagh, J.E.T. Smith, S. Sharma and S.M. George, "Volatile Etch Species Produced During Thermal Al_2O_3 Atomic Layer Etching", *J. Phys. Chem. C* **124**, 287 (2020).

[2] Y. Lee and S.M. George, "Thermal Atomic Layer Etching of Al_2O_3, HfO_2, and ZrO_2 Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures", *J. Phys. Chem. C***123**, 18455 (2019).

[3] Y. Lee, C. Huffman and S.M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem. Mater.***28**, 7657 (2016).

5:00pm **ALE2-MoA-15 Blocking Thermal Atomic Layer Etching with Removable Etch Stop Layers**, ***David Zywotko,*** University of Colorado - Boulder*; O Zandi, J Faguet, P Abel,* TEL Technology Center, America, LLC*; S George,* University of Colorado - Boulder

Thermal atomic layer etching (ALE) can be performed using sequential fluorination and ligand-exchange reactions. For example, thermal Al_2O_3 ALE can be achieved using HF for fluorination and $Al(CH_3)_3$ (trimethylaluminum (TMA)) as the metal precursor for ligand-exchange [1]. Sequential exposures of HF and TMA lead to Al_2O_3 etch rates of 0.47 Å/cycle at 285°C. The ability to block thermal ALE selectively will be useful for advanced nanofabrication. This study demonstrates how thermal Al_2O_3 ALE can be blocked with removable ZrF_4 etch stop layers. In situ quartz crystal microbalance (QCM) measurements were utilized to monitor the etching and the effect of the etch stop layers.

The ZrF_4 etch stop layers could be deposited on Al_2O_3 using tetrakis(ethylmethylamido) zirconium and H_2O at 285°C. These reactants deposit ZrO_2 layers that are then converted to ZrF_4 during the subsequent HF exposure. Because $Al(CH_3)_3$ does not undergo ligand-exchange with ZrF_4 [2], the ZrF_4 layer serves as an etch stop layer. QCM measurements revealed that an initial ZrO_2 thickness of just one monolayer prior to fluorination was able to completely inhibit thermal Al_2O_3 ALE. Prior to reaching a ZrO_2 thickness of one monolayer, the etching inhibition was proportional to the ZrO_2 fractional coverage. The ZrF_4 etch stop layer was observed to arrest the thermal Al_2O_3 ALE for >100 ALE cycles.

The ZrF_4 etch stop layer could then be easily removed by a ligand-exchange reaction with $AlCl(CH_3)_2$ (dimethylaluminum chloride (DMAC)) [3]. The ZrF_4 etch stop layer could be applied and removed repeatedly without changing the Al_2O_3 etch rate. X-ray photoelectron spectroscopy (XPS) studies observed no trace of Zr on the Al_2O_3 surface after 7 cycles of DMAC and HF sequential exposures. Area selective deposition of the ZrF_4 etch stop would lead to area selective etching using HF and TMA as the reactants. Area selective deposition could be achieved based on selective reactant adsorption or substrate-dependent nucleation delays.

[1] Younghee Lee, Jaime W. DuMont and Steven M. George, "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994 (2016).

[2] Younghee Lee, Craig Huffman and Steven M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem. Mater.***28**, 7657 (2016).

[3] Younghee Lee and Steven M. George, " Thermal Atomic Layer Etching of Al_2O_3, HfO_2, and ZrO_2 Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures", *J. Phys. Chem. C***123**, 18455 (2019).

5:15pm **ALE2-MoA-16 Mechanism of the HF Pulse in the Thermal Atomic Layer Etch of HfO_2 and ZrO_2: A First Principles Study**, ***Rita Mullins,*** Tyndall National Institute, Ireland*; S Natarajan,* Aalto University, Finland*; S Elliott,* Schrödinger, Inc.*; M Nolan,* Tyndall National Institute, Ireland

HfO_2 and ZrO_2 are two high-k materials that are crucial in semiconductor devices. Atomic level control of material processing is required for fabrication of thin films of these materials at nanoscale device sizes. Thermal Atomic Layer Etch (ALE) of metal oxides, in which up to one monolayer of the material can be removed per cycle, can be achieved by sequential self-limiting fluorination and ligand-exchange reactions at elevated temperatures. However, to date a detailed atomistic understanding of the mechanism of thermal ALE of these technologically important oxides is lacking. In this contribution, we investigate the hydrogen fluoride pulse in the first step in the thermal ALE process of HfO_2 and ZrO_2 using first principles simulations. We also present a thermodynamic analysis approach to compare reaction models representing the self-limiting (SL) and continuous spontaneous etch (SE) processes taking place during an ALE pulse. Applying this to the first HF pulse on HfO_2 and ZrO_2 we find that thermodynamic barriers impeding continuous etch are present at ALE relevant temperatures. Explicit calculations of HF adsorption on the oxide surfaces allow us to investigate the mechanistic details of the HF pulse. A HF molecule adsorbs dissociatively on both oxides by forming metal-F and O-H bonds. HF coverages ranging from 1.0 ± 0.3 to 17.0 ± 0.3 HF/nm^2 are investigated and a mixture of molecularly and dissociatively adsorbed HF molecules is present at higher coverages. Theoretical etch rates of -0.61 ± 0.02 Å /cycle for HfO_2 and -0.57 ± 0.02 Å /cycle ZrO_2 were calculated using maximum coverages of 7.0 ± 0.3 and 6.5 ± 0.3 M-F bonds/nm^2 respectively (M = Hf, Zr).

5:30pm **ALE2-MoA-17 Thermal Atomic Layer Etching of Ta_2O_5 and TaN using BCl_3 and HF: Evidence for a Conversion-Etch Mechanism**, *N Johnson,* ***Steven M. George,*** University of Colorado - Boulder

Ta_2O_5 ALE was demonstrated using BCl_3 and HF as the reactants. The Ta_2O_5 ALE surface chemistry could proceed via a fluorination and ligand-exchange mechanism or a conversion-etch mechanism. The experimental results support a conversion-etch mechanism. BCl_3 is believed to convert the surface of Ta_2O_5 to a B_2O_3 surface layer via the favorable conversion reaction $Ta_2O_5 + 10/3\ BCl_3(g) \rightarrow 5/3\ B_2O_3 + 2TaCl_5(g)$ [ΔG°(250°C = -38 kcal]. HF can then spontaneously etch the B_2O_3 surface layer via the favorable reaction $B_2O_3 + 6HF(g) \rightarrow 2BF_3(g) + 3H_2O(g)$ [ΔG°(250°C = -17 kcal] [1]. In contrast, HF fluorination of Ta_2O_5 to TaF_5 or $TaOF_3$ is thermochemically unfavorable.

In situ spectroscopic ellipsometry and *ex situ* x-ray reflectivity measurements were employed to study Ta_2O_5 ALE. Evidence for the conversion of Ta_2O_5 to B_2O_3 was provided by the dependence of the Ta_2O_5 etch rate on BCl_3 exposure and BCl_3 pressure. The Ta_2O_5 etch rate increased progressively with both longer BCl_3 exposures and higher BCl_3 pressures. The longer BCl_3 exposures and higher BCl_3 pressures convert more Ta_2O_5 to B_2O_3. Using three BCl_3 exposures (130 mTorr for 30 s) and one HF exposure, the Ta_2O_5 etch rate was 1.05 Å/cycle at 250°C (Figure 1). Under these conditions, the Ta_2O_5 etch rates increased with temperature ranging from 0.36 Å/cycle at 200°C to 1.96 Å/cycle at 295°C. Ta_2O_5 etch rates also increased at higher BCl_3 pressure. The etch rates varied from 0.48 to 1.46 Å/cycle using one BCl_3 exposure (30 s) at BCl_3 pressures from 130 to 1000 mTorr, respectively (Figure 2).

TaN ALE was also demonstrated using an O_3 oxidation step to oxidize TaN to Ta_2O_5. The Ta_2O_5 was then etched using BCl_3 and HF as the reactants. TaN ALE was performed using supercycles defined by an O_3 exposure followed by 60 Ta_2O_5 ALE cycles using BCl_3 and HF as the reactants. The etch rate was 38 Å/supercycle at 250°C (Figure 3). This high TaN etch rate was attributed to the large Ta_2O_5 thickness produced by O_3 oxidation. The oxidation of TaN using O_3 was studied using x-ray reflectivity measurements. TaN oxidation was observed to be fairly self-limiting at Ta_2O_5 thicknesses of 60-70 Å after longer O_3 exposures at 250°C.

[1] N.R. Johnson and S.M. George, "WO_3 and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Mechanisms" *ACS Appl. Mater. Interfaces***9**, 34435 (2017).

ALD Fundamentals
Room Arteveldeforum & Pedro de Gante - Session AF-MoP

ALD Fundamentals Poster Session

AF-MoP-2 A Novel Approach to Evaluate LEIS Data of 2D SnS_2 to Quantify the First and Second Atomic Layer Coverage*, P Brüner,* IONTOF GmbH, Germany*; M Mattinen, M Ritala,* University of Helsinki, Finland*; **Thomas Grehl**,* IONTOF GmbH, Germany

With the strong interest in 2D materials in recent years, the number of requests for Low Energy Ion Scattering (LEIS) analysis of this class of films has increased. As LEIS is sensitive to the outer atomic layer of the sample, it is ideally suited to determine the composition of 2D materials. While other techniques struggle with the extremely thin layer, and the substrate usually contributes to the analytical signal even for closed films, the surface peaks in LEIS only correspond to a single atomic layer.

In addition to the composition of the outer atomic layer, the LEIS spectra also contain information about the composition of the first few nm of the sample. Close to the surface, this information has monolayer depth resolution. Since no sputtering is involved, this method does not suffer from correlated artefacts or transients and has sufficient depth resolution for 2D materials.

In this study, we analysed SnS_2 films [1] on Si and sapphire wafers. Specifically, we developed a novel approach to quantify the signal from deeper layers: By subtracting the surface peaks and fitting the remaining in-depth signal, we can quantify the coverage of the second atomic layer. In this way, the quality of the films can be judged very accurately, and for films with complex island growth additional information can be gained.

We will demonstrate both the general approach to thin film analysis using LEIS, as well as the specific method shown here for the first time. This includes the sample cleaning from atmospheric contamination by sample heating in UHV or by exposure to atomic oxygen. Island growth is studied, showing the different trends in island formation for the two different substrates: while strong multilayer growth is found for the Si substrate, growth on sapphire has a consistently higher fraction of the film with monolayer thickness.

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AF-MoP-3 The Structure and Properties of Titanium Nitride Layers Grown by Plasma Enhanced Atomic Layer Deposition on Different Substrates*, **Valentina Korchnoy**,* Technion - Israel Institute of Technology, Israel*; I Krylov,* Tower Semiconductor Ltd., Israel*; X Xu, Y Qi, K Weinfeld, M Eizenberg, D Ritter,* Technion - Israel Institute of Technology, Israel

Low resistivity TiN films are essential for most microelectronic applications. Film resistivity is determined by electron scattering from foreign atoms, grain boundaries and film surfaces, and often serves as an indication for the film quality. Substrate plays a major role during ALD of polycrystalline films. First deposition cycles determine density and orientation of the initial nuclei, which affects the entire film structure. We report the effect of various substrates on structure and properties of TiN films grown by plasma-enhanced atomic layer deposition using TDMAT as a precursor. TiN films were deposited at 300 °C using N_2, NH_3, N_2/H_2 and Ar gas mixtures, on various types of amorphous, polycrystalline and single crystalline substrates. The substrates were Si covered by thermally grown 100nm thick SiO_2 (amorphous), and covered by an additional 10 nm interfacial layers: $Al2O_3$, HfO_2, WO_3, $Ta2O_5$ (amorphous), or MoO_3, TiO_2 (polycrystalline). Resistivity of the films deposited on MoO_3 or TiO_2 was lower by a factor of about 2, for all types of plasma gas studied (Fig.1). Shape and size of TiN grains deposited on MoO_3 or TiO_2 layer are significantly different from those deposited on the SiO_2 layer (Fig.2). They consist of large (~35 nm) rectangular grains. The grains deposited on SiO_2 are V-shaped and much smaller.

Growth of TiN films on single crystalline substrates: hexagonal (sapphire) or cubic ($SrTiO_3$ and MgO) was also investigated. Resistivity of TiN films deposited on single crystalline substrates is lower than those deposited on amorphous SiO_2 layer (Fig.3). The lowest film resistivity was obtained for TiN films grown on cubic substrates: $SrTiO_3$ and MgO. Postdeposition annealing reduced the film resistivity due to the improvement of crystalline quality. The resistivity became comparable to the bulk TiN value (13 μΩ.cm). A clear peak was obtained by XRD for films grown on (111) and (001) oriented MgO substrates (Fig. 4), indicating that the deposited films consist of highly oriented grains. Grain orientation is determined by substrate.

The substrate strongly affects morphology, orientation, and resistivity of thin PEALD TiN films. Films grown on amorphous substrates exhibit the smallest grain size and the highest resistivity among all investigated substrates. Polycrystalline substrate acts as a “seed” layer for the formation of large rectangular shaped TiN grains, which contribute to low resistivity. The lowest bulk value of TiN resistivity (~20 μΩ.cm) was achieved in the TiN films, which were deposited on single crystal substrates. The preferred crystallographic orientation of the films, either (111) or (001), does not affect film resistivity.

AF-MoP-4 Novel Slenium ALD Precursors*, **Jaroslav Charvot**, D Pokorný, F Bureš, R Zazpe, J Macák,* University of Pardubice, Czech Republic

Atomic layer deposition of metal chalcogenides steadily attracts more and more attention. These compounds possess interesting properties that may be utilized in semiconducting materials, photocatalysis, hydrogen evolution etc. Nevertheless, precursor portfolio for selenium deposition is very limited. Highly toxic H_2Se or insufficiently reactive Et_2Se (Et_2Se_2) were later replaced with bis(trialkylsilyl)selenides, which proved to be sufficiently volatile, thermally stable and versatile precursor for metal selenide thin layers fabrication. This work presents cyclic silylselenides bearing one or two atoms of selenium as new ALD precursors. They possess volatility and thermal stability similar to previous bis(trialkylsilyl)selenides, however rigid nature of these cycles render them higher air stability. The syntheses of precursors will be described along with their proper analyses (GC/MS, multinuclear NMR). Thermal behaviour was studied by TGA and DSC. All three target molecules were used as Se precursors in ALD by reacting them with $MoCl_5$ to give corresponding $MoSe_2$ thin layers on different substrates.

AF-MoP-11 Atomic Layer-Deposited Superconducting Niobium Nitride for Quantum Device Applications*, E Knehr,* Institute of Micro- and Nanoelectronic Systems, Karlsruhe Institute of Technology, Germany*; **Mario Ziegler**, S Linzen,* Leibniz Institute for Photonic Technologies Jena, Germany*; A Kuzmin, K Ilin,* Institute of Micro- and Nanoelectronic Systems, Karlsruhe Institute of Technology, Germany*; R Stolz, E Ilichev, H Schmidt, M Siegel,* Leibniz Institute for Photonic Technologies Jena, Germany

Highly uniform and homogeneous superconducting thin films are of interest for applications in quantum detection and, e.g., for novel devices based on quantum phase slips. One of the most widely used materials for these purposes is niobium nitride (NbN) because of its relatively high critical temperature and short relaxation time, among others [1,2]. Conventionally, NbN films are deposited by reactive magnetron sputtering. However, atomic layer deposition (ALD) has the advantage of precise thickness control and potential deposition of thin films with high uniformity.

The development of superconducting NbN films fabricated by plasma-enhanced ALD has already been shown in [3,4]. The deposition process utilizes (tert-butylimido)-tris(diethylamino)-niobium (TBTDEN) as precursor and a hydrogen plasma to form monolayers of NbN. These ALD-grown NbN films exhibit — favorable for many applications — smaller diffusion coefficients while having similar critical temperatures compared to magnetron sputtered NbN films [5]. Furthermore, our ALD-grown films have the advantage of high kinetic inductivity and a well-defined superconductor-insulator transition (SIT) within the film thickness range of 3-4 nm due to the realized highly disordered film [4].

For future applications, uniform films showing the described properties over large areas are required. For this purpose, we investigate the homogeneity of NbN samples distributed over an area with a diameter up to eight inches during deposition. By measuring both structural (e.g. AFM, XRD) and electrical properties (e.g. T_c, j_{sw}) of these films, we examine the suitability of ALD-NbN for applications requiring uniform thin films over large areas. A small spread of these properties leads to higher yield during fabrication, especially for large area devices such as radiation detector arrays. We will discuss the achieved minimum of electrical parameter spread and corresponding maximum of applicable wafer area.

In addition, we studied the influence of the downstream reactivity of the hydrogen plasma on the NbN thin film properties by varying the distance between the IC-plasma source and the substrate surface.

As an exemplary application, we report on the detection properties of superconducting nanowire single-photon detectors (SNSPDs) made from ALD-NbN thin films.

AF-MoP-12 Carbenes Can Make a CVD Process into an ALD Process by Surface Passivation*, **Aya Kadri**, M Griffiths,* Carleton University, Canada*; J Masuda,* Saint Mary's University, Canada*; S Barry,* Carleton University, Canada

Atomic layer deposition of gold has been explored in the past but all processes to date utilize energetically enhanced coreagents.[1] In order to use milder secondary reagents (either oxidants or reductants), Au precursors need to exhibit higher thermal stability. Alkylgold(I) phosphine compounds have been explored for ALD in the literature due to their unique surface reactivity and a broad ligand selectivity. However, it has been shown that $(PMe_3)AuMe$ undergoes surface-mediated bimolecular reductive elimination to produce ethane.[1]

This study exploits the stability of surface bound carbenes to slow the reactivity of carbene adducted Au(I) alkyls (NHC-Au-R) at gold surfaces. It has been shown that N-heterocyclic carbenes (NHCs) form stronger passivating layers on an Au metal surface than do phosphines.

An *in-situ* quartz-crystal microbalance analysis showed that the precursor (1,3-dimethyl-2-imidazolidinylidene)AuMe exhibits very strong passivation. Literature suggests that isopropyl wingtip groups on the carbene allow the carbene to stand upright on the surface rather than laying flat which makes it much more difficult to remove.[2] Finally, fluorination of the Au(I)-bonded alkyl ligand should improve precursor volatility and thermal stability.

The thermal properties of (1,3-diisopropyl-2-imidazolidinylidene)$AuCF_3$ (**1F**) were studied but **1F** was found to behave poorly (1 Torr of vapour pressure at 189 C) with respect to its hydrogen-bearing counterpart (1,3-diisopropyl-2-imidazolidinylidene)$AuCH_3$ (**1**) (157 C). Further effect of fluorination on the thermal stability and volatility was explored by comparing the thermal properties of **1** and **1F** with the corresponding compound adducted with the unsaturated carbene (1,3-diisopropyl-2H-imidazol-2-ylidene)$AuCH_3$, **2**, 1 Torr vapour pressure of 141 C).

Finally, structural modifications to carbenes will be discussed, where a variety of R-substituted carbenes will be adducted to both $Au\text{-}CH_3$ and $Au\text{-}CF_3$ moieties, and their thermal properties assessed.

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AF-MoP-14 High Wet Etch Resistance SiO_2 Films Deposited by Plasma-Enhanced Atomic Layer Deposition using 1,1,1-Tris(Dimethylamino)Disilane*, **Su Min Hwang**,* University of Texas at Dallas*; H Kim, Z Qin,* The University of Texas at Dallas*; A Ravichandran,* University of Texas at Dallas*; J Lee,* The University of Texas at Dallas*; Y Jung,* University of Texas at Dallas*; S Kim,* Kangwon National University, Republic of Korea*; J Ahn,* Hanyang University, Republic of Korea*; B Hwang, L Lee, X Zhou,* DuPont*; J Kim,* University of Texas at Dallas

With the complexity in device integration such as high aspect ratio trenches and 3D structure increasing, requirements for ALD SiO_2 films have been more stringent. In particular, the selection of silicon precursors is important for low-temperature ALD SiO_x with high-film quality, e.g., higher wet-etch-resistance and free of catalysis or corrosive by-product.[1] Among the numerous Si precursors that are available, an amino-based silicon precursor is considered a good candidate. Recently, extensive researches on ALD of SiO_x thin films using various aminosilane precursors such as tris(dimethyl-amino)silane (TDMAS), di(isopropylamino)silane (DIPAS), and bis(diethylamino)silane (BDEAS) have been widely reported.[2,3] Most researches on ALD SiO_x have been based on amino-mono-silane precursors, hence a comprehensive study of ALD SiO_x using an amino-di-silane precursor with overall comparisons has been scarce.

Herein, a novel precursor, 1,1,1-tris(dimethylamino)disilane (TADS), was investigated using thermal atomic layer deposition (tALD) and plasma-enhanced atomic layer deposition (PEALD) for growth of SiO_x thin films in a temperature range of 115 – 480 °C. In both ALD processes, TADS exhibits self-limiting growth behavior as a function of precursor and oxygen exposure time. In the case of the tALD process, TADS yields a relatively lower growth rate (0.06 nm/cycle), while showing comparable film density and excellent conformality (> 95% step coverage). In the PEALD SiO_2 process, TADS demonstrates not only a higher or at least comparable growth rate but also a higher bulk film density. As a result, the PEALD SiO_2 films deposited using TADS show a lower wet etch rate of 1.6 nm/min in 200:1 HF which is comparable to the wet etch rate of thermal oxide. Analyzed with FT-IR, the SiO_2 films contain predominant Si−O bonds and a low level of Si−H and O-H bonds. The FT-IR results are consistent with the observed high wet etch resistance. Furthermore, the SiO_2 films deposited at 310°C show at least 75% step coverage in high aspect ratio nanotrenches, suggesting that TADS is applicable for conformal high-quality SiO_2 films on 3D structures.

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AF-MoP-15 Applying a Figure of Merit to Known Copper Precursors*, **Atilla Varga**, M Griffiths,* Carleton University, Canada*; J Masuda,* Saint Mary's University, Canada*; S Barry,* Carleton University, Canada

Copper metal thin films continue to dominate the manufacturing of microelectronics as interconnects for silicon integrated circuits. Copper reduces propagation delays, power consumption, and size of the interconnects in the circuits, which makes it a highly sought after metal in the field of nanotechnology.[1] Copper nitride thin films are also an area of interest for applications such as chemical sensors, photodetectors, and their optoelectronic energy conversion properties are useful as semiconductors for photovoltaic applications.[2] Finally, copper oxide thins films are used as semiconductors and have many applications in the optoelectronic industry due to their tunable band gaps and interesting properties, most notably superconductivity at relatively high temperatures.[3]

ALD has been used to deposit these copper-containing thin films, and a large variety of different precursors have been studied. There are numerous industrial and academic labs developing processes, precursors, and technologies that incorporate copper thin films. This has resulted in a wide range of ligand choice and precursor design strategies that has produced a wide variety of excellent copper precursors. Herein, the general strategies for copper precursor design, the history of copper precursors, and our analysis of precursor merit will be presented.

Our group has developed a figure of merit for ALD precursors, which incorporates the volatility and thermal stability of a precursor (Equation **1**). Using the figure of merit, a given precursor’s usefulness can be visualized and compared to other known precursors. From the copper literature body, a figure of merit will be presented. From this the variety of precursors for different types of film composition can be compared and evaluated. These precursors range from the most utilized copper (I) amidinates[4], guanidinates, and iminopyrrolidinates, as well as more recent precursors such as copper (II) imines[5] and N- heterocyclic carbenes (Figure **1**). In addition, novel copper precursors being developed by our group will also be presented.

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AF-MoP-16 Conformality in Aluminum Oxide ALD Process Analyzed using the 3rd-Generation Silicon-Based Lateral High-Aspect-Ratio Test Structures*, **Jihong Yim**,* Aalto University, Finland*; O Ylivaara,* VTT Technical Research Centre of Finland Ltd, Finland*; M Ylilammi, V Korpelainen,* VTT Technical Research Centre of Finland, Finland*; E Haimi, E Verkama,* Aalto University, Finland*; M Utriainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland

Atomic layer deposition (ALD) has an excellent inherent conformality among deposition techniques. Yet ALD’s conformality is not self-guaranteed. To experimentally analyze the conformality, various latera-high-aspect-ratio (LHAR) test structures have been developed.[1]

This work aims (i) to introduce the 3rd-generation microscopic LHAR conformality test chips, PillarHall-3, which was improved from the 1st-generation concept[2] but not yet reported in detail in a scientific publication, and (ii) to investigate the effect of experimental parameters on the conformality of alumina ALD thin films. PillarHall-3 consists of a lateral channel of 500 nm (nominal height) under a polysilicon membrane supported by silicon pillars. For the typical nominal height of 500 nm, the aspect ratio is up to 10000:1. We will present investigations on how process parameters (number of ALD cycles, Me_3Al (TMA) pulse time, and purge time) and physical dimension of test chips influence the TMA-H_2O alumina ALD process at 300°C. We have re-implemented the model of Ref. 3 in Matlab and extract the lumped sticking coefficient from experimental data in this work. We analyzed the saturation profile by spectroscopic reflectometry line scans (spot size ca. 5 µm) and the elemental profiles by SEM-EDS after removal of the top membrane. We measured the surface topography by atomic force microscope (AFM). We will report uncertainty components and their effects on conformality analysis.

For the different number of ALD cycles, the penetration depth at 50% of film thickness, $PD^{50\%}$, decreased with increasing film thickness. This is explained by the narrowing of the channel by the film and a thereby higher aspect ratio experienced by the process.[3] For increasing TMA pulse times, the overall shape of the saturation profile changed inferring the change of film growth mechanism from TMA-limited to H_2O -limited growth. For different purge time, the height of the constant thickness region and growth per cycle slightly decreased when the purge time increased, while $PD^{50\%}$ increased. The overall shape of the saturation profile remained the same.

The PillarHall-3 design presents quick means to characterize the saturation profile of ALD processes and allows one to experimentally extract a slope at $PD^{50\%}$, which is related to the fundamental kinetics of the ALD growth process.[4]

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AF-MoP-17 Growth and Characterization of Aluminum Nitride using TMA, and NH_3 by Atomic Layer Deposition*, Y Lin, C Kei, **Chan-Yuen Chang**, C Yang, C Chen,* National Applied Research Laboratories, Republic of China

Aluminum nitride (AlN) has attracted lots of attention because of its excellent chemical, electrical, and optical properties. Wurtzite AlN is a wide direct-bandgap material which is a promise material for deep-ultraviolet, 5G resonator/filter and surface acoustic wave devices. We have deposited AlN films on Si(100) substrates by home-build atomic layer deposition (ALD) using TMA and NH_3 as a nitriding agent. The thickness and refraction index were measured by ellipsometry. The composition was determined by energy-dispersive X-ray spectroscopy (EDS). The surface and cross-sectional images were analyzed by scanning electron microscopy (SEM) and transmission electron microscope (TEM), respectively. The SEM image (shown in **Figure 1**) shows that AlN film present a uniform and continuous surface. According to the cross-sectional TEM image (shown in **Figure 2**), a dense and continuous AlN film was deposited. The growth rate was about 0.97Å/cycle at 400℃. The refraction index was about 1.94 that declined from theoretical value could be attribute to the presence of oxide in the AlN/Si interface and the top of AlN film (the cross-sectional EDS data was shown in **Figure 3**).

AF-MoP-18 Thermal SiN_x Using NH_3 and Anhydrous Hydrazine as Nitriding Agents*, S Hwang, **Dan Le**, A Ravichandran, A Kondusamy,* University of Texas at Dallas*; D Alvarez, J Spiegelman,* RASIRC*; J Kim,* University of Texas at Dallas

Silicon nitride (SiN_x) is perceived as a quintessential component in microelectronics for scaling next generation ultra-large-scale integration (ULSI) technology with possible applications as a passivation layer, sidewall spacer, and contact etch stop liner.[1] Deposition of ultrathin and uniform SiN_x films with high conformality is required for ULSI due to application restrictions, such as thickness and complicated surface areas.[2] In general, the plasma-enhanced ALD (PEALD) process allows a low temperature process for such film deposition, but potentially results in poor conformality, creates surface damage, and is not applicable on sensitive substrates. The thermal ALD (tALD) process can overcome these issues; however, it requires a higher deposition temperature range for SiN_x films.[1] In this study, we focus on establishing a high quality SiN_x tALD deposition process at relatively low temperatures (350 °C – 650 °C) for ammonia (NH_3) and evaluate the properties of films deposited using hydrazine. Furthermore, films grown by hydrazine will be compared to films grown with ammonia with the same process conditions, silicon precursor, and temperature range.

In this experiment, hexachlorodisilane (HCDS) is used as the source of silicon, along with BRUTE hydrazine and ammonia as the precursors for nitrogen. A PEALD/ tALD chamber (Rocky Mountain Vacuum Tech Inc.) is employed to deposit SiN_x films with a working pressure between 150 – 160 mTorr. Furthermore, to eliminate the possibility of condensation of precursor or residual products, the chamber walls and precursor delivery lines are heated to 120 °C and 100 °C, respectively. The experimental temperature range is established from 350 °C to 650 °C. At the temperature range of 450 °C – 550 °C, the index of refraction (R.I.) of SiN_x films deposited using hydrazine is up to 2.0, which further coincides with the earlier reported result, with a R.I. as high as 2.1.[2] Additionally, the atomic force microscopy (AFM) indicates that films grown with hydrazine have a smooth surface, with an RMS as low as 0.14 nm. It is further determined that the SiN_x films roughness is independent of temperature. Moreover, the GPC of SiN_x films deposited using ammonia is less than half of the GPC of films grown with hydrazine at a temperature range of 500 °C – 550 °C. The experiment details and detailed results will be presented.

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AF-MoP-19 Observation of Transient Response of Langasite Crystal Microbalance (LCM) at High Temperature*, **Masafumi Kumano,*** Tohoku University, Japan*; K Hikichi,* Technofine Co. Ltd, Japan*; M Omote,* XMAT Corporation, Japan*; Y Ohashi, A Yoshikawa, S Tanaka,* Tohoku University, Japan

Langasite $Ca_3TaGa_3Si_2O_{14}$ (CTGS) is a new candidate for a high temperature microbalance measurement1). It keeps piezoelectricity in a high temperature range even close to its melting point without any phase transition, and a large crystal can be potentially grown in an industrial scale. Therefore, CTGS is a promising material for a microbalance in ALD tools working at high temperature.

The turnover temperature (T_0) of the temperature coefficient of frequency (TCF) of CTGS can be adjusted by the cut angle, and the 2nd order TCF is -0.046 ppm/ºC^2 at 395ºC. The TCF is comparative to that of BT-cut quartz, but thermal transient signal comparable with a mass loading signal generates, when a pulsed gas flow at high temperature gives relatively large non-stational thermal perturbation to the crystal surface. To find a reliable signal pattern during ALD process, the detail of the transient frequency response must be examined.

Fig. 1 shows a frequency to temperature model diagram of CTGS with and without mass loading (Δm) on the crystal. A CTGS langasite crystal microbalance (LCM) has the resonance frequency maxima (a_0 and a_1) at T_0. In an ALD or ALD-like cycle of TMA/H_2O, surface molecular reaction is very fast, and a mass gain Δm in each cycle, 45 ng/cm^2 for monoatomic layer TMA2), is so small that the thermal effect can be neglected. Under this assumption, a relatively slow transient response of the LCM may be thermal perturbation through gas molecular heat transfer or radiation heat equilibrium.

In this study, the LCM transient response was observed in three cases; (T_0, T)=(323ºC, 327ºC) in case 1, (448ºC, 440ºC) in case 2 and (365ºC, 372ºC) in case 3, where T is reactor temperature. The thermal decomposition temperature of TMA is 323ºC, and ALD cycle was applied only in case 1, while TMA thermally decomposed in cases 2 and 3. Multi-point temperatures around the crystal were controlled within 0.1ºC, which is necessary to stabilize the LCM response for this purpose. As shown in Fig. 2, local heating or cooling occurred on the crystal in each case as expected from Fig. 1. At a larger time scale, the LCM frequency envelope gave a straight line of 1.9 Hz/cycle in ALD at 323ºC, as shown in in Fig. 3.

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AF-MoP-20 Atomic Layer Deposition of Niobium Nitride Thin Film with $NbCl_5$ and NH_3, ***Moo-Sung Kim**, S Lee,* Merck Performance Materials Ltd. Korea, Republic of Korea*; S Ivanov,* Versum Materials, Inc

Due to some problems of Cu metal interconnect such as Cu diffusion into Si substrate and poor adhesion on SiO_2 substrate, the role of diffusion barrier materials is very important in nano scale process. Accordingly, the transition metal nitride such as TiN_x, TaN_x, MoN_x, WN_x and NbN_x have been widely studied to solve these problems. Among them, NbN_x is one of promising materials because of chemical insensitivity, good thermal stability and mechanical characteristics. Another important point for diffusion barrier is whether it can be conformally deposited on deep trench pattern. ALD method can make a uniform film at a relatively low temperature through self-limiting reaction, even at a trench or hole pattern where the aspect ratio is high.

In this study, we have performed the atomic layer deposition of NbN_x thin film with $NbCl_5$ and NH_3 at deposition temperature from 300 to 500°C. ALD saturation characteristics, ALD window and linearity of NbN_x were investigated on various substrates such as Si, SiO_2, Al_2O_3 and TiN. The thickness and resistivity were measured with XRF and 4-point probe, respectively. To confirm a chemical composition of NbNx film, RBS and SIMS were analyzed. The films have also been characterized with XRD and XRR for crystallinity and film density, respectively. The step coverage was identified with deep trench pattern of high aspect ratio (A/R = 15 ~ 18) by TEM.

The ALD window of NbN_x film was observed from 400 to 450°C. The resistivity of NbN_x film decreased gradually as the deposition temperature increases. It was ~ 1,900 µohm-cm at 350°C whereas at 500°C, it was only ~ 700 µohm-cm. The chemical composition was formed Nb_4N_5 at all conditions on Si substrate. Interestingly, Nb:N= 1:1 composition was shown on SiO_2 substrate. The Cl impurities decreased from ~7 to 0 at % as the deposition temperature increases from 350 to 500°C. Clear NbN peaks were observed in XRD analysis. These main peaks were well matched with c-Nb_4N_5 reference, and with SIMS and RBS data. The film density was increased from 6.63, 7.16, and 7.31, at 350, 450 and 500°C, respectively. The step coverage became worse slightly as the temperature increased, and 10Torr chamber pressure showed better step coverage than 20 and 30Torr. More than 95% step coverages at middle and bottom were achieved in deep trench pattern with A/R of 17.

AF-MoP-21 Atomic Layer Deposition of Vanadium Oxides using Vanadyl Acetylacetonate as Precursor, *P Juan,* Ming Chi University of Technology, Republic of China*; **Wen-Hao Cho**,* National Applied Research Laboratories, Republic of China*; C Kuo,* National Central University, Republic of China*; G Li,* Ming Chi University of Technology, Republic of China*; C Chen, C Yang, C Kei,* National Applied Research Laboratories, Republic of China

Among the vanadium oxides, VO_2 has attracted lots of attention due to its remarkable metalinsulator transition or semiconductor-metal transition behavior. Several thin film deposition techniques including sputtering, evaporation, pulsed laser deposition and chemical vapor deposition have been used to prepare VO_2. In this study, vanadium oxides were deposited by atomic layer deposition (ALD) using $VO(acac)_2$ (vanadyl acetylacetonate) and O_2 as precursors. The thickness of vanadium oxides thin film at different substrate temperature was measured by spectral ellipsometry. The growth rate of vanadium oxides at 420°C and 380°C were 0.34 nm and 0.14 nm per cycle respectively. The growth rate of vanadium oxides was temperature-sensitive. The surface and cross-sectional images were analyzed using scanning electron microscopy. The composition analysis of vanadium oxides films that fabricated at different substrate temperature were carried out by X-ray photoelectron spectroscopy (XPS). From the narrow scan XPS spectra (Figure 1), the vanadium oxides films deposited at 380°C shows a peak at ~516.3 eV demonstrating the presence of VO_2 while the vanadium oxides films deposited at 420°C shows a peak at ~515.7 eV demonstrating the presence of V_2O_3.

AF-MoP-26 Density Functional Theory Study on the Reducing Agent for Atomic Layer Deposition of Tungsten using Tungsten Chloride Precursor, *R Hidayat, **Yewon Kim**, T Chowdhury,* Sejong University, Republic of Korea*; S Kim,* Yeungnam University, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

The three-dimensional vertical NAND architecture requires the excellent gap filling of tungsten (W) into the high-aspect-ratio patterns. Tungsten hexafluoride (WF_6) has been the tungsten precursor for either chemical vapor deposition (CVD) or atomic layer deposition (ALD) technique. Since WF_6 damages the electrical properties of underlying dielectric layers, the fluorine-free tungsten precursor is requested. The use of tungsten chlorides, such as WCl_5 or WCl_6, can be a potential solution, but it has not been explored to find the suitable reducing agent for these precursors. In this work, we studied various molecules as the reducing agent for the ALD of tungsten using tungsten chloride precursor. We used the density functional theory (DFT) calculation to simulate the reactions between the –Cl* surface group and reducing agents during the second half-reaction of the ALD process. The reducing agents considered in this study include atomic hydrogen (H), hydrogen molecule (H_2), silane (SiH_4), borane (BH_3), trimethylaluminum (TMA), triethylaluminum (TEA), and $AlH_2(^tBuNCH_2CH_2Nme_2)$. We compared all possible reaction pathways of reducing agents for the removal of chlorine atom from a chlorine-passivated tungsten cluster . We determined the most favorable reaction pathway and found that H, BH_3, and SiH_4 can be the reducing agents for the ALD of W. Our calculation shows that aluminum compounds would form tungsten carbide film, which agrees well with the literature [1,2]. This study will provide the basis for a better understanding of the selection and the design of the reducing agent for ALD of metal films.

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AF-MoP-27 Density Functional Theory Study on the Surface Reaction of the Hafnium Precursor with a Linked Amido-Cyclopentadienyl Ligand, ***Romel Hidayat**, H Kim,* Sejong University, Republic of Korea*; H Kim, Y Byun, J Lee,* Mecaro, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

Hafnium oxide (HfO_2), a high dielectric constant (k) material, has been used as the gate dielectric of CMOS devices. It also had been used as the capacitor dielectrics in DRAM devices and was replaced by zirconium oxide (ZrO_2). Since the ferroelectricity of HfO_2-based thin films has recently been demonstrated, the interest in HfO_2 has increased again because HfO_2-based ferroelectrics have very high k values but are compatible with CMOS processes, unlike perovskite materials. Potential applications are nonvolatile logic, ferroelectric RAM, and DRAM devices. Hafnium chloride ($HfCl_4$) and tetrakis(ethylmethylamino)hafnium (TEMAH) were the most studied as hafnium precursors. $HfCl_4$ is a solid and is concerned about corrosive byproducts. TEMAH showed relatively low ALD temperatures, which limits the densification and crystallization of the deposited film [1]. Therefore, there is an increasing demand for Hf precursors that are capable of high-temperature conformal deposition. In this study, we studied heteroleptic Hf precursors with a linked amido-cyclopentadienyl (Cp) ligand by density functional theory (DFT) to enable high-temperature ALD. Pyrolysis and hydrolysis reactions of Hf compounds were simulated to expect the thermal stability and the reactivity with hydroxyl groups. The precursors with the linked ligand showed higher activation energies for pyrolysis and lower activation energies for hydrolysis as compared with $CpHf(NMe_2)_3$. The thermal stability of hafnium precursors was examined by the change in color and ^{1}H-NMR spectrum at elevated temperatures, and the better stability of the precursors with the linked ligand has been confirmed. We also investigated the effects of Alkyl groups in the precursors. Finally, we constructed and optimized a hydroxylated monoclinic HfO_2 surface and then simulated the surface reaction of the precursors. Precursors with the linked ligand showed low activation energies for the serial ligand exchanging reactions, which are significantly lower than those of $CpHf(NMe_2)_3$. DFT study shows that the Hf precursors with the linked ligand are promising due to their high reactivity and excellent thermal stability.

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AF-MoP-28 Crystallized ZnO Room-Temperature Atomic Layer Deposition and its Application, ***Kazuki Yoshida**, K Saito, M Miura, K Kanomata, B Ahmmad, S Kubota, F Hirose,* Yamagata University, Japan

Room temperature ALD (RT-ALD) is a promising method for forming metal oxide films on not heat tolerant flexible substrates [1]. We reported a zinc oxide (ZnO) thin film deposited by an RT-ALD system. ZnO is an oxide semiconductor material with a wide bandgap. It also has high visible light transmittance, low electrical resistivity, and low-temperature deposition is possible. Additionally, ZnO has higher water corrosion resistance compared to alumina (Al_2O_3). To achieve its full potential as an electronic and barrier materials the film should be crystallized. We developed the ZnO ALD although it was found that the deposited ZnO film was crystallized even by the RT process. In this conference, we show the observation results of crystallization and discuss its applicability.

We used a p-type Si (100) as a substrate of the RT-ALD. All the samples were cleaned by ultrasonic cleaning using acetone, isopropyl alcohol, and deionized water. The substrate temperature was RT during the ALD process. We used dimethylzinc (DMZ) as a precursor and plasma excited humidified Ar as oxidization gas. For one cycle of ALD, the precursor was exposed at 400000 L and the oxidation time was 300 s with an RF power of 200 W. We confirmed the crystallinity of ZnO by using X-ray diffraction (XRD) and high-resolution TEM (HRTEM). The anti-corrosion resistance to water was tested by immersing ZnO and Al_2O_3 coated Si substrate into hot water (90 ˚C) for 5min respectively.

Figure 1 shows the in-plane XRD pattern obtained from RT-ALD ZnO. We clearly confirm diffraction peaks coming from (100) and (101) [2] at 31.7˚ and 36.2˚. We also confirm weak peaks of (002) and (102) [2] at 34.5˚ and 47.2˚. The cross-sectional HRTEM image is shown in figure 2. We find the crystallized grains in the ZnO layer deposited on amorphous Al_2O_3. We consider the ZnO is the polycrystal although this film was obtained from the room temperature deposition. We assume that this zinc oxide crystallization in RT is caused by reaction heat at the oxidization of DMZ by plasma excited humidified argon.

Figure 3 shows the results of the hot water corrosion test. The sample with only Al_2O_3 (Fig. 3. (a)) showed obvious corrosion after immersion, as shown in Fig. 2. (b). In contrast, when ZnO was coated on Al_2O_3 (Fig. 3. (c)), no corrosion was observed after immersion (Fig. 3. (d)). We succeeded in fabricating the crystallized ZnO thin film with enough water resistance by using RT-ALD. In the conference, we will release a gas barrier rate data with the ZnO and Al_2O_3 laminated film.

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AF-MoP-30 Modelling of Low-Temperature Atomic Layer Deposition of Silicon Nitride using Plasma Excited Ammonia, *Kentaro Saito, K Yoshida, M Miura, K Kanomata, B Ahmmad, S Kubota, F Hirose,* Yamagata University, Japan

Silicon nitride (SiNx) has been attracting much attention since it is expected as gas barrier and anticorrosion coats. The SiNx film deposition has been performed by chemical vapor deposition (CVD) and atomic layer deposition (ALD). These conventional processes were performed at a temperature of 300 °C and higher. For application of SiNx to organic films, the low temperature (low-T) deposition process has been demanded. A low-T ALD of SiNx using tris(dimethylamino) silane (TDMAS) as a Si precursor and plasma-excited ammonia is studied using multiple internal reflection infrared spectroscopy (MIR-IRAS).

An n-type Si substrate was used as a prism for MIR-IRAS. The size of the prism was 10×45 mm^2 and its resistivity was 1000 Ωcm. 45° bevels were formed on its two short edges. The prism was set in a reaction chamber for the measurement. If the IR spectra before and after the processes are defined as I_r and I_0, respectively, the absorbance (Abs) was calculated from the equation, Abs = $\log10(I_r/I_0)$. TDMAS was used as the Si precursor. In the nitridation step, ammonia and argon were mixed with a volume ratio of 7:3, followed by being excited through a quartz tube with an RF power of 250 W and a frequency of 13.56 MHz. The flow rate of the mixed gas was 10 sccm. Ammonia molecules in the mixture were dissociated to NH radicals and some fragments. Plasma excited ammonia was provided in the chamber. All the experiments were performed at RT.

We observed the surface reaction to confirm TDMAS adsorption and examine if the plasma-excited ammonia generated nitride on the TDMAS adsorbed surfaces at RT. Fig. 1 shows IR spectra obtained from a TDMAS adsorbed surface with exposures from 1000 to 400000 L at RT. Peaks at 2964, 2880, and 2805 cm^{-1} correspond to C-H vibrations in adsorbed TDMAS. The positive peak indicates the TDMAS adsorption on the surface at RT. Fig. 2 shows IR spectra measured from plasma excited ammonia treated TDMAS saturated surface. Negative peaks at 2965, 2878, and 2804 cm^{-1} indicate that the silicon nitride was generated there at RT. Based on the IRAS data, we discuss the reaction model of the silicon nitride low-T ALD.

AF-MoP-33 Investigating the Reaction Chemistry of Atomic Layer Deposited SnOx on Perovskite using In-situ Quartz Crystal Microbalance, *Adam Hultqvist, J Jacobsson, S Svanström, T Törndahl,* Uppsala University, Sweden*; U Cappel,* Royal Institute of Technology, Sweden*; H Rensmo, E Johansson, G Boschloo, M Edoff,* Uppsala University, Sweden

The recent lead halide perovskite solar cell efficiencies have been high, but there is still a big question regarding the device stability under operation. A key to stability is to form high quality interfaces to the perovskite that do not degrade and which do not allow for inter diffusion of elements on either side of the interface. Inorganic materials have seemingly suitable properties, but the resulting interfaces to the perovskite, especially the upper one typically lacks in quality. The reason is that most deposition techniques damage the soft and temperature sensitive perovskite and that the remaining processes are not able to make materials with good enough quality or coverage.

Atomic layer deposition (ALD) would be a good choice to grow conformal inorganic materials on perovskite as it does not require high thermal or kinetic energy. Unfortunately, studies have shown that the perovskite is sensitive to the reaction chemistry of most low temperature ALD processes. The thermal $Sn(N(CH_3)_2)_4$ and H_2O process used to grow SnO_x seems promising as it does not damage the perovskite bulk and is able to reach a saturated growth per cycle without much process inhibition. However, the resulting solar cell performance is poor. Previous studies suggest that this relates to the non-ideal perovskite/SnO_x interface that forms as a result of the ligands reacting detrimentally with the perovskite surface during the initial ALD cycles. In this contribution we further analyze these initial cycles using in-situ quartz crystal microbalance (QCM) monitoring complemented by hard and soft X-ray photoemission spectroscopy (SOXPES and HAXPES) and resulting solar cell performance.

To mimic the conditions of the solar cell fabrication, the QCM crystals are coated with a partial solar cell stack with the bare perovskite on top and are then placed inside the ALD reactor. The initial growth dynamics are monitored as a function of the growth temperature, chemical conditions, perovskite types and capping layers as PCBM, C60 and the recently popular nucleation layer PEIE. These results are directly correlated to solar cell performance and to the chemical environment of the buried perovskite/thin SnO_x interface measured by SOXPES and HAXPES. The perovskite integrity before and after the saturated growth per cycle are also analyzed by QCM to get a better understanding of the complete process.

AF-MoP-34 Development of Indium Precursors for Deposition of Indium Oxide, *Takashi Ono, K Yamamoto, S Kamimura, C Dussarrat,* Air Liquide Laboratories, Japan

Indium oxide is a major component of many technologically important thin films. Owing to its electrical properties and transparency in the visible region, it has been widely studied as transparent conducting oxides (TCOs), thin-film transistors (TFT), gas sensors, and catalysts. Among these various applications, we can find binary, ternary and even quaternary materials like InZnO, InGaO, InSnO (ITO) and InGaZnO, either for low temperature (e.g. TCO) or high temperatures (channel material) applications. Recently, there has been an enormous interest in the next generation of see-through transparent electronics such as transparent TFTs, organic light-emitting diodes (OLEDs) and photovoltaics.

In this study, we have carried out the investigation of several types of indium precursors, and found that some of them have suitable thermal properties. Those were evaluated by atomic layer deposition (ALD) process using ozone as oxygen source. Impurities in the deposited films were found to be below the detection limit by XPS, RBS/HFS measurements. Film characterization and thermal properties of synthesized precursors will be reported. The relationships between molecular structures and the corresponding GPC will be discussed.

AF-MoP-36 Studying the Co-Reactant Role During Plasma-Enhanced Atomic Layer Deposition of Palladium, *Ji-Yu Feng, M Minjauw, R Ramachandran, M Van Daele, H Poelman,* Ghent University, Belgium*; T Sajavaara,* University of Jyväskylä, Finland*; J Dendooven, C Detavernier,* Ghent University, Belgium

Palladium (Pd) is an attractive noble metal for a wide range of applications in catalysis, nanoelectronics and energy storage devices. ALD has emerged as a powerful method for the synthesis of Pd nanostructures with precise dimensions control. Unlike most other noble metal processes, the main Pd ALD process using palladium(II)hexafluoroacetylacetonate [$Pd(hfac)_2$] is based on true reducing surface chemistry, involving a reducing co-reactant such as H_2.[1] Based on the current understanding, H surface species from the dissociation of H_2 by the Pd surface during the co-reactant step, can eliminate ligands of incoming $Pd(hfac)_2$ molecules during the precursor pulse, releasing Hhfac as reaction product.[2]

This work investigates the role of different plasmas and plasma sequences governing the Pd-PEALD growth, using $Pd(hfac)_2$ as precursor. Except for the process using only O_2 plasma (O_2*), ALD processes including a reducing agent (H_2* and NH_3*) enable successful Pd growth at 100℃, showing a clear difference in GPC ranked from high to low as follows:

O_2*+H_2*>NH_3*≈H_2*>H_2*+O_2*, and a trend of increasing GPC with temperature for the first three processes in contrast to a stable GPC for the H_2*+O_2* process. Moreover, the GPC of processes with a H_2* step prior to the precursor pulse decreases when longer pumping times are applied after the H_2* pulse. XPS and ERD reveal the presence of carbon in the films deposited by the processes using only reducing agents (H_2* and NH_3*), while no hydrogen could be detected. Almost no carbon remains in the films deposited by the processes with an additional O_2* step, in accordance with previous work.[3]

The observed differences in GPC and film composition are linked to the surface chemistry based on in vacuo XPS characterizations. In short, O_2* removes most of the precursor ligands and its fragments, and oxidizes the Pd surface. H_2* is able to reduce an oxidized Pd surface and can remove fluorine and oxygen on the surface, but some carbon remains. The highest GPC is achieved when a clean metallic Pd surface is exposed to the precursor, while oxygen and carbon species on the surface prove to be growth inhibitors. The key growth facilitator is hydrogen which resides on the Pd surface in those processes with the H_2* step directly before the precursor pulse. Moreover, the amount of hydrogen on the Pd surface available for the precursor reaction is an important factor in determining the GPC dependence on temperature and pumping time.

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AF-MoP-37 Plasma Enhanced Atomic Layer Deposition of Carbon Incorporated Silicon Oxynitride (SiON) Thin Films Using Novel Organochlorodisiloxane Precursors*, Z Qin,* The University of Texas at Dallas*; S Hwang, A Ravichandran,* ***Dan Le****, Y Jung,* University of Texas at Dallas*; B Hwang, L Lee, X Zhou,* DuPont*; J Kim,* University of Texas at Dallas

Incorporating carbon to lower dielectric constant and maintain good wet etch resistance and high thermal and electrical stabilities of SiN_X films has recently been considered as an effective method to reduce resistive-capacitive (RC) delay and parasitic capacitance which deteriorate device performance. However, the films deposited from some aminosilane precursors and O_3 cannot retain C content above 150°C[1], and plasma enhanced atomic layer deposition (PEALD) of carbon incorporated Si-based dielectric films is found to be challenging after three approaches, (1) use of C-containing Si precursor with N-containing plasma, (2) use of a three-step process consisting of sequential Si precursor exposure, C precursor exposure and N-containing plasma exposure and (3) use of a Si precursor with CO/O_2 plasma, were evaluated[2]. Furthermore, the thermal stability of the carbon in the resultant PEALD films was not examined.

In this research, two novel C-containing Si precursors, 1,1,3,3-tetrachloro-1,3-divinyldisiloxane (CVDSO) and 1,3-dichloro-1,3-dimethyl-1,3-divinyldisiloxane (CMVDSO), were investigated using a hollow cathode PEALD system in a temperature range of 230−570 °C. The $-CH=CH_2$ groups in these molecules contain carbon-carbon π bonds which may participate in chemical reactions such as polymerization or hydroamination and be beneficial for carbon incorporation [2], [3] . In the temperature range of 310−480 °C, both CVDSO and CMVDSO exhibit self-limiting growth behaviors with NH /N plasma gas mixture. With both NH_3/N_2 and N_2 plasmas, the thin films deposited at 310 °C from CMVDSO show a carbon content of 5~6% after 60 s gas cluster ion beam sputtering using XPS. The N_2 plasma film of CMVDSO has an almost unchanged carbon content after a RTA treatment at 800℃ for 1 min. For CVDSO, only the N_2 plasma film exhibits a similar result. These results suggest that both precursors may have the capability to incorporate carbon with a desirable thermal stability in films. The different carbon incorporation behaviors of these two precursors with NH_3/N_2 and N_2 plasmas may be explained by the H radical ions generated in NH_3/N_2 plasma that can abstract surface -Cl, $-CH=CH_2$ and $-CH_3$ at different rates [4]. The detailed experimental results will be presented.

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AF-MoP-40 Reactive Ballistic Transport in Horizontal Macrotrenches Under ALD and CVD Conditions: A Comparison with Vertical Structures*,* ***Angel Yanguas-Gil,*** Argonne National Laboratory

Horizontal macrotrench configurations have long been used as substrates to characterize the conformality of thin film growth processes and to extract kinetic information in both CVD and ALD. An attractive feature of macrotrenches is that, as long as transport remains ballistic, they provide a simpler way of characterizing growth profiles while maintaining essentially the same geometry of a vertical trench. However, one important distinction is the geometry at the entrance of the feature, particularly when it is fabricated as a recessed structure. Surfaces near the entrance of the macrotrench can create virtual sources that can affect the transport of species, and under reactive transport can produce differences in film thickness between the top and bottom walls.

In this work we establish a comparison between the ballistic transport inside macrotrenches with different configurations and a conventional vertical trench, both under ALD conditions and under simple CVD conditions characterized by a non self-limited constant sticking probability. In particular, we focus on the impact that geometry has on the effective sticking probability of the structure and on the asymmetry in growth rates between the top and bottom walls. Finally, we benchmark the validity of the diffusive model, and the break down of the diffusive approximation near the entrance.

AF-MoP-44 Understanding the Influence of *In-situ* Ar-Plasma Annealing Processes on the Film Properties of ALD-Grown AlN Layers*,* ***Saidjafarzoda Ilhom****, A Mohammad, D Shukla, J Grasso, B Willis,* University of Connecticut*; A Okyay,* Stanford University*; N Biyikli,* University of Connecticut

In this report we have investigated the impact of *in-situ* layer-by-layer Ar-plasma treatment on the AlN growth and film properties in a hollow-cathode plasma-assisted ALD reactor. AlN thin films were grown on Si(100) substrates using trimethylaluminum (TMA) as metal precursor and $Ar/N_2/H_2$ plasma as the nitrogen co-reactant. Growth experiments have been performed at 200 °C substrate temperature and 100 W rf-power, 30 seconds plasma exposure, and 50/50/50 sccm $Ar/N_2/H_2$ plasma gas compositions. Additionally, each unit ALD-cycle was followed by an *in-situ* Ar-plasma annealing process, which consists of Ar-plasma exposure for 20 seconds in the range of 50 – 300 W rf-power. *In-situ* and *ex-situ*ellipsometry was employed to measure the thickness and optical property variations of the films. Film thicknesses ranged between 33.8 – 46.05 nm with refractive indices of 1.70 – 2.10 scanned over the 50 – 300 W Ar-annealing rf-power. X-ray diffraction (XRD) showed AlN hexagonal wurtzite crystal structure for the non-annealed baseline sample, which had a refractive index of 1.97. On the other hand, AlN films grown with lower *in-situ* Ar-annealing rf-power (50 – 100W) showed amorphous crystal structure with reduced refractive index (1.70 – 1.76). Interestingly, although increasing the *in-situ* annealing plasma power (150 – 300 W) led to higher refractive indices (1.95 – 2.10), the films still exhibited amorphous-like crystal properties. Also, samples with Ar-annealing powers of (150 – 200 W) displayed relatively high absorption component within the UV-VIS range of the electromagnetic spectrum. Additionally, x-ray reflection (XRR) method was utilized to analyze the density of the samples, which ranged between 2.91 – 3.14 g/cm^3. Furthermore, XPS will be employed to study the chemical bonding and elemental composition of the samples. The role of *in-situ* Ar-annealing rf-power in film optical behavior and crystal structure evolution will be discussed based on the correlation of spectroscopic ellipsometry, XRD, XRR, and XPS results.

AF-MoP-45 Thin-Film Deposition from $Mo(CO)_6$: The Effect of Co-Reactants and Temperature on Film Purity*,* ***Phillip Chen****, S Nguyen, B Hendrix, T Baum,* Entegris, Inc.

In 1970, it was reported that $W(CO)_6$ and $Mo(CO)_6$ could produce high-purity thin-films with low film resistivity [1]. Contrary to this earliest report, numerous studies with the same precursors demonstrated that the deposited films were highly contaminated with carbon impurities. In subsequent studies, films from these precursors were amorphous with very poor film resistivity [2, 3]. In this work, we report our recent findings on $Mo(CO)_6$ and its deposited films. We specifically explored the effects of substrate temperature, reactor pressure and co-reactant identity towards thin-film purity.

At low substrate temperatures (<300°C), H_2, Ar and CO_2 co-reactants can alter the ratio of carbon in the deposited films, sometimes depositing cubic Mo_2C. Annealing these films can produce cubic or hcp Mo_2C, under some conditions. NH_3 co-reactant deposited films of lower carbon content. The best as-deposited resistivities from low temperature deposition were around 150μΩ-cm. Annealing films to 800°C, resulted in lower resistivity films for some conditions.

At high substrate temperatures (>500°C), films with low as-deposited resistivity can be achieved. The addition of water as a co-reactant, allows the formation of high-purity Mo films with low film resistivity, 20μΩ-cm. The choice of co-reactants, pulse sequence and pulse times can alter the deposited Mo film properties.

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AF-MoP-46 Feasibility of Boron Nitride Film Growth at Lower-than 250°C Substrate Temperature via Hollow-Cathode Plasma-ALD: In-situ Monitoring of Plasma Composition Effect, ***Adnan Mohammad**, D Shukla, S Ilhom, B Willis, J Grasso,* University of Connecticut*; A Okyay,* OkayayTech*; N Biyikli,* University of Connecticut

Hexagonal boron nitride (h-BN) can be used as a good lubricant at both low and high temperatures. In addition, h-BN has excellent chemical and thermal stability, which makes it an ideal material for extreme and harsh environments. The conventional synthesis of h-BN is carried out using high-temperature CVD or sintering techniques, both power-hungry methods. Our previous work on h-BN via plasma-enhanced ALD demonstrated as-grown crystalline h-BN deposition above 350 °C substrate temperature, where the boron precursor was most probably facing thermal decomposition. However, at reduced substrate temperatures (250 °C), we did not observe any film growth. Our current study demonstrates that BN film growth is indeed possible even at 200 °C, within a customized remote plasma-ALD reactor featuring large-diameter hollow-cathode plasma source and reduced source-to-substrate distance.

BN thin films are deposited in a hollow-cathode plasma-assisted ALD (HCPA-ALD) chamber with TEB precursor and various nitrogen plasma chemistries including different compositions of N2, H2, and Ar gases. We also employed real-time in-situ ellipsometric monitoring of the deposition experiment, where individual half cycle surface reactions including chemisorption, ligand removal, nitrogen/impurity incorporation, and etching processes could be observed and correlated with the ex-situ measured material properties. The substrate temperature is varied between 200 and 250 ° C, the N2 carrier gas flow is kept at 10 sccm, and Ar-purging gas flow at 50 sccm. Throughout the saturation curve and long-run linearity experiments, the operation pressure was within 0.5 - 1.1 Torr, depending on the plasma gas composition and related gas flows. The saturation studies are carried out to determine the optimized growth conditions, where the growth-per-cycle (GPC) parameter is traced for different precursor pulse time (15 and 30 ms), rf-plasma power (100 W to 250 W) and plasma-gas chemistries (N2-only, N2/H2, Ar/N2, Ar/N2/H2 at varying ratios). The growth recipe for the 1000-cycle long runs in order to achieve thicker films for material characterization is chosen based not only on the average GPC values obtained over 10-cycle periods, but as well on the individual half cycle behavior: clear chemisorption and plasma-assisted ligand removal characteristics. The different plasma compositions studied are (i) Ar/N2 at 50/50 sccm; (ii) N2-only at 50 sccm; and (iii) N2/H2 at 50/10 sccm. The as-deposited films exhibit amorphous character evidenced by XRD measurements. Spectroscopic ellipsometer and XPS studies will be presented as well as post-deposition vacuum annealing to improve crystallinity.

AF-MoP-47 Ti-Doped ZnO Thin Films by Atomic Layer Deposition: Growth Mechanism Study and Influence of Process Parameters on Material Properties, ***Damien Coutancier**,* IPVF-CNRS, France*; O Fournier,* IPVF-EDF, France*; S Zhang,* IPVF-CNRS, France*; S Bernardini,* IPVF-Total, France*; F Donsanti,* IPVF-EDF, France*; N Schneider,* IPVF-CNRS, France

Transparent conductive oxides (TCO) thin films are used in a wide range of optoelectronic devices. Despite its favourable properties, indium tin oxide has to be replaced due to indium scarcity. One of the main candidates is doped-ZnO, which has tunable properties by adding a large range of elements (Al, Ga, Mg, Ti,…)[1]. Atomic layer deposition (ALD) has been reported to grow Ti-doped ZnO (TZO) thin films by introducing TiO2 cycles into the ZnO matrix. The as-grown TZO films show excellent transmittance and conductivity; their structural, electrical and optical properties have been investigated as a function of the TiO2/ZnO cycle ratio [2–4], the thickness [5] and the deposition temperature[6]. However, no investigations on neither the growth mechanism of ALD-TZO film, nor applications as TCO have been reported.

Here, we report an ALD process to synthetize TZO films from diethylzinc, titanium tetrakis(isopropoxide) and water. The growth mechanism was investigated by in situ quartz-crystal microbalance measurements to monitor the mass changes at every step of the cycle. It evidenced different insertion modes of titanium depending on the precursor introduction, as well as the etching of Zn-Et terminated surface fragments by TTIP. The order of the precursor introduction affects the doping mechanism and consequently the final TZO film properties.

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AF-MoP-48 Effect of Deposition Temperature on Titanium Nitride in Plasma-Enhanced Atomic Layer, ***Heli Seppänen**, E Österlund, H Lipsanen,* Aalto University, Finland

Titanium nitride (TiN) is an interesting material in many fields of electronics due to its electrical properties and compatibility with other materials. It has been studied as gate metallization in CMOS transistors [1, 2] and as diffusion barriers for both MEMS [3] applications and copper [4]. Recently, it has also been suggested as a replacement for gold in plasmonic applications [5]. Atomic layer deposited (ALD) TiN is often grown using a thermal process at high temperatures (>300 °C) with $TiCl_4$ and ammonia (NH_3) as precursors. However, the process with $TiCl_4$ and NH_3 as precursors has not been studied with plasma-enhancement, which also allows lower deposition temperatures.

This study investigates the electrical and microstructural properties of TiN thin films deposited at different temperatures. Additionally, the effect of annealing on the properties is studied. The deposited TiN films are characterized using spectroscopic ellipsometry, X-ray diffraction (XRD) and sheet resistance measurements. The results show a decrease in sheet resistance in the film from 120 Ω/□ to 35 Ω/□ with rising deposition temperature. Furthermore, the crystallinity of the TiN films (Supplementary, Figure 1) is also enhanced with higher temperature.

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AF-MoP-50 Infrared Spectroscopy of SiNx Grown by Atomic Layer Deposition on Structured Substrates, ***Yuji Otsuki**, Y Suzuki, M Kagaya, K Oshimo, H Murakami, K Ouchi,* Tokyo Electron Technology Solutions Limited, Japan

In the microelectronics industry, microfabrication is performed on nanometer scales, and it is often necessary to grow a film on a nanoscale structured substrate such as a line-and-space pattern and a via hole. In the case of film growth on a structured substrate, the uniformity of film quality is important, and film quality improvement requires understanding of the physical properties of the film. However, few methods exist for characterizing films with complex structures, particularly sidewalls and bottoms of trenches. Energy dispersive X-ray spectrometry provides information on elemental composition, but does not provide details on physical properties or structure such as chemical bonds. Therefore, typical practice is to examine the detailed physical characteristics of the film on the blanket wafer instead of the structured sample, and to infer the physical characteristics of the structured sample from the results of the blanket wafer examination.

Vibrational spectroscopy is a non-invasive technique and is applicable to semiconductors and insulators. It can be used not only to identify chemical bonds, but also to investigate microscopic structures such as bond length and bond angle. Therefore, vibrational spectroscopy of a blanket sample is typically used to estimate the film quality of a structured sample. To our knowledge, however, few studies apply vibrational spectroscopy to the pattern sample itself.

In this study, we applied infrared (IR) spectroscopy to structured samples themselves and evaluated the physical properties directly. SiNx grown by plasma-enhanced atomic layer deposition was selected as a model sample, and grown on both bare-silicon and line-and-space-patterned substrates. It became clear that the IR spectral line shapes differed between the blanket and structured samples. The intensity ratio between Si–N stretch vibration and vibration of impurities in the film suggests that the number densities of NH, NH_2, and SiO species of the structured sample were higher than those of the blanket sample. This indicates that the film quality of the structured sample was lower than that of the blanket sample. This disparity may be due to the unlikelihood of ions or radicals reaching the side and bottom of the trench during deposition, resulting in insufficient nitridation. This method accomplished the challenging task of directly measuring the physical properties of a film grown on the side and bottom surfaces of a trench, and showed the importance of such a measurement.

AF-MoP-51 Enabling Strong Magnetoelectric 2-2 Composites Made of AlN Films Grown by Plasma-Enhanced ALD on Magnetostrictive Foils for Energy Harvesting Applications*, **Tai Nguyen**, N Adjeroud, S Glinsek, Y Fleming, J Guillot, J Polesel-Maris,* Luxembourg Institute of Science and Technology, Luxembourg

Synthesis of AlN films with controlled crystalline orientation is always challenged by demanding high deposition temperatures (>300°C) and the presence of impurities such as carbon and oxygen [1, 2]. Recent studies presented the growth of preferably oriented (002) AlN films at 250°C by plasma-enhanced ALD (PEALD) [3]. However, the piezoelectric (PE) response of such ALD layers has not been demonstrated yet. Our current study highlights the effect of thermodynamic parameters on growing the preferentially (002) oriented AlN film, then measuring its direct piezoelectric coefficient $e_{31,f}$. By using the highly conformal coating and the low temperature growth by PEALD, we were able to design 2-2 magnetoelectric (ME) composites with a high-quality interface by stacking AlN films on 15µm-thick nickel, 12.5µm-thick iron, and 15µm-thick cobalt foils. In these 2-2 ME composites, the interface between the magnetostrictive layer and the PE layer plays a crucial role to improve the ME coupling [4]. Yet, it can be easily deteriorated by poorly conformal coating techniques and high-temperature processes because of roughness, lattice mismatch, and a large difference in thermal expansion coefficient between both materials [4]. Therefore, the PEALD processing emerges as a very suitable methodology to solve the above-mentioned issues.

In the present work, AlN films were grown by PEALD with control of the deposition temperatures and the purging time between the trimethylammonium pulse and the plasma discharge as critical parameters to achieve (002)-oriented films (Table 1). XRD results (Fig. 1) shown that the preferably (002) oriented film grown as increasing the deposition temperature as well as the purging time. The XPS surveys (Fig, 2) confirm the high-quality AlN films with low impurities level (1% of carbon and 6-7% of oxygen). The direct $e_{31,f}$ coefficient is evaluated by the 4 point-bending method setting up on an aixACCT instrument. The highest $e_{31,f}$ of 0.37 $C.m^{-2}$ was obtained for a 590nm-thick AlN film processed at 250 °C with the purging time of 30s (Fig. 3). The ME transverse coefficient was measured out of resonance by exposing the 2-2 composite to a DC bias magnetic field varying from -180 to 180 Oe superimposed by a weak AC magnetic field of 8.5 Oe at 46 Hz (Fig. 4). The ME transverse coefficients were measured at 2.8, 0.3, and 0.15 $V.cm^{-1}.Oe^{-1}$ for AlN films deposited on nickel, iron, and cobalt foils, respectively. Although the ME composites are made by magnetostrictive and piezoelectric materials with intrinsic moderate performances, the ME coefficient would be strong enough for utmost promising application devices as energy harvesters and magnetic sensors.

AF-MoP-53 On the Fundamentals of ALD: The Importance of Getting the Picture Right*, **Riikka Puurunen**,* Aalto University, Finland*; R van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) has become of global importance as a fundamental building block for example in semiconductor device fabrication, and also gained more visibility (e.g., the Millennium Technology Prize 2018). In recent years, the number of ALD processes has increased, new groups have entered the field, and fundamental insights have been gained. At the same time, significantly varying views exist in the field related to the description and meaningfulness of some core ALD concepts. Open, respectful but critical scientific discussion would be needed around these concepts - for example at this AVS ALD/ALE conference, the world's largest conference on ALD.

The discussion on terminology of ALD that started in the 2005 surface chemistry review [1] is continued in this contribution, taking into account recent progress reported in leading reviews such as Ref. 2. We start by considering the concept of "ideal ALD". How should it be defined so that the well-recognized practical benefits of ALD are maintained, while no unnecessary utopian requirements are created? We propose that the repetition of well-separated saturating, irreversible chemisorption reactions (which by definition saturate at a monolayer of the chemisorbed species) is sufficient to reproduce the benefits of ALD. A requirement of "full monolayer growth" (of the ALD-grown material), progressed e.g. in numerous cartoons of ALD, is not needed. There should also be no reason to expect a constant growth per cycle (GPC) within the ALD window (the saturating chemistry is typically weakly temperature dependent), although such a scheme is repeatedly reproduced in the literature.

Other fundamental concepts will be pointed out, where mix-ups have been created. For example, although the GPC (or etch per cycle in Atomic Layer Etching) is a saturation-related concept and not a time-related kinetic parameter, Arrhenius plots have been sometimes created to extract "activation energies" of some process from these "growth/etch rates (per cycle)". Also, "Langmuir adsorption" has been adopted as a way to model ALD in a simplified, lumped way. Notably, Langmuir adsorption assumes no interaction between adsorbed species, contrasting some recent discussions of "cooperative effects" in ALD. Also, concepts of "adsorption isotherm" and amount adsorbed vs. time ("saturation curve"), although fundamentally different, have been mixed.

We hope that the discussion on the fundamentals of ALD will be intensified, and that the discussion will help the field progress and flourish in the future.

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AF-MoP-59 In-situ Real-Time and Ex-situ Spectroscopic Analysis of Al_2O_3 Films Prepared by PEALD*, **Paul Plate**, F Naumann, J Reck, H Gargouri, B Gruska, A Blümich,* SENTECH Instruments GmbH, Germany*; A Mahmoodinezhad, C Janowitz, K Henkel, J Flege,* BTU Cottbus-Senftenberg, Germany

In-situ techniques provide a very powerful means to further improve atomic layer deposition (ALD) processes and their preparation equipment. Ellipsometry has widely been used to investigate thin films prepared by ALD. Consequently, in-situ ellipsometry has been developed to monitor ALD growth in operando.[1]

In this work in-situ real-time ellipsometry (irtE) with a very high time resolution of 24 ms was used to investigate the growth of inductively coupled plasma enhanced (ICPE) ALD of Al_2O_3. Utilizing this technique, it is possible to resolve each step of the ALD cycle in detail and in real-time. The combination of in-situ measurements with ex-situ ellipsometry (UV-VIS-NIR-SE and IR-SE) and X-ray photoelectron spectroscopy (XPS) allows correlating surface effects observed by in-situ ellipsometry with the bulk properties of the ALD layers. For benchmarking, an Al_2O_3 film deposited by thermal ALD (T-ALD) with a very similar equipment was used.

The ICPEALD films were deposited at substrate temperatures ranging from 80 to 250 °C, while the reference T-ALD layer were prepared at 200 °C. The influence of the plasma exposure step was studied by varying plasma parameters such as plasma power and pulse duration.

The Al_2O_3 ICPEALD process exhibits a higher growth rate than its thermal counterpart. However, XPS measurements revealed an increase in the amount of incorporated carbon compared to the layer prepared by T-ALD. Simultaneously, the refractive index decreased. In-situ measurements indicated an adsorption process, which is not typical for an ALD process. Additionally, IR measurements pointed to the presence of CH_x species, in agreement with the XPS results. A correlation was found between the duration and power of the plasma pulse and the non-stoichiometric composition of the ICPEALD aluminum oxide films. The irtE technique was successfully used to minimize the incorporated carbon and improve the film quality by optimizing the plasma parameters, resulting in high-quality Al_2O_3 layers. [2]

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AF-MoP-60 Conformality of TMA/H_2O and TMA/O_3 Processes Evaluated using Lateral High-Aspect-Ratio Structures*, **Sakari Lepikko**,* Aalto University, Finland*; O Ylivaara,* VTT Technical Research Centre of Finland Ltd, Finland*; J Yim, E Verkama,* Aalto University, Finland*; M Utriainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen, R Ras,* Aalto University, Finland

Atomic layer deposition (ALD) is a fast-growing technique in manufacturing modern electronics due to its ability to produce uniform and conformal thin films with sub-nanometer precision even within high-aspect-ratio cavities. However, reaction kinetics and deposition parameters set the limits how deep the film can be grown conformally within a high-aspect-ratio structure. In this work, we use lateral high-aspect-ratio structure for comparison of thickness profiles of two aluminum oxide Al_2O_3 deposition processes: trimethylaluminum $Al(CH_3)_3$ (TMA) with either water H_2O (denoted as TMA/H_2O) or ozone O_3 (denoted as TMA/O_3) as co-reactants. The processes are performed with Veeco-CNT Savannah S200 ALD reactor on PillarHall® LHAR3 test structures in otherwise the same conditions except for the co-reactant pulse. This structure has a lateral trench with gap height of 500 nm and depth of 1 mm, resulting in aspect ratio of 2000.

The thickness profiles obtained with spectroscopic reflectometry show four main differences between the processes. The initial plateau at low depths describes the growth per cycle (GPC). It is 30% higher for TMA/H_2O than for TMA/ O_3. Since the TMA dose is the same in both processes, we conclude that O_3 generates less hydroxyl groups than H_2O, which affects GPC [1]. The plateau is followed by a steep slope. The slope at half-thickness value is related to the sticking coefficient of limiting reactant [2]. The slope in this case corresponds to the sticking coefficient of TMA in both processes, indicating that TMA is the limiting reactant in these deposition conditions. The depth of half-thickness value describes the diffusion length of the reactants under the deposition conditions. This value is slightly higher for TMA/O_3 even though the limiting TMA dose is the same in both processes. TMA/O_3 diffuses therefore slightly longer into trenches than TMA/H_2O. However, the total volume of deposited film remains smaller for TMA/O_3 due to smaller GPC. The total area beneath the thickness profile curve, which equals to cross-sectional area of the film, for TMA/O_3 is 20% smaller than for TMA/H_2O.

Lastly, TMA/H_2O is compared to another TMA/H_2O process deposited in Picosun R-150 ALD reactor on a similar PillarHall® structure [3]. The processes are otherwise nearly identical except for half-thickness depth. This is due to larger dose used in the Picosun reactor increasing the diffusion length of precursors.

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AF-MoP-62 Atomic Layer Modulation using Steric Hindrance of Precursors*, H Lee,* ***Chi Thang Nguyen****,* Incheon National University, Republic of Korea

Atomic layer deposition (ALD) is a technique frequently used through the supercycle manner to fabricate multicomponent thin films. The stoichiometry of thin film can be controlled by changing the ratio of each ALD cycle. These days, most of applications require reduced film thickness with high stoichiometric uniformity in few nanometers. However, the conventional supercycle approach has limitations in reduction of thickness because it requires a certain thickness to achieve the desired stochiometric uniformity. In addition, the stoichiometric uniformity of the multicomponent ALD films does not well matched with the calculated value by the cyclic ratio due to unknown mixing mechanisms. In this work, we proposed a different approach by ALD using steric hindrance effects of precursors. Two precursors with different molecules size are sequentially exposed to the surface, and the stoichiometry of the film is determined and controlled by the adsorption coverage ratio of precursors based on steric hindrance of two precursors. The experiments were conducted using a ruthenium precursor, dicarbonyl-bis-(5-methyl-2,4-hexanediketonato)Ru(II) (Tanaka Kikinzoku Kogyo) with two Al precursors, trimethylaluminum (TMA) and dimethylaluminum isopropoxide (*DMAI)* (Lake Materials). The adsorption coverages by steric hindrance effects of precursors on the SiO_2 substrate surface were simulated by Monte Carlo (MC) method. The density functional theory (DFT) calculation was also performed to estimate the favorable adsorption of each precursor on the surface, supporting the experimental results and interpretation of atomic layer modulation (ALM) thin films. The theoretical calculation results were consistent with the analyzed stoichiometry of the films. The results in this work have a big potential to fabricate a nanometer-thick multicomponent ALM film for various applications.

AF-MoP-63 Tungsten Films Grown by Plasma-Enhanced Atomic Layer Deposition with Newly Synthesized Metalorganic and Halide Precursor*,* ***Yujin Lee****, S Seo, T Nam, H Lee, H Yoon, S Lee,* Yonsei University, Republic of Korea*; J Seo, J Seok,* Hansol Chemical, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea

For continuous scaling down of semiconductor devices, metal deposition has been developed as a plug filling process for interlayer connecting. Tungsten (W) has a wide range of industrial applications since it has a relatively good electrical conductivity and a high electromigration durability due to its high melting point of 3380 °C. [1] Among various techniques, atomic layer deposition (ALD) has been investigated to find the most feasible way to grow uniform, dense, conformal, and conductive W thin film to thicknesses of a few nanometers in more complicated structures, since its growth mechanism is entirely based on self-limited surface reaction.

To date, several W precursors have been employed. Among them, the halide precursors have been widely used as precursors for metal deposition since it can fabricate a high-purity film compared to metal organic precursors. Tungsten hexafluoride (WF_6) is the most widely reported halide-based precursor to date due to its simple structure and high reactivity. However, the toxic by-product (HF) can provoke the interfacial Si consumptions and corrosion of devices. In this respect, in halide-based precursors, fluorine (F)-free tungsten precursors have recently received attention, but study on development of F-free tungsten precursor is still in its infancy. In contrast, the organic precursor is free from the formation of corrosive by-product. However, the carbon species derived from the organic ligand of the precursor can deteriorate film properties and device performance. For this reason, studies for pure tungsten metal deposition with organic precursors have not been reported. Eventually, since the halide and organic precursors have their own strengths and weaknesses, there has been considerable controversy over the choice of precursors between the two groups.

In this work, we fundamentally investigated PE-ALD process of W on SiO_2 substrate, using newly synthesized tungsten halide and metalorganic precursor. We analyzed the growth characteristics, chemical composition, crystallinity, and the results were correlated to the effects of the precursor ligands. In addition, the electrical properties, including resistivity depending on the ALD cycles, and conformality at trench were evaluated for potential application.

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AF-MoP-64 Metal Aminoalkoxide Precursors for ALD Metal Oxide Films*,* ***Atsushi Sakurai****, H Sato,* Adeka Corporation, Japan*; A Saito,* Adeka Corporation, Republic of Korea*; M Hatase, A Nishida, T Yoshino, M Enzu, N Okada, A Yamashita,* Adeka Corporation, Japan

Innumerable ALD precursors for metal oxide films have been well investigated over the past two decades and those efforts have contributed to current semiconductor industries. As we anticipate future expansion of ALD processing into photovoltaic, solid-state battery, and power devices, new materials could be helpful to meet various R&D requirements in those areas. For years, we have been investigating many kinds of ALD high-k precursors for Hf, Zr, and Al-oxide films, but the new industries require other kinds of metal precursors for the deposition of oxides of Sn, Ni, and Co, etc. For pure metal film growth, metal alkoxide precursors are not always preferred to O-free precursors in consideration of their poor reactivity with an H_2 reducing agent. On the other hand, metal alkoxide precursors could be promising candidates to deposit high purity metal-oxide thin films as they could easily react with O-based co-reactants such as H_2O and O_3. As a result, we would like to propose metal aminoalkoxides precursors as high purity, high vapor pressure, low melting point, sufficiently thermal stabile and synthetically viable options for high volume manufacturing. During the presentation, we will summarize physical properties (TGA, DSC, etc.) of metal aminoalkoxides: $M[OCHRCH_2NR'R'']_n$ （M = Sn, Cu, Ni, Co, Hf, Y, etc.） followed by some ALD processing using O-based co-reactant and metal-oxide film data (XPS, SEM, etc.).

AF-MoP-65 Surface Reaction Mechanism during Atomic Layer Deposition of Al_2O_3 using Water, Methanol, and Ethanol as the Oxidants*, H Kim,* ***Seunggi Seo****, W Woo, I Oh,* Yonsei University, Republic of Korea*; B Shong,* Hongik University, Republic of Korea

Atomic layer deposition (ALD) is a vapor phase thin film deposition technique based on self-limited surface reaction. Since ALD could deposit thin films with high quality, good uniformity, high conformality, and sub-nanometer thickness controllability, [1] ALD has been regarded as one of the most suitable deposition technologies for semiconductor device fabrication.

Since thin films of alumina (Al_2O_3) have wide range of applications such as high-k dielectric material for electronic devices, mechanical and chemical protective coatings, diffusion barriers, and optical coatings, [2-5] For the deposition of Al_2O_3, trimethylaluminum (TMA) have been the most widely used for Al precursor. And water (H_2O) is widely utilized as the oxygen source in ALD Al_2O_3 processes, because H_2O shows facile ligand exchange reaction during ALD.

However, ALD Al_2O_3 processes with H_2O reactant showed undesirable substrate oxidation issue. For example, there was an unwanted interface oxide between ALD deposited Al_2O_3 film and Si substrate. The interface oxide could reduce the dielectric constant of the deposited thin films and increase leakage current density. [6-7] To avoid the oxidation of substrates, it is necessary to develop a new ALD process by using oxidants with lower oxidation potential than that of H_2O. Despite its technical importance, ALD Al_2O_3 processes with weaker oxidants such as alcohols have rarely been investigated. [8] For this reason, the chemical reaction mechanism between surface adsorbed precursor and reactant has not been clearly identified.

In this work, we fundamentally investigated ALD process Al_2O_3 on Si substrate, using TMA and various oxidants (water (H_2O), methanol (MeOH), and ethanol (EtOH)). Furthermore, we investigate the reaction mechanism of various alcohol oxidants during ALD of Al_2O_3. Density functional theory (DFT) calculations at B97D3 level of theory were performed using Gaussian 09 suite of programs.

Our developed ALD processes showed typical ALD growth characteristics. The saturated growth rates with H_2O, MeOH, and EtOH were 1.3, 0.10, and 0.96 Å/cycle, respectively. From this study, we revealed that the beta-hydrogen transfer reaction of EtOH could easily oxidize surface methyl group into surface hydroxyl.

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AF-MoP-66 Evaluation and Investigation on Reaction Mechanism of Novel Hf Alkoxide Precursors for Atomic Layer Deposition of HfO₂

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With the scaling down of semiconductor devices, due to the decrease of reliability of gate oxide against electric breakdown and increase of leakage current caused by direct tunneling of electron, SiO_2 based dielectric was replaced by high-k dielectrics. Among the various high-*k* dielectric materials, HfO_2 is considered as one of the most suitable material owing to its high dielectric constant, good thermodynamic stability and high bandgap energy. Atomic layer deposition of high-quality HfO_2 has emerged as a key technology for ultrathin and high-k gate dielectrics. Among the various type of Hf precursors, alkoxide precursors are considered as attractive precursor to deposit C-free films owing to its strong inherent metal-oxygen bonding. However, conventional alkoxide precursors could not be applied to ALD HfO_2 process due to non-saturated growth characteristics caused by undesired reaction. Chain reaction of hydrolytic decomposition that is hydrolysis of alkoxide precursors continuously occurs by water vapor or surface hydroxyl generated from the β-hydride elimination. In addition, alkoxide precursors require relatively high deposition temperatures due to ligand exchange reactions between alkoxide ligands and surface hydroxyl groups due to strong Hf—O bonding but are difficult to apply to ALD due to limited thermal stability. There is a need for new Hf precursors which can overcome the limitations of conventional alkoxide precursors and possess the advantages of alkoxide precursors. In this study, we developed ALD HfO_2 process using newly synthesized Hf alkoxide precursors by Korea Research Institute of Chemical Technology as designed for deposition of carbon-free HfO_2.New type of β-diketonates ligand was employed to improving thermal stability and inhibition of undesired reactions in ALD process. In addition, Cyclopentadienyl ligand was employed to develop heteroleptic precursor that is most widely employed ligand to improve thermal stability and volatility of precursor. We investigated the impact of ligand substitution on growth characteristics, chemical compositions, film density and crystallinity of ALD HfO_2 using new precursors. The electrical properties including the dielectric constant and leakage current density were evaluated for applications. Furthermore, we theoretically investigated the effects of ligand substitution on mechanism of precursor intermolecular reactions which can cause non-saturated growth by density functional theory (DFT) calculations used for revealing the reaction energy and pathways.

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AF-MoP-67 Phase-Induced Surface Free Energy Control of Plasma Enhanced Atomic Layer Deposition HfO₂ Thin Films

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Surface free energy of material is considered one of thermodynamic functions of the equilibrium state between atoms within solid/liquid interfaces, and it is directly related to the wettability of materials. Finely tunable surface free energy of materials can be utilized for various applications in need of controlling wetting behaviors depending on the types of liquids.

Ceramic films on solid surfaces have been used to adjust the wettability of materials as a robust coating. Among them, the control of wettability using hafnium oxide (HfO_2) film has been recently studied. However, due to the unpredictable factors stemming from different deposition methods, the surface free energy of HfO_2 films still lacks systematic research. Besides, the HfO_2 films showed only limited range of contact angles so far. In this paper, the surface free energy of HfO_2 films was comprehensively investigated for its determinants. With delicate control of film thickness by plasma enhanced atomic layer deposition (PE-ALD) technique, the changes in surface free energy of HfO_2 thin films were analyzed by measuring contact angles, chemical compositions, surface roughness, and film crystallinity. By minimizing ambiguous effects from other factors, we concluded that the surface free energy of PE-ALD HfO_2 films was mainly dependent on the changes of film crystallinity. Based on the control of surface free energy induced by film crystallinity, it was demonstrated that PE-ALD HfO_2 thin films showed a wide range of wetting behaviors to various types of liquids with different surface tensions.

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AF-MoP-69 Room Temperature ALD using High-Purity Ozone Gas

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Recently, low temperature (<100°C), thin (3 - 50nm) conformal metal oxide film deposition has garnered much attention for its applications as a gate dielectric, gas barrier, and as optically transparent protection on a low-heat-resistant electronic/optical devices, such as GaO high mobility devices and inorganic/organic (laminated) electro-luminescent devices. Until now, it has been demonstrated that surface-adsorbed precursors can be oxidized to metal oxides by energetically & electrically activated radicals (OH or O) generated from remote plasmas (H_2O or O_2) at low temperatures[1]. However, low temperature ALD faces two challenges: (1) due to the difficulty of exhausting residual water vapor in the chamber, a longer purge time after H_2O plasma treatment is required, which reduces the throughput; and (2) there is a tradeoff between radical concentration and the lifetime of the radicals; thus, to keep the uniformity and conformity all the way to the bottom of a high aspect ratio trench, it has been necessary to reduce radical concentration.

To overcome these challenges, we used H_2O-free, energetically thermal (equilibrium) and electrically neutral, highly concentrated (≥99%) O_3 gas as an oxidizing source. ≥99% O_3 gas works as a damage-less oxidizing source to various precursors in ALD processes; H_2O, NO_x and heavy metal contaminants are 3-4 orders of magnitude lower compared to when conventional ozonizers are utilized. In addition, due to the long lifetime of the O_3 gas at <100°C (longer than 10,000 sec), the gas can be applied to batch (e.g. 25 wafers) processing ALD equipment.

We evaluated film qualities of Al_2O_3 deposited by TMA (Trimethyl Aluminum) and ≥99% O_3 at room temperature. The typical growth rate per cycle was 0.16nm/cycle, which is higher than that of O-plasma and H_2O ALD at 200°C (0.12nm/cycle) [2].

To validate the dependence of the film quality on ozone concentration used, and the mechanism of the deposition at room temperature, we've conducted microscopic analysis using XPS, SIMS and molecular dynamic simulation. We have found that the new energetically allowable chemical path to generate OH radicals using highly concentrated O_3 with intermediates from TMA contributes the film quality. The influence of several process parameters and the concentration of ozone gas on the film quality, conformality and electric properties and a water vapor transmission rate will also be discussed detail in the presentation.

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AF-MoP-70 Atomic Layer Deposition of Zinc Oxide Thin Films using a Liquid Cyclopentadienyl-Based Precursor, bis(n-propyltetramethylcyclopentadienyl)Zinc

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Thin-film transistors using amorphous In-Ga-Zn-O (IGZO) has attracted attention due to their high mobility. We have reported the atomic layer deposition (ALD) of In_2O_3 and Ga_2O_3 thin films using cyclopentadienyl-based precursors, and these films have negligibly low carbon impurities [1, 2]. To deposit an IGZO thin film, a Zn precursor is required in addition to these precursors. Here, we report the results of the study on ALD using a cyclopentadienyl-based Zn precursor, which is also expected to deposit high-purity ZnO thin films.

As a liquid Zn precursor, bis(n-propyltetramethylcyclopentadienyl)zinc, $Zn(Cp^{pm})_2$, was synthesized. The compound was analyzed using differential scanning calorimetry to determine the thermal decomposition temperature, and it was estimated to be around 240 °C. Therefore, the growth temperature was set to 200 °C, which is the growth temperature of In_2O_3 and Ga_2O_3 films [1, 2]. The vapor pressure of the $Zn(Cp^{pm})_2$ was determined by directly measuring the equilibrium vapor pressures of the liquid and gas phases at a constant temperature. From the obtained vapor pressure, the precursor temperature was set to 120 °C.

ZnO thin films were deposited 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 (WpO) . Based on the ALD-In_2O_3 and Ga_2O_3 films deposition, a ZnO thin film was deposited for 10 cycles with pulse times for $Zn(Cp^{pm})_2$, H_2O, and O_2 plasma of 0.1, 3.0, and 50 s, respectively. The thickness of the ALD-ZnO film was as thin as 0.19 nm. Compared with GaCp*, which is used for Ga_2O_3 films deposition [1], $Zn(Cp^{pm})_2$ has a lower reactivity with H_2O. Therefore, the H_2O pulse time of WpO process was extended to 30 s, and the thickness of the ZnO film consequently increased to 0.27 nm. In the same WpO condition, the ZnO film thicknesses linearly increased to 0.47 and 0.64 nm as ALD cycles increased to 30 and 50, respectively.

For comparison, ALD using solely H_2O as an oxidant was also investigated. The film thickness at 10, 30, and 50 cycles were 0.11, 0.20, and 0.21 nm, respectively, and the film growth became saturated around 30 cycles. On the other hand, film growth was possible using solely O_2 plasma with a pulse time of 50 s, though the uniformity of film thickness became poorer.

Thus, this $Zn(Cp^{pm})_2$ is promising as an ALD precursor for a high-purity ZnO film.

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AF-MoP-71 High Volatility Precursors for ALD Process of Rare Earth Oxides

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Rare Earth Oxides (REOs) are recognized for their unique characteristics: a wide band gap, high dielectric constant, and high refractive index. As a result of those properties, REOs' films have been widely investigated for many applications such as a dielectric insulator, superconductor, optical film, and barrier film. Therefore, various rare earth precursors have been developed and suggested for decades.

From the aspects of cost-benefit, homoleptic precursors with Metal-Oxide bonds like $M(thd)_3$ and $M(OtBu)_3$ have been studied. However, they do not have either high reactivity with a co-reactant or high volatility or high thermal stability. On the other hand, metal-aminoalkoxides are widely known having good reactivity and thermal stability. In this work, novel homoleptic rare earth aminoalkoxide precursors with high volatilily, thermal stability, and reactivity was developed.

2-Dimethylamino-2-methylpropanol (dmamp), which is the most common aminoalcohol ligand, was used to synthesize $Y(dmamp)_3$. Low vapor pressure of $Y(dmamp)_3$ (1.0 torr @ 234°C) is a practical issue for commeical ALD processes. Novel YAA-6 precursor was synthesized with a new desinged aminoalcohol lingand. Vapor pressure of YAA-6 was higher than that of $Y(dmamp)_3$ (1.0 torr @ 196°C), which was an significant advantage considering low vapor pressure of REOs' precursors. Thermal stability of YAA-6 measured by DSC was high (~335°C) enoguh for practical ALD applications. Furthermore, having been heated at 200°C for more than 4 months, YAA-6 did not decompose obviously detected by TG-DTA measurement. YAA-6 precursor was applied to deposited Y_2O_3 thin film with O_3 reactant. Self-limited film growth on Si and SiO_2 substrates was observed at 250°C (Fig. 2 (a)). In addition, smooth Y_2O_3 films were observed by XSEM measurements (Fig. 2 (b)).

As a conclusion, the novel Yttrium precursor with the new aminoalkoxides lignad showed high volatility and thernal stabiltiy. Smooth ALD Y_2O_3 films were sucessfully deposited by the new Yttrium precursor. Finally, the same aminoalkoxide lingad was applied to other rare earth metal precursors such as DAA-6, EAA-6, TAA-6, BAA-6, and LAA-6. These precursors also showed high volatility and thermal stability (Table 2), which made them promsing candidates for ALD of REOs.

AF-MoP-74 Atomic Layer Deposition of Yttrium Oxide Films and their Properties of Water Wettability

***Bo Zhao**, F Mattelaer, G Rampelberg, J Dendooven, C Detavernier,* Ghent University, Belgium

Atomic layer deposition (ALD) of yttrium oxide (Y_2O_3) is investigated, using the liquid precursor $Y(EtCp)_2(iPr\text{-}amd)$ as the yttrium source in combination with H_2O, O_2 plasma and H_2O plasma. Saturation is confirmed for each investigated reactant. The saturated GPC is 0.74 Å/cycle, 0.83 Å/cycle and 1.03 Å/cycle for H_2O, O_2 plasma and H_2O plasma, respectively (Figure 1). The three processes exhibit a similar ALD window from 150 to 300 ˚C (Figure 2a). All the as-deposited Y_2O_3 films are pure (with C and N impurity levels below 0.5 at. %), smooth and with a polycrystalline cubic structure (Figure 2b), while the densities for the plasma-enhanced processes (O_2 plasma and H_2O plasma) are slightly higher than that of the thermal process .

The as-deposited Y_2O_3 films are hydrophobic with water contact angles over 90°. The water contact angle gradually increased and the surface free energy gradually decreased as film thickness increased, reaching a saturated value at Y_2O_3 film thickness of about 20nm. The hydrophobicity was retained during post-ALD annealing at 500 °C in static air for 2 h. Exposure to polar and non-polar solvents influences the Y_2O_3 water contact angle. The reported ALD process for Y_2O_3 films may find potential applications in the field of hydrophobic coatings.

The authors would like to thank Air Liquide for supplying the precursor and for interesting discussions.

AF-MoP-75 Hollow-Cathode Plasma-Assisted Atomic Layer Deposition of III-Nitrides: How the Substrate and Plasma Chemistry Impacts the Raman Spectroscopy Analysis of GaN and InN Thin Films

M Alevli, N Gungor, Marmara University, Turkey*; S Ilhom, A Mohammad, **Deepa Shukla**, N Biyikli,* University of Connecticut

Raman spectroscopy is a powerful analytical method that allows deposited films to be evaluated without complex sample preparation or labeling. However, a main limitation of Raman spectroscopy in thin film analysis is the extremely weak Raman intensity that results in low signal-to-noise ratios. Therefore, it is of critical importance to utilize any opportunity that increases the intensity of the Raman signal and to understand whether and how the signal enhancement changes with respect to the substrate material and material growth conditions employed. Our plasma-enhanced ALD experiment results show clear differences in the spectroscopic response from both GaN and InN films on different substrates. We demonstrate that the substrate surface has a pretty strong influence on the ALD-grown material properties: the spectroscopic Raman bands were observed for the GaN and InN films grown on sapphire substrates, whereas films on silicon substrates do not exhibit any characteristic Raman signal. The upshift of the E_2-high peak frequencies is corresponding to a compressive strain within the GaN films grown on sapphire, whereas a tensile strain character in InN films on sapphire is confirmed by the decrease in E_2-high mode frequency. In this work, we compare the effect of these two substrates on the structural, compositional, surface, and optical properties of GaN and InN films. Furthermore, the impact of utilized nitrogen plasma composition will be studied via Raman spectroscopy and XRD analysis, which depicts the critical H_2/N_2 ratio parameter. We'll also discuss and present our theoretical modeling efforts and compare with the spectroscopic optical measurements.

AF-MoP-76 Effect of Ligand Structure on Crystallinity of Atomic Layer Deposited Titanium Dioxide*, **Sanghun Lee**,* Yonsei University, Republic of Korea*; W Noh,* Air Liquide Laboratories Korea, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea

Titanium dioxide (TiO_2) exhibits not only amorphous but also various crystal structures such as brookite, anatase and rutile. Owing to the diversity in crystal phase, TiO_2 is a versatile material for photocatalysis, corrosion resistance coatings, microelectronic devices, and hard mask applications and its crystallinity is critical factor for their performance at the same time. With an increase in demand of highly conformal TiO_2 coating in these areas, atomic layer deposition (ALD) has been regarded as an indispensable technique for those applications and it led to an explosive growth in research on ALD TiO_2. The numerous of researches have been focused on its crystal structure, and it was widely studied that the crystallinity of TiO_2 was critically dependent on process temperature, film thickness or oxidants. Of course, the type of precursors also influences on crystallinity, as M. Ritala reported that crystalline growth of ALD TiO_2 was dependent on ligand size of alkoxide precursor.[1] However, there have been only a few studies on effect of precursor on TiO_2 crystallinity, while various metal organic precursors were developed for ALD TiO_2.

In this study, we developed ALD TiO_2 process for hard mask application where high etch selectivity and obtaining amorphous phase of TiO_2 is very important. We had comparative studies on ALD TiO_2 varying titanium precursors, one is based on alkylamide ligand while the other one is based on alkoxide with cyclopentadienyl ligand. To evaluate as hard mask material, we compared etch rate and investigated the crystallinity of ALD TiO_2. From our analysis of X-ray diffraction (XRD), we noticed that use of precursor based on alkylamide more easily evokes crystalline phase at the same film thickness and process temperature.

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AF-MoP-84 Homoleptic and Heteroleptic Alkoxide Precursors for Deposition of Aluminum Oxide Thin Films*, **Liao Cao**, F Mattelaer, G Rampelberg,* Ghent University, Belgium*; F Hashemi, R van Ommen,* Delft University of Technology, Netherlands*; M Tiitta,* VOLATEC, Finland*; J Dendooven, C Detavernier,* Ghent University, Belgium

Aluminum oxide is widely used as a barrier layer, dielectric film and encapsulation material due to its excellent chemical and thermal stability, high field strength and high resistivity. Controlled deposition of aluminum oxide thin films via atomic layer deposition (ALD) is a well-developed process with applications ranging from semiconductor electronics to large-scale coatings. The most commonly used precursor for deposition of Al_2O_3 via a thermal ALD process is trimethylaluminum (TMA). TMA has a high vapor pressure and is very reactive towards most surfaces, acting as an ideal precursor for deposition of Al_2O_3 at various temperatures. However, TMA is pyrophoric, toxic, corrosive and relatively expensive when aiming to coat surfaces at large scale, such as coating powders or roll-to-roll processes. Thus, alternative low-cost and safe precursors for deposition of alumina would facilitate economical and environmentally sustainable manufacturing.

Alkoxides are a class of precursors with less severe safety issues and lower cost, but also less reactivity than alkyls. In this work, we investigate several homoleptic aluminum alkoxides as precursors for deposition of Al_2O_3 in combination with different reagents including water, oxygen plasma and ozone. Aluminum tri-isopropoxide (TIPA) presents a growth window of Al_2O_3 from 140°C up to 300°C by using water and oxygen plasma as co-reactant. Aluminum tri-sec-butoxide (ATSB) also presents a wide growth window from 100°C up to 300°C, but with a small decomposition component above 200°C. The growth rates of deposition processes with both precursors are comparable to the thermal ALD of TMA and water (1.1Å/cycle) and all investigated processes generate smooth and conformal films.

We have also explored specially synthesized heteroleptic precursors in the hope of inheriting certain advantageous aspects from the homoleptic cases, e.g. the thermal stability of TIPA and the high vapor pressure of ATSB. Aluminum di-isopropoxyl-sec-butoxide (AiP_2sB_1) and Aluminum isopropoxyl-di-sec-butoxide (AiP_1sB_2) were synthesized and investigated with water and plasma as co-reactant to deposit Al_2O_3. The results show that the synthesized heteroleptic precursors can offer higher vaporization ability and easier precursor handling. The ALD parameters indicate a higher growth rate and wider temperature window than their homoleptic counterparts for both water and plasma processes.

The most promising homo- and heteroleptic precursors have been evaluated for large-scale coating in an atmospheric pressure ALD setup for coating powders.

AF-MoP-85 The Role of Steric Hindrance During Plasma Enhanced ALD of SiO_2*, **Chenhui Qu**, M Kushner,* University of Michigan

Plasma enhanced atomic layer deposition (PE-ALD) consists of at least two steps – precursor and plasma exposure, with gas purging between steps. In PE-ALD of SiO_2, the Si-containing precursor is first deposited, typically in a plasma-free environment, in a self-limiting step. The Si-containing precursor is typically an organic molecule, such as bis[diethylamino]silane, BDEAS $[SiH_2(N(CH_3)_2)_2]$ or tris[dimethylamino]silane 3DMAS $[SiH(N(CH_3)_2)_3]$. The surface is then exposed to an oxygen-containing plasma to remove the ligands, oxidize the Si and prepare the surface for the next passivation step. PE-ALD should be capable of depositing the equivalent of 1 monolayer/cycle. However, deposition per cycle is typically much less than 1 monolayer, and sometimes as small as 0.1 monolayers per cycle even for fully passivated, self-limiting processing. One cause of this low deposition rate is the steric hindrance caused by the Si precursor. The precursors are simply large molecules which, when adsorbed, block possible adsorption sites for other precursors. The end result is a cessation of passivation of the surface without passivating all available sites – that is, self-limiting while not being saturated. In PE-ALD, during plasma exposure, high-energy ions, hot neutrals, and UV/VUV photons can also produce defects in the film that can lead to non-saturating coverage.

In this paper, results from computational investigations of PE-ALD of SiO_2 will be discussed with a focus on the consequences of the steric hindrance of Si precursors on deposition rate and film quality (measured by defects or film density). The system is a capacitively coupled plasma sustained in Ar/O_2 gas mixtures at 1-5 Torr for the oxidation step. The target features are either blanket deposition or trench and vias with a 20-50 nm opening and an aspect ratio (AR) of 10-20. The modeling platforms are the Hybrid Plasma Equipment Model (HPEM) for the reactor scale and the Monte Carlo Feature Profile Model (MCFPM) for the feature scale. The MCFPM, a voxel-based simulator, was improved to enable deposition of large molecules that produce steric hindrance of adjacent surface sites by resolving the precursor as the central Si atom and ligand groups. The ligand groups are co-deposited with the Si so that the steric hindrance is naturally included. Results from parametric studies will be discussed for deposition rate and defect generation as a function of the degree of steric hindrance (size of precursor), plasma conditions (reactant fluxes, ion energies) and feature topology (AR, reentrant features).

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AF-MoP-86 Machine Learning for Atomic Layer Deposition: Process Optimization Based on Growth Profiles*, **Angel Yanguas-Gil**, J Elam,* Argonne National Laboratory

In recent years the areas of machine learning and artificial intelligence have experienced a tremendous growth. However, the bulk of the development has focused on non-scientific datasets, primarily visual data. In this work, we show how we can adapt some of the existing methodologies to the field of atomic layer deposition, in particular to accelerate process optimization using ex-situ data such as reactor growth profiles.

One of the challenges of artificial neural networks is that they require large amounts of training data. In order to overcome this limitation, we have used reactor scale simulations to build two synthetic datasets, one focused on 1D growth profiles for a cross-flow cylindrical reactor, and one with 2D growth profiles for a model wafer-scale reactor. In order to ensure good transferability, the simulation tools used for this work were first validated against experimental data in our laboratory.

We have then trained artificial neural networks with different architectures against these datasets to explore their ability to encode and generate growth profiles that are physically correct and consistent with ALD behavior. We have applied this approach to solve a one-step optimization problem, in which the goal is to provide optimal dose times based on just a single growth profile. After training the network for one-step optimization, the Pearson correlation between dose profiles predicted by the network and the ground truth from a testing dataset is 0.995. Our results show that artificial neural networks are capable of learning ALD profiles and provide excellent surrogate models. Similar approaches could be used for other applications, such as optimal growth profile reconstruction, the extraction of kinetic data from 2D profiles, or to evaluate the ideality of an ALD process.

AF-MoP-90 Plasma-Enhanced ALD of as-Grown Crystalline VO_x and the Evolution of its Phase Structure via Critically Tuned Post-Deposition Annealing Process*, **Adnan Mohammad**, D Shukla, S Ilhom, K Joshi, B Willis, B Wells, N Biyikli,* University of Connecticut

Vanadium dioxide (VO2) shows a low-temperature (~70 °C) phase-transition behavior due to a structural change from monoclinic phase to a tetragonal rutile phase structure. This character is defined as MIT (metal-to-insulator transition), which can be used in electrical and optical switches. In the relatively narrow ALD-grown VOx literature, growth of VOx is predominantly reported with thermal ALD recipes, in which TEMAV or VTIP are utilized as the vanadium precursor and either H2O or ozone (O3) as the oxygen co-reactant. While the as-grown films have been reported to be mostly amorphous, post-deposition annealing enabled to achieve different crystal phases of VOx, including VO2. On the other hand, no significant report is yet found on VOx films grown via plasma-enhanced ALD (PEALD), where O2 plasma is used as the coreactant. An optimized PEALD recipe towards obtaining as-grown crystalline VOx films might attract interest for certain applications where post-deposition annealing would be prohibitive.

In this work we report on the low-temperature crystalline VOx deposition in a remote-plasma ALD reactor featuring an inductively coupled plasma (ICP) source, in which we utilized TEMAV and O2 plasma as the metal precursor and co-reactant, respectively. The parameters used for the PEALD experiments are 0.03 s of TEMAV pulse with 20 sccm of Ar-carrier flow, 100 sccm Ar-purge for 10 sec, 50 sccm O2 plasma at 100W for 10 s, and finally another 10 s of Ar purge. In addition, the TEMAV precursor cylinder is heated at 115 °C in order to provide sufficient amount of precursor vapor into the growth chamber. The as-grown films are subsequently annealed in a high-vacuum chamber to observe the change in the film phase structure as a function of annealing temperature and pressure. The annealing temperature was scanned from 450 to 600 °C, while the annealing pressure was changed between 0.5 mTorr to 5 mTorr, which is controlled by O2 gas flow. The x-ray diffraction (XRD) measurements revealed crystalline V2O5 phase for the as-deposited films. A shift in the diffraction peak is observed at the samples were annealed at 0.5 mTorr, 450 and 600 °C, at which they exhibited V4O9 and monoclinic VO2 crystal phases, respectively. Increasing the annealing pressure to 5 mTorr on the other hand, has drastically reduced the XRD peak intensities and resulted in an amorphous-like VOx film. Temperature-dependent electrical characterization of the VO2 samples will be performed to verify the MIT character of the films and the results will be correlated with high-resolution x-ray photoelectron spectroscopy measurements.

AF-MoP-92 Investigating the Role of N_2 Plasma Composition on the Atomic Layer Growth of InN Films Using Hollow-Cathode Plasma Source*, S Ilhom, A Mohammad, D Shukla, J Grasso, B Willis,* University of Connecticut*; A Okyay,* Stanford University*; **Necmi Biyikli,*** University of Connecticut

In this work, we have studied the influence of N_2 plasma composition on the growth of indium nitride (InN) thin films at low substrate temperatures via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD). InN films were deposited on Si(100) substrates using trimethylindium (TMI) and variants of N_2 plasma (N_2-only, Ar/N_2, and $Ar/N_2/H_2$) as the metal precursor and nitrogen co-reactant, respectively. ALD growth experiments have been performed within 50 - 150 W plasma power range and 160 - 240 °C substrate temperature. *In-situ* ellipsometry was employed to observe individual ligand exchange events in real-time during the growth process. Additionally, *ex-situ* characterizations were done to identify the optical, structural, and chemical properties of the grown InN films. X-ray diffraction (XRD) results showed that only the samples grown at 200 and 240 °C with 100 W rf-power displayed single-phase hexagonal crystalline structure with peak intensity values increasing as a function of substrate temperature. Moreover, varying the plasma chemistry such as addition of H_2 to Ar/N_2 led to significant microstructural changes resulting in crystalline In_2O_3films. As such, x-ray photoelectron spectroscopy (XPS) measurements are carried out to further understand the possible reactions taking place with varying N_2 plasma compositions. XPS results revealed that films with Ar/N_2 plasma show near-ideal stoichiometric In:N ratios (~1:1), which becomes more nitrogen rich when only N_2 plasma is employed. However, films grown with $Ar/N_2/H_2$ plasma composition showed significant O incorporation in the films confirming the transformation from InN to In_2O_3 phase. Spectroscopic ellipsometer is utilized to study the spectral absorption characteristics of the optimal InN films with Ar/N_2 plasma to extract the corresponding optical band edge. Films grown at 200 and 240 °C exhibited high absorption components with optical absorption band edges at 2.10 and 1.78 eV, respectively, indicating crystalline InN films, while 160 °C sample with relatively lower absorption and larger band gap of 2.24 eV reminds of more porous and amorphous films with higher carbon-oxygen impurity content.

AF-MoP-93 As-Grown Crystalline β-Ga_2O_3 Films via Plasma-Enhanced ALD at Low Substrate Temperatures*, **Saidjafarzoda Ilhom**, A Mohammad, D Shukla, J Grasso, B Willis,* University of Connecticut*; A Okyay,* Stanford University*; N Biyikli,* University of Connecticut

Growing wide bandgap semiconductors, such as Ga_2O_3 and GaN at very low and CMOS compatible temperatures has attracted great research attention. In the current flexible electronics era, there is a great demand for producing high quality and in particular as-grown crystalline thin films of these materials at lower substrate temperatures.

We report on the low-temperature, as-grown crystalline Ga_2O_3 films on various substrates (Si, sapphire, glass, and Kapton) via a hollow-cathode plasma-assisted ALD system. The films were deposited using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Growth experiments were performed at 200–240 °C substrate temperature and 30–200 W 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 20 seconds scanned over 50–300 W rf-power. Both *in-situ* and *ex-situ* ellipsometry was employed to measure the thickness and optical properties of the films. The thickness of the films without Ar-annealing stage, ranged between 20.74–39.30 nm and as-grown refractive indices were between 1.75–1.67 within the scanned plasma power range. The relatively significant amount of thickness gain (39.30 nm) and reduced refractive index of the films (1.67) at the increased plasma powers (200 W) reminds of a possible plasma re-deposition of carbon-rich reaction byproducts or increased incorporation of oxygen atoms. X-ray diffraction (XRD) showed that Ga_2O_3 films grown without *in-situ* plasma annealing exhibited amorphous structure irrespective of both substrate temperature and rf-power. However, with the introduction of *in-situ* Ar-annealing the thickness of the films ranged between 22.9–31.4 nm with refractive indices of 1.75–1.79. The increased refractive index (1.79) and reduced thickness gain (31.4 nm) at 250 W Ar-annealing power indicates possible densification and crystallization of the films. Indeed, XRD and XRR confirmed that *in-situ* Ar-plasma treated films grow in a monoclinic β-Ga_2O_3 crystal phase with further improving crystallinity and film density (from 5.07 to 5.80 g/cm^3) with increasing Ar-annealing rf-power. X-ray photoelectron spectroscopy (XPS) measurement results of the β-Ga_2O_3 samples grown under varying *in-situ* Ar-annealing plasma conditions will be discussed as well, which provides additional insight into the elemental composition of the films that might help to understand the changes in the structural, optical, and electrical properties. A future outlook will be provided to overcome the challenges to achieve device quality layers on low-temperature compatible flexible substrates.

AF-MoP-94 Aluminum Oxide ALD with Hydrogen Peroxide: Comparative Study of Growth and Film Characteristics for Anhydrous H_2O_2, H_2O_2/H_2O Mixtures, H_2O and Ozone*, J Spiegelman, **Dan Alvarez**,* RASIRC*; K Andachi, G Tsuchibuchi, K Suzuki,* Taiyo Nippon Sanso Corporation, Japan

Thermal low temperature ALD has seen a resurgence in activity due to difficulties found with plasma approaches on 3D surfaces. Hydrogen peroxide reactivity may benefit low temperature growth rates and achieve improved film properties. We studied:

· Gas-phase hydrogen peroxide, delivered from an anhydrous, ampoule-based formulation by use of a membrane delivery system.

· High concentration H_2O_2/H_2O delivery by *in situ* concentration methods and use of a membrane vaporizer as a gas generator.

ALD studies on Al_2O_3 films have been conducted with the use of Trimethyl Aluminum (TMA). Growth rates of H_2O_2/H_2O, H_2O, H_2O_2 and O_3 have been observed at 100-350°C. As has been reported, growth rates drop with increased temperature. Previous works have explained that surface de-hydroxylation occurs with increasing temperature, and the slope of this decrease is significantly less for anhydrous hydrogen peroxide. This can be attributed to surface re-hydroxylation with the use of dry H_2O_2, where this oxidant can easily split into hydroxy radicals HO. The overall higher growth rates for H_2O_2/H_2O and H_2O may be attributed to the increased vapor pressure of these oxidants which provides added reactant material to the substrate surface. The H_2O_2/H_2O combination leads to the highest overall growth rate, where the effects of H_2O_2 augment the fast growth rate of water.

Initial FT-IR study was performed on films grown with H_2O_2/H_2O and H_2O; the measured signal for the hydrogen peroxide films is approximately 20% stronger. Though this measurement is somewhat qualitative, it implies that films grown with hydrogen peroxide have higher film density.

Composition of films grown by all four oxidant methods was measured by XPS; all films have near stoichiometric Al_2O_3 composition, within the experimental error of the instrument.

Initial wet etch rate studies (7.14% buffered HF) were performed on H_2O_2/H_2O and H_2O films grown at 200°C. In this instance, H_2O_2/H_2O film has an etch rate of 69.9nm/min vs 81.5nm/min for water: a 15% improvement in etch resistance.

Electrical properties of resultant Al_2O_3 films have been examined. For films grown at 300C, Dielectric Breakdown Strength was measured. Here, film grown with H_2O_2/H_2O was significantly greater than both water and ozone grown films; anhydrous hydrogen peroxide was similarly improved, but to a lesser degree. An analogous result was obtained when measuring leakage current.

An extensive film property data set with all oxidants will be presented in the temperature range of 100-350C. Correlations to surface chemistry will made along with suggestions on how to tailor film properties for specific applications.

AF-MoP-95 Indium Aluminum Nitride Growth Kinetics and Crystallinity Studied Using *In Situ* and *Ex Situ* Synchrotron X-ray Scattering*, Jeffrey Woodward,* ASEE*; S Rosenberg,* Sandia National Laboratories*; S Johnson,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; N Nepal,* U.S. Naval Research Laboratory*; K Ludwig,* Boston University*; C Eddy, Jr.,* U.S. Naval Research Laboratory

Indium aluminum nitride (InAlN) is an attractive material system due to its capabilities for lattice matching and polarization engineering with indium gallium nitride and aluminum gallium nitride. While conventional methods of epitaxial growth of InAlN are challenged by a large miscibility gap and the significant differences in optimal growth conditions for the constituent indium nitride (InN) and aluminum nitride (AlN) binary compounds, InAlN alloys throughout the entire compositional range have been successfully achieved in the form of ultra-short period superlattices known as digital alloys (DA) using plasma-assisted atomic layer epitaxy (ALEp)[1]. However, the realization of ALEp-grown InAlN films of sufficient quality for device applications requires a deeper understanding of the nucleation and growth kinetics, and their correlation with the resultant crystalline structure. To this end, grazing incidence small-angle X-ray scattering (GISAXS) using synchrotron radiation has been established as an effective technique for the real-time *in situ* study of nanoscale surface topography during the ALEp growth of III-N films[2]. In addition, access to a synchrotron light source motivates the use of grazing incidence wide-angle X-ray scattering (GIWAXS), which probes order at atomic length scales, as a powerful method to investigate the crystal lattice of the film.

In this work, we present real-time *in situ* GISAXS and *ex situ* GIWAXS studies of InAlN DA ALEp growth on GaN performed at the ISR and CMS beamlines of Brookhaven National Laboratory's NSLS-II, respectively. Two sample sets were investigated – one in which the target stoichiometry was varied across the entire compositional range, and another in which the superlattice period was varied while the target stoichiometry remained fixed at 62% InN. The GIWAXS results indicate that order within the InAlN crystal structure increases with both the In content and the superlattice period.

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AF-MoP-96 Potential of Guanidinate and Amidinate Gallium Complexes as Precursors for Atomic Layer Deposition*, N Schneider,* ***Paul-Alexis Pavard,*** CNRS-IPVF, France*; S Bellemin-Laponnaz,* CNRS, France*; C Gosmini,* École Polytechnique CNRS, France*; D Lincot,* CNRS-IPVF, France*; A Auffrant,* École Polytechnique CNRS, 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 also 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.

This communication focuses on the development of new efficient gallium precursors to be used in the ALD of oxygen-free gallium-containing sulphide thin films.[1] The target ligands are guanidinate and amidinate, as these are known for their relative ease of synthesis and their thermal stability. Indeed, amidinate guanidinate-based complexes of tantalum, titanium and lanthanides have been tested as ALD precursors.[2] A series of gallium guanidinate and amidinate complexes were synthesized by tuning the substituents on both the endocyclic carbon atom of the ligand backbone and the ones on the nitrogen atoms, or by inserting alkyl or halide ligands in the coordination sphere of the gallium centre.[3,4] The evolution of the formed complexes was followed by in-situ NMR. To shed light on the transport of the reagents in ALD, transport conditions were mimicked by subliming gallium complexes.

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

Atomic Layer Etching Poster Session

ALE-MoP-3 Density Functional Theory Study on the Reactions of Fluorine-Containing Molecules on Silicon Nitride Surface*, Tanzia Chowdhury,* *R Hidayat, H Kim,* Sejong University, Republic of Korea*; T Mayangsari,* Universitas Pertamina, Indonesia*; S Park,* Wonik IPS, Republic of Korea*; J Jung, W Lee,* Sejong University, Republic of Korea

Silicon nitride is one of the most extensively used silicon-based materials in semiconductor devices. It has been used as gate spacers and diffusion barriers for many decades and was recently introduced to the charge trap layer and the sacrificial layers for three-dimensional (3D) NAND devices. The integration of silicon nitride into these devices often requires selective removal of silicon nitride against other materials, such as silicon oxide or silicon, and vice versa. With the continuing device miniaturization, atomic-scale processes such as atomic layer etching (ALE) has been developed for controlled removal of thin layers. ALE consists of the modification of the surface and the removal of the modified layer. The species used to modify the surface plays a crucial role in the overall process. The ALE of silicon nitride was reported by the modification by CH_3F gas adsorption and the removal of the modified layer by Ar ion bombardment [1]. However, the comparative study on the interaction of different gaseous fluorine-based molecules with the silicon nitride surface is yet to be presented. Ab initio atomic-scale simulation can be a convenient method to study the underlying surface chemistry as well as to outline new etching process routes. Previously, we modeled and simulated the initial fluorination reactions of SiO_2 and Si surfaces by various fluorine-containing gas molecules [2]. In the present study, density functional theory (DFT) calculations have been employed to investigate the initial reaction of fluorine-containing molecules on an NH_2 and NH-terminated Si3N4 surface. We chose a comprehensive set of hydrofluorocarbons and hydrogen fluoride, such as CF_4, CHF_3, CH_2F_2, CH_3F, and HF. Surface reaction mechanisms were studied by modeling and simulation of possible reaction pathways to determine the adsorption energy, activation energy, reaction energy, and desorption energy. Finally, we compared the reactions on the Si_3N_4 surface with the reactions on the OH-terminated SiO_2 and H-terminated Si surfaces.

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ALD for Manufacturing
Room Arteveldeforum & Pedro de Gante - Session AM-MoP

ALD for Manufacturing Poster Session

AM-MoP-1 Comparative Study of ALD Barrier Oxides for Moisture Barrier Applications in LED Manufacturing*, Sebastian Taeger,* *M Mandl,* OSRAM Opto Semiconductors GmbH, Germany*; R Ritasalo, T Pilvi,* Picosun Oy, Finland*; R Tomasiunas, I Reklaitis,* Vilnius University, Lithuania

Light emitting diodes (LEDs) have been tremendously successful in the last decade, both in replacing traditional light sources in most lighting applications and enabling new products related to signaling, visualization and illumination. This success story was accompanied by a significant technological evolution of LED devices, making them significantly more complex. Besides this, upcoming challenges like integration of LEDs and ICs on chip level and the development of micro-LEDs will pose new challenges for materials and processes required for LED manufacturing.

Atomic layer deposition (ALD) technique has traditionally been used for controlled deposition of high-quality thin films for the semiconductor industry. Furthermore, its capability to deposit a wide range of materials as conformal and pinhole-free films on challenging substrates and topographies makes it a valuable tool for LED makers to tackle the challenges ahead.

Used in LED devices, ALD films can serve or contribute to electrical and chemical passivation layers, reflective or anti-reflective coatings and moisture barriers for example. Choosing the right combination of materials and processes for each application based on existing literature is not easy since most studies focus either on a specific material or specific materials properties.

In this work we have done a material screening of several ALD oxides, including varying oxygen source (H_2O/O_3) and deposition temperature (100°C-300°C depending on material) to find the best solutions for LED applications. The selected materials included Al_2O_3, Ta_2O_5, SiO_2, Nb_2O_5, TiO_2, HfO_2, ZrO_2, and Y_2O_3. The PICOSUN® 200 Advanced ALD reactor was used for the depositions.

Electrical, optical, morphological and chemical properties of the films were studied. For comparison of water vapor transmission rates (WVTRs) in a realistic setup, a specific capacitive sensor developed by OSRAM [1] was employed.

This sensor device basically consists of a hygroscopic sensor dielectric placed between metal electrodes. The top electrode is perforated to enable moisture penetration into the sensor dielectric. The whole device is encapsulated with the moisture barrier material under test. In a controlled hot and humid environment, water molecules penetrating though the barrier layer are absorbed in the sensor dielectric and increase the capacity of the sensor. From the rate of capacity increase, the WVTR of the barrier layer can be derived.

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AM-MoP-3 Advanced 3D Particle Functionalization using Self-Limiting Reactions in Fluidized Bed Reactor Technology*, Didier Arl,* *T Da Cunha, A Maulu, N Adjeroud, K Menguelti, M Gerard, D Lenoble,* Luxembourg Institute of Science and Technology, Luxembourg

High specific surface powders in polymeric or inorganic matrices requires a fine control of their properties. The design of these nanoscopic agents is linked to the development of nanotechnology processes which can be transferred from planar substrates to complex 3D surfaces. In this framework we showed how self-limiting reactions inspired by Atomic Layer Deposition can be applied to functionalize powder by using a specifically designed Fluidized Bed Reactor. A specific interest has been given to work in non-saturated regime with nickel or Cobalt acetylacetonate to obtain well controlled metal nanocatalysts of 5-10nm diameter. Depending on the process window, some interesting properties have been demonstrated such as ferromagnetic behavior or the systematic recover of the Metal-Carbide phase that increase the throughput of Carbon Nanotubes growth. These activated nanostructures can expressly improve the electrical, the thermal or the mechanical properties of some related composites depending on how some processing parameters such as exposure time, pressure or local temperature can be tailored.

AM-MoP-5 Wafer Scale Conformality using Lateral High Aspect Ratio Test Structures*, Oili M.E. Ylivaara,* *F Gao,* VTT Technical Research Centre of Finland Ltd, Finland*; R Puurunen,* Aalto University, Finland*; M Utriainen,* VTT Technical Research Centre of Finland, Finland

The development of the conformal thin film process is at high importance, especially in 3D memory applications. High aspect ratio structures, new materials, and demanding geometries are challenges for the tool manufacturers, material developers, and in inspection and testing. PillarHall® Lateral High Aspect Ratio (LHAR) silicon test chip has proven its value in conformality metrology and elemental mapping of the trench wall [1-5] where single chip on the center of a carrier has been a typical approach. Here, we examined the PillarHall® test chip compatibility to wafer level conformality mapping using specially designed PillarHall® LHAR4 small chips, on a 150-mm wafer scale with a silicon-based chip holder to enable attachment of multiple chips on a selected wafer locations. Studied process was Al_2O_3 made by ALD at 300 °C using 500 cycles in Picosun R-150 ALD reactor with variable pulse-purge sequences. Chips were stabilized in the process chamber for 30 minutes at ALD temperature, before the process was started.The film thickness was measured with spectroscopic reflectometry SCI FilmTek 2000M using 49 pts and 100 pts measurement for full wafer and for the LHAR4 chip, respectively. The film thickness on planar surface, 150-mm wafer was 47.3±0.2 nm which was in-line with the film thicknesses measured from opening of the LHAR4 chips, varying from 45.8 to 48.3 nm. The half thickness penetration depth, $PD^{50\%}$ varied a from 184 to 232. The reason and repeatability for the variation in the $PD^{50\%}$ across the 150-mm wafer are still unconfirmed and can be e.g. due to small gradients in temperature and pressure, and precursor flow designs in the reactor system. Although reasons of conformality variations at wafer level are not well-known, PillarHall® provides information of the minimum reachable aspect ratio. This information can be used to develop experimentally process parameters for specific aspect ratio requirements for the full wafer area. Furthermore,the presented platform enables easy and fast methodology to improve understanding of the factors influencing on the wafer level conformality.

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AM-MoP-6 P-Type Semiconductor Cu_2O Deposited via Atmospheric Pressure Spatial Atomic Layer Deposition: A Step Towards Low-Cost Photovoltaic Solar Harvesters*, Abderrahime Sekkat,* *D Bellet,* Grenoble INP/CNRS, France*; A Kaminski-Cachopo,* IMEP-LaHC, France*; G Chichignoud,* SIMAP, France*; D Muñoz-Rojas,* Grenoble INP/CNRS, France

Cuprous oxide (Cu_2O) is a non-toxic and abundant p-type semiconductor with a direct band gap around 2.1 eV and a large visible absorption coefficient. It has been studied and developed for several devices such as solar cells, thin film transistors or batteries. In this study, an innovative technique for depositing conformal and high-quality thin films, AP-SALD (Atmospheric Pressure Spatial Atomic Layer Deposition), is used to deposit Cu_2O at low temperatures (up to 260 °C), under atmospheric pressure for photovoltaic applications. AP-SALD is an alternative approach to conventional ALD in which the precursors are separated in space rather than in time, allowing fast deposition rates as compared to conventional ALD (up to nm/s in some cases).

The aim is to optimize the low-cost Cu_2O deposition by AP-SALD on different substrates, even flexible, with a control over growth rate and transport properties (mobility and concentration of carriers). The effect of deposition parameters has been carefully studied, and mobility values of 91 $cm^2V^{-1}s^{-1}$ have been obtained, close to values associated to epitaxial Cu_2O thin films or Cu_2O single crystals. Optimized Cu_2O thin films, combined with n-type ZnO also deposited by AP-SALD, lead to all-oxide solar harvesters with efficiency rivaling values for similar devices made with high temperature and/or vacuum approaches. This shows that AP-SALD is a suitable approach to fabricate all-oxide solar harvesters, on both glass and flexible substrates.

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

EM-MoP-5 First Principles Modelling of Growth of Hybrid Organic-Inorganic Films*, **Arbresha Muriqi**, M Nolan,* Tyndall National Institute, Ireland

Organic-inorganic hybrid materials are a unique class of materials with unique properties which means they are useful in flexibile devices. Molecular layer deposition (MLD) offers novel pathways for the fabrication of such hybrids by using metallic precursors and a vast range of organic precursors. To investigate and understand the mechanism of growth and stability a combination of theoretical and experimental data is needed.

In this contribution, we present a first principles investigation of the molecular mechanism of the growth of hybrid organic−inorganic thin films of aluminium alkoxides, known as ”alucones” grown by MLD. We focus on the interactions between precursors and this is explored by analyzing the MLD reaction products between the post-TMA Monomethyl-Al_2O_3 (Al-CH_3-Al_2O_3) and Dimethyl-Al_2O_3 ($Al(CH_3)_2$-Al_2O_3) surface and the organic precursors ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG) and tetraethylene glycol (FEG). The energetics of the reaction of alumina with ethylene glycol (EG) and glycerol (GL) precursors are also investegated in detail to assist the interpretation of experimental findings regarding the differences in the hybrid films grown by EG and GL. The DFT calculations show that while the organic precursors can bind to the TMA fragements via formation of Al-O bonds and loss of CH_4, it is most favorable for the organic precursors to lie flat and create so-called double reactions through two terminal hydroxyl groups with the surface fragments, where the terminal groups bind to Al. For EG this potentially removes all the active sites and growth will be less favourable. For GL the third hydroxyl group is available and growth can proceed. We also showed that the TMA in the next pulse reacts favourably with this OH from GL. The longer the chain length the harder it is for the organic precursor to stay straight and not create double reactions. This investigation contributes to the understanding of growth process of EG-alucones and GL-alucones at the molecular level and is valuable in supporting experimental data on hybrid film growth.

EM-MoP-7 Thermal Atomic Layer Deposition of Aluminum Nitride using a Liquid Aluminum Dihydride Complex and Ammonia*, J Choi, D Ma, J Kim,* UP Chemical Co., Ltd., Republic of Korea*; T Chowdhury, R Hidayat, H Kim, W Lee,* Sejong University, Republic of Korea*; **Wonyong Koh**,* UP Chemical Co., Ltd., Republic of Korea

Aluminum nitride is a wide bandgap III-V compound with excellent thermal conductivity, high electrical resistivity, diffusion barrier properties, piezoelectric properties, and self-protection in oxidizing environments at high temperatures. It has been studied for various applications in electronics, optoelectronics, and microelectromechanical systems. Aluminum nitride thin films can be fabricated by physical vapor deposition, high-temperature chemical vapor deposition, and atomic layer deposition (ALD) techniques. ALD has several advantages including low process temperature, atomic-scale control of film thickness, and excellent step coverage on nanostructures. Aluminum chloride ($AlCl_3$), trimethylaluminum (TMA), tris(dimethylamido)aluminum (TDMAA), and tris(diethylamido)aluminum(TDEAA) were investigated as the aluminum precursor, and ammonia (NH_3) was used as the co-reactant. $AlCl_3$ is a solid and needs high deposition temperatures (≥500°C). Corrosive byproducts are also a concern. TMA exhibits a very narrow ALD temperature window near 350°C, below which the growth rate is very low due to poor reactivity of NH_3. Above that temperature, the TMA decomposes, resulting in the growth rate higher than monolayer growth. TDMAA and TDEAA have better reactivity with NH_3, but the thermal decomposition of the precursor limits the ALD temperatures to 250°C or lower, resulting in low film densities, low crystallinity, and high oxygen concentration [1]. In this work, we prepared high-quality ALD aluminum nitride films using a liquid aluminum dihydride complex and NH_3 at 300°C or higher temperatures. The deposited thin film had a composition in which the ratio of Al and N was 1: 1. Oxygen impurities were not detected by XPS after sputter etching of the surface layer. The ALD aluminum nitride of this work showed nearly 100% step coverage in the pattern with the aspect ratio of 10. The reaction of the precursor of this work with NH_3 or NH_2-terminated AlN surface was simulated by density functional theory (DFT) calculation and was compared with the reactions of other aluminum precursors.

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EM-MoP-9 Quinizarin: A Large Aromatic Molecule Ideal for Atomic Layer Deposition*, **Per-Anders Hansen**, O Nilsen,* University of Oslo, Norway

Atomic layer deposition is a remarkable synthesis tool due to the vast array of materials that can be deposited and the complexity of structures that can be designed. The low temperature layer-by-layer approach even allows organic and inorganic components to be combined as hybrid or composite materials. However, for organic and hybrid materials, it is challenging to find suitable precursors with large aromatic systems that are also can be sublimed and have necessary reactivity. This is a major barrier for using organic components for dye sensitized solar cells or luminescence, visible light photochemistry, chemical sensors and organic electronics with this technique.

In this work we introduce a well known orange dye molecule, quinizarin. This molecule has a large conjugated aromatic system with strong absorption of visible light and show strong luminescence both in solution and its resulting complex together with aluminium ions. Interestingly, quinizarin also show surprisingly good properties for film deposition due to reactive –OH groups and low sublimation temperature (130 °C). Strongly coloured pink hybrid films was deposited with trimethylaluminium and quinizarin at 175 °C with a growth rate of 0.76 nm/cycle with about 15 % thickness gradient for samples space 5 cm apart along the gas stream. The low sublimation temperature, good reactivity and large conjugated system of quinizarin opens up for explorations of solid state hybrid and organic films based on this molecule along many different technological paths.

EM-MoP-10 Superconducting and Insulating Nitride-Based Thin Films Deposited by Plasma Enhanced Atomic Layer Deposition*, I Gonzales Diaz-Palacio, L Ehmcke,* Universität Hamburg, Germany*; K Furlan,* Technische Universität Hamburg, Germany*; M Wenskat, W Hillert, R Blick, **Robert Zierold**,* Universität Hamburg, Germany

New concepts and materials for superconducting radio frequency (rf) systems have to be investigated to replace the bare niobium cavities, which are close to the theoretical performance limit nowadays. These novel approaches have the potential to further push the achievable accelerating fields and to reduce rf losses which in turn decrease operational costs or increase operational flexibility.

Here we report about thin film deposition of titanium nitride, niobium nitride, and mixtures of them by plasma enhanced atomic layer deposition from tetrakis(dimethylamino) titanium (TDMAT) and (t-butylimido)tris(diethylamino) niobium (TBTDEN) as metalorganic precursors. An adjustable ratio of nitrogen and hydrogen gas is used as co-reactant.

Structural and superconducting properties of the deposited thin films are characterized and optimized with respect to the deposition parameters, e.g. plasma power, plasma time, gas composition, and temperature. Specifically, in addition to the critical temperature and field, we reveal (i) a transition to an effective 2D electronic system and (ii) weak antilocalization in our titanium nitride films in low temperature magnetotransport studies proving the high quality and low impurity content.[1,2]

Furthermore, we compare the physical and structural properties of the superconducting thin films grown on insulating aluminum nitride, which has been deposited from trimethyl aluminum and a N_2/H_2-plasma without vacuum break, to oxygen- and hydroxyl group-terminated substrates such as Al_2O_3 or SiO_2 coated silicon wafers.

Our experimental studies lead to new insights in the ALD growth of superconducting nitrides and might be a stepping stone to ALD-deposited superconducting-insulator multilayer structures, which are treated as one of the most promising approaches to overcome the physical limitations of bare niobium cavities.

We acknowledge financial support by the German Federal Ministry of Education and Research (BMBF) via the project SMART.

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EM-MoP-15 Low Temperature Thermal a-SiC Deposition Using Pulse CVD and ALD*, **Susumu Yamauchi**, M Fujikawa,* Tokyo Electron Technology Solutions Limited, Japan*; T Miyahara,* TEL Technology Center, America, LLC

Semiconductor manufacturing processes are becoming increasingly complex and miniaturized year by year in order to achieve high performance, low power consumption and low manufacturing costs. From thin films point of view, this can be translated that thin films are required to be deposited at lower temperature, with high conformality and sometimes required to have high etch selectivity to other materials.

Despite enormous number of thermal SiO_2 and SiN deposition at low temperature < 450 ℃, not many thermal a-SiC deposition have been reported at low temperature. Most of SiC have been deposited at > 700 ℃ which might not be favorable to implement in manufacturing. On the other hand there are a lot of precedent reports of a-SiC deposition at low temperature which have done by plasma process. The authors agree with the usefulness of plasma enhanced deposition, but in the coming semiconductor manufacturing process with advanced scaling, there are concerns of conformality and plasma-induced damages.

Therefore, the authors have utilized thermal reaction without plasma enhancement to a-SiC thin film deposition (CVD, pulse-CVD and ALD) at low temperature. Several acetylene compounds have chosen as carbon precursor and disilane (Si_2H_6) has chosen as silicon precursor respectively. All of samples were deposited with CVD/ALD capable vacuum reactor. Precise process control has been established over wafer temperature, pressure and gas flow at every single process step. Detail physical characterization was carried out to study a-SiC film properties. Firstly, films were measured with SEM and ellipsometry to obtain thickness as well as deposition rate or growth per cycle (GPC). XPS measurement showed stoichiometry of deposited film and spectra were deconvoluted to analyze distribution of bond state as further research. EDX combined with TEM was also implemented to some of samples. Film density was measured with XRR. In-film hydrogen concentration was measured by HFS. Conformality of deposited film was inspected with TEM and SEM.

Thermal a-SiC was successfully deposited at ≥ 400 ℃. Typical deposition rate or GPC of pulsed CVD and ALD were 0.60 Å/cyc and 0.32 Å/cyc respectively. Film stoichiometry were Si/C/O = 51/47/2% with pulse-CVD and Si/C/O = 49/44/7% with ALD respectively. XPS peaks deconvolution for both Si2p and C1s indicated that ≥ 80% of silicon and carbon formed Si-C bond. Film density was ~ 2.3 g/cm^3. Step coverage of film was confirmed with A/R = 1:3 to 1:7 trenches and which showed good conformailty. Dry etch rate was 8.2 to SiO_2 and 7.8 to SiN respectively.

EM-MoP-16 Novel Approach for Conformal Chemical Vapor Phase Deposition of Ultra-Thin Conductive Silver Films*, **Sabrina Wack**, P Lunca Popa, N Adjeroud, R Leturcq,* Luxembourg Institute of Science and Technology, Luxembourg

The present work demonstrates a novel approach for the conformal deposition of ultra-thin conductive silver (Ag) films on complex substrates. Using an original multi-step plasma-enhanced approach, we demonstrate the deposition of conductive silver films with thickness down to 11 nm. Conductive ultra-thin Ag films are commonly deposited by physical vapor deposition techniques (metal evaporation or sputtering). However, these are line-of-sight methods that do not allow conformal deposition on substrate with complex morphology (e.g. trenches) [1]. Non line-of-sight methods such as the ones based on chemical vapor phase deposition (Chemical Vapor Deposition-CVD or Atomic Layer Deposition-ALD) usually produce non-electrically-conductive films for thickness below 20-50 nm due to island formation by Volmer-Weber growth mode for metal layers on oxide-based substrate [2]. Moreover, conductive ultra-thin silver films based on ALD (down to 22 nm) [3], require low-temperature deposition (below 120 ºC), with a very narrow process temperature window (about 10 ºC).

The deposition is based on Ag(fod)(PEt_3) as silver precursor, and H_2 plasma as reducing agent. An acceptable process temperature window (> 30 ºC), and a deposition temperature larger than 120ºC for enhanced uniformity and deposition rate have been demonstrated. In these conditions, highly uniform deposition on bent and batched samples have been performed. 20 nm thick films exhibit a resistivity down to 40 μΩ·cm. The resistivity increases up to 1.4 mΩ·cm when reducing the thickness down to 11 nm. The critical thickness as low as 11 nm is thus very close to the state-of-the-art for sputter-deposited thin films [4], and well below the 22 nm obtained with ALD [3]. The obtained Ag thin film also demonstrates a high reflectance up to 94% and a low absorbance of 3% in the infrared region for a film thickness of 36 nm, showing the high quality of the films. This quality is confirmed by morphological analysis using scanning electron microscopy and atomic force microscopy, as well as by the structural (X-ray diffraction) and chemical (energy dispersive X-ray spectroscopy) properties. This new processing approach opens a very interesting path for the use of ultra-thin silver films for electronic and optoelectronic applications.

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EM-MoP-17 When ALD Outperforms MOCVD: Direct Comparison of Epitaxial InN Films*, **Chih-Wei Hsu**, P Deminskyi, I Martinovic, J Palisaitis, H Pedersen,* Linköping University, Sweden

The successful development of III-nitride semiconductors and their alloys for light-emitting and power electronics has attracted tremendous attention over the past few decades. InN, with direct band gap of 0.7 eV and high carrier mobility, has been suggested to play a key role in extending the LED toward infrared and lifting the operating frequency of a high-electron-mobility transistor. However, the utilization of InN in device structures is rare due to the challenges of integrating high quality InN as active layers in between other matrix material.

In this work, homogeneous and epitaxial InN layers with well-controlled thickness grown on GaN and SiC by using plasma ALD is presented and compared to InN grown by conventional Metal-Organic Chemical Vapor Deposition (MOCVD). Trimethyl indium and NH_3 are used as precursors in both plasma ALD and MOCVD with the main difference of it being supplied in a plasma discharge in the case of plasma ALD. The morphological and structural properties of the resulting materials are characterized by using scanning electron microscopy, atomic force microscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The surface profiles and the surface roughness of InN grown by ALD are nearly identical to those of GaN and SiC. In contrast, scattered hill-rock features are observed on InN grown by MOCVD. Despite the difference in morphology, the InN grown by ALD and MOCVD have the same hexagonal wurtzite structure and is epitaxially grown on GaN and 4H-SiC with the growth direction of <0002>. The full-width-half-maximum of XRD rocking curve of InN (0002) is well-reproduced depending on the quality of underlying material; the measured values for our ALD grown InN (0002) are between 150-200 arcsecond for InN on GaN and between 20-30 arc seconds for InN on 4H-SiC. This result is better than any other reported value for InN (0002) rocking curves. The observation of interference fringes in the vicinity of InN (0002) suggests very smooth InN layer with sharp interface grown by ALD. Such features are absent in InN grown by MOCVD. The well-resolved lattice images obtained in our TEM investigation further confirm the epitaxial relationship between InN and its underlying materials.

In summary, the InN grown by ALD results in smooth and homogeneous films with good crystalline quality while the InN grown by MOCVD results in hill-rock structures after relaxation. Our results suggest that ALD is a promising growth technique that can enable the use of InN layer in optoelectronic applications.

EM-MoP-19 Solution-Based ALD Routes Towards Thin Films of Organic-Inorganic Hybrid Perovskites*, **Vanessa Koch**, M Barr, P Büttner, I Mínguez-Bacho, D Döhler, J Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany

Organic-inorganic hybrid perovskites are not yet accessible with conventional Atomic Layer Deposition from the gas-phase (gALD). Therefore, a method to deposit such materials in a precise and controllable manner is necessary. We present two procedures to grow organic-inorganic hybrid perovskite thin films with 'solution Atomic Layer Deposition' (sALD), a technique which transfers the principles of ALD from the gas phase to liquid processing at ambient conditions. The first route entails two steps: the successful deposition of polycrystalline PbS thin films on planar and nanostructured substrates *via* sALD with subsequent conversion to the hybrid perovskite methylammonium iodoplumbate (methylammonium lead iodide, MAPI, $CH_3NH_3PbI_3$). The second route paths the way to a direct deposition of hybrid perovskites including lead-free phases. These materials can then serve as light-absorbing layers in thin film solar cells.

EM-MoP-21 Development of ALD Copper Oxide and Al:Cu_xO Films*, J Avila, C Eddy, Jr., **Virginia Wheeler**,* U.S. Naval Research Laboratory

Thin film metal oxide semiconductors that exhibit p-type conductivity are advantageous for a wide variety of applications, such as photovoltaics and high power electronics. Copper containing materials, like Cu_2O and $CuAlO_2$, are promising p-type oxides due to O-Cu-O structure facilitating hole carriers through copper vacancies.[1,2] Additionally, the wide bandgap of $CuAlO_2$ (3.5 eV) results in ~70% transparency of visible light[1], which is useful for transparent conductors. ALD of Cu_2O or $CuAlO_2$ would allow conformal thin films on a variety of substrate materials and complex architectures required for many new applications. There are few studies demonstrating the growth of either Cu_2Oor $CuAlO_2$ by ALD,[2] and even fewer showing the systematic effect of digitally doping of Cu_2O films with increasing amounts of Al on film quality. In this work, the chemical, structural, and electrical properties of ALD grown Al:CuO films will be assessed as a function of increasing amounts of Al.

Due to its relatively high growth rate, deposited crystallinity,[3] and stoichiometric modularity, Bis(dimethylamino-2-propoxy)copper(II) (or Cudmap) was used with ozone to deposit CuO films at 150°C CuO films were digitally doped with individual Al_2O_3 -cycles using trimethylaluminum (TMA) and ozone. The ratio of Al_2O_3 to CuO cycles was varied from 2-50 cy%. Initial films indicate that only 2 cy% of Al is needed to reach stoichiometric 1:1 ratio with Cu, and dramatically changes the properties of the film resulting in increased growth rate and reduced film crystallinity. Furthermore, XPS analysis of a 50 cy% films, indicates that TMA reduces the CuO film to a mixed Cu--$^{+}$/Cu^{2+} oxidation state.

The influence of crystallinity on the electrical properties of Al:CuO films was studied through post-deposition annealing. Initially, CuO films were annealed to determine the parameters required to crystallize and reduce CuO to Cu_2O, the necessary stoichiometry for $CuAlO_2$ films. Oxygen pressure was crucial to attaining continuous films with the required crystalline structure and phase, while temperature and time were less impactful. Specifically, a low pressure of 0.1 mTorr of O_2 is required to achieve crystalline Cu_2O from the as-deposited CuO ALD film. Using the established optimized annealing conditions, the effect of Al incorporation on the final film crystallinity, morphology and electrical properties was assessed as a means towards realizing usable p-type oxide films for optoelectronic devices.

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EM-MoP-23 Photoactive Hybrid Thin Films by Molecular Layer Deposition*, Melania Rogowska,* *P Hansen,* University of Oslo, Norway*; H Valen,* Nordic Institute of Dental Materials, Norway*; O Nilsen,* University of Oslo, Norway

Photoreactive surfaces can be utilized in solar cells, light sensors and photocatalytic processes for water purification systems or antimicrobial coatings. One of the promising method to design such photoactive materials is to extend the light absorption towards the visible light region by combining inorganic transition metal clusters with highly aromatic organic molecules. Molecular layer deposition (MLD) is a suitable tool to fabricate such structures with an excellent thickness control.

In this study we have produced organic-inorganic hybrid materials with photoactive properties based on 2,6-naphthalenedicarboxylic acid as the absorber and organic building unit, and Ti, Zr, Hf or Y as metal centre. We characterized the growth dynamics and physicochemical properties of our surfaces with in-situ QCM, FTIR, UV-Vis and photoluminescence (PL) measurements. The films are amorphous as deposited and prove strong photoactivity and photoluminescence. The growth dynamics

is dependent on the choice of a metal and our current focus is in identifying the effect of chemistry on the growth and material properties.

In all deposited systems, the strong near-UV absorption of the organic precursor is broadened and

red-shifted when the organic molecule binds to a metal atom. The PL characterization proves that the presence of different metal clusters change the optical emission of hybrid systems and moreover

Ti-O clusters quench the emission from the organic linker. It was also found that the emission of light from the photoactive materials decreases upon UVC exposure, showing photobleaching effect.

EM-MoP-24 Inducing Conductivity into Parylene C by Vapor Phase Infiltration of In_2O_3*, Oksana Iurkevich,* *E Modin,* CIC nanoGUNE BRTA, Spain*; I Šarić, R Peter, M Petravić,* University of Rijeka, Croatia*; M Knez,* CIC nanoGUNE BRTA, Spain

The development of material for future electronics does not only rely on increasing the computational efficiency, but also on including completely novel functionalities, such as foldability. Hybrid organic-inorganic materials are especially promising for this task as they may combine the properties of inorganics, such as electronic conductivity, with the flexibility of organic polymers.

A hybrid system, consisting of a semiconducting material blended with a polymer matrix, may be beneficial over conventional approaches that rely on coatings and well-defined interfaces between the two materials. Vapor phase infiltration (VPI) meets this challenge by allowing diffusion of a precursor into the bulk of a soft substrate. VPI on polymer substrates leads to the formation of a gradient hybrid layer with altering density and smooth transition from the bulk polymer to the inorganic thin film on the surface (Fig.1). This gradient layer can compensate mechanical stress and suppress crack formation upon bending, thus preventing the loss of electrical conductivity upon bending, folding, or stretching.

In this work, we developed a VPI process of indium oxide by exposure of parylene C to alternating pulses of trimethylindium and water precursors. Parylene C is a CVD-deposited polymer with high thermal tolerance. The infiltration process was performed in the temperature range from 130 to 210ºC. Despite the film growth even at low temperatures, the sheet resistance of those structures remained high at 130ºC. Substitution of the water with hydrogen peroxide allowed to decrease the sheet resistance value by five orders of magnitude and highlighted the importance of the oxygen source choice. For higher infiltration temperatures this difference decreased to one order of magnitude for water and H_2O_2 precursors. However, the precursor choice made a significant impact on the infiltration depth, chemical distribution of the elements, and crystallinity. Moreover, transmission electron microscopy showed that in the case of hydrogen peroxide, there is no thin inorganic film growing on top of the surface, but the whole surface remained hybrid. Such functionalization of the dielectric polymer with electronically conductive material is a promising approach for the development of novel foldable organic electronic devices.

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

EM-MoP-26 Solution Atomic Layer Deposition of Cu-BDC SURMOF Thin Films*, Maïssa K. S. Barr,* *S Nadiri,* Friedrich-Alexander University of Erlangen-Nürnberg, Germany*; D Chen, P Weidler,* Karlsruhe Institute of Technology, Germany*; H Baumgart,* Old Dominion University*; J Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany*; E Redel,* Karlsruhe Institute of Technology, Germany

Transferring the principles of atomic layer deposition (ALD), known with gaseous precursors, to precursors dissolved in a liquid generalizes established methods such as the 'layer by layer' growth or the 'successive ion layer adsorption and reaction' (SILAR). This 'solution ALD' (sALD) shares the fundamental properties of standard 'gas ALD' (gALD), especially the self-limiting growth and the ability to coat deep pores.

It is particularly interesting in the case of ionic solid or polymers. In the specific case of metal-organic fameworks (MOF), the use of sALD appears as a method of choice. Indeed the usual processes such as spray coating, spin coating and dip coating do not offer a control at the scale of individual units (molecules or ions). So far, only few processes from the gas phase, including ALD, have been reported due to the competition of the growth and the thermal decomposition of the MOF at elevated temperature under vacuum.

In the following the deposition of a surface-anchored metal-organic framework (SURMOF) is described. The optimization of the deposition conditions is studied for the growth of Cu-BDC by sALD. Copper acetate and benzene-1,4-dicarboxylic acid (BDC) are used as the copper source and the linker, respectively. The purge and pulse durations are varied independently and demonstrate the self-limiting feature of this sALD reaction. The morphology of the films is observed by scanning electron microscopy and atomic force microscopy. The films are crystalline MOF is identified by x-ray diffraction and TOF-SIMS. The thin SURMOF films obtained by sALD exhibit a quality superior to layers obtained by spray and dip coating: in particular, the films are continuous and uniform after only 10 cycles already.

EM-MoP-29 ALD-Grown Gallium Oxide Thin Films with Properties Close to Bulk Wafers*, Elham Rafie Borujeny,* *K Cadien,* University of Alberta, Canada

Gallium oxide is a wide bandgap material (Eg ~ 4.6eV - 5.2eV) with a large breakdown field (~ 8MV/cm). These properties make gallium oxide a promising material for power semiconductor applications [1]. A comprehensive study of gallium oxide thin films grown by ALD is presented in this work, and ~40nm-thin films with properties close to bulk gallium oxide wafers are obtained.

Gallium oxide films were deposited on C-plane sapphire, p-Si (100), n-Si (111) and p-Si (110) wafers as well as glass slides using a Kurt J. Lesker ALD 150-LX™ system equipped with a remote inductively coupled plasma (ICP) source. Depositions were done at a substrate temperature range of 50°C to 450°C. In-situ ellipsometry measurements were performed and the results were used to predict the quality of the films at different deposition conditions. 1-D and 2-D XRD patterns were collected to study crystallinity of the films. AFM measurements were performed to study surface morphology of the films. Electrical resistivity of the films was measured using van der Pauw method. Characterization results confirmed robustness of ellipsometry as a fast, non-contact and non-destructive technique for predicting structure and property of the films, which is especially beneficial for highly resistive thin films of emerging wide bandgap materials such as gallium oxide.

As a result of this work, low temperature gallium oxide thin films with resistivity and breakdown voltage values close to bulk wafers have been successfully deposited by ALD. An example cross section TEM image of a film grown at 275°C is shown in the attachment to present the crystalline quality of the film both at the interface and throughout the bulk of the film.

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EM-MoP-30 Crystalline GaN Film Growth at a Thermal Budget Approaching 100°C Using Hollow-Cathode Plasma-Assisted Atomic Layer Deposition

***Deepa Shukla**, A Mohammad, S Ilhom, N Biyikli,* University of Connecticut

The III-nitride wide bandgap semiconductor material family features attractive properties to be integrated with low-temperature materials such as transparent glass and polymeric flexible substrates. Towards such an integration, our plasma-assisted atomic layer deposition (PA-ALD) efforts concentrated on achieving a minimal deposition thermal budget not exceeding 200 °C. Our previous efforts demonstrated the effectiveness of the hollow-cathode plasma source in obtaining relatively low-impurity GaN layers at a substrate temperature of 200 °C. Using our customized hollow-cathode PA-ALD (HCPA-ALD) reactor, in this work, we achieved crystalline hexagonal GaN films at growth temperatures as low as 120 °C. To the best of our knowledge, this corresponds to the lowest growth temperature for crystalline GaN films via remote-plasma ALD.

GaN thin films were successfully deposited using HCPA-ALD on Si(100) substrates using triethylgallium (TEG) and $Ar/N_2/H_2$ or N_2/H_2 plasma as metal precursor and nitrogen co-reactant, respectively. Saturation curve study revealed an optimal plasma power of 150W and plasma duration of 20 s. The temperature range for the saturation experiments was 100 – 240 °C and each growth parameter variation was carried out for 10-cycle sub-runs. The sensitivity of the multi-wavelength *in-situ* ellipsometer has provided sufficient resolution to capture the subtle changes in the growth-per-cycle (GPC) parameter. The temperature variation of the GPC demonstrates a slight increase with temperature till 200 °C, where after it reaches a plateau, indicating a possible ALD temperature window for the TEG-N_2/H_2 surface growth reaction. Structural, chemical, and optical characterizations were performed to evaluate and compare film quality of GaN films grown at different substrate temperatures. The influence of plasma gas composition on film crystallinity has been characterized using grazing-incidence x-ray diffraction (GIXRD) and it was observed that the absence of Ar plasma during the growth process enhances the preferred (002) crystalline orientation by suppressing (100) & (001) neighbor peaks. In addition, we found that the optimal N_2/H_2 flow ratio is 1:2, reaching the highest (002) peak intensity. High-resolution XPS measurements revealed near-ideal stoichiometry with relatively low oxygen incorporation and below-deteccarbon content lower than the XPS-detection limits. High-resolution TEM imaging confirms the polycrystalline structure along with the crystal planes within the film grown at 120 °C. A detailed analysis comparing previously published reports on PA-ALD grown GaN will be presented.

ALD Applications
Room Van Rysselberghe - Session AA2-TuM
ALD for Batteries and Energy Storage I & II

Moderators: Arrelaine Dameron, Forge Nano, Neil Dasgupta, University of Michigan

9:00am **AA2-TuM-3 Ultrathin TiN by Thermal ALD as Electrically Conducting Li-ion Diffusion Barrier for Integrated 3D Thin-Film Batteries***, **Jan Speulmanns**, A Kia, S Bönhardt, M Czernohorsky, W Weinreich,* Fraunhofer IPMS, Germany

Upcoming autonomous microelectronic devices for the Internet-of-Things require ultralow power consumption enabling on-chip energy storage. Integrated 3D thin-film batteries (TFB) are a promising solution to meet these demands [1]. Enhancement and an in-depth understanding of Li-ion diffusion barriers are crucial factors to enable these devices. The diffusion of Li-ions into the Si substrate would damage surrounding components, detach the battery, and lead to a loss of capacity.

Titanium nitride (TiN) is an excellent Li-ion diffusion barrier and current collector [2]. Thin films manufactured by plasma-enhanced atomic layer deposition (ALD) proved superior blocking properties compared to sputtered layers, e.g., the insertion of around 0.02 Li per TiN formula unit was achieved for a 32 nm thick film [3]. Additionally, a sufficient specific resistivity of 200 μΩ cm as a current collector was shown. Orientation with low surface energy and reduced film contents of oxygen and chlorine were key factors for the performance. However, the employed remote plasma ALD was challenging for a conformal coating of structured substrates. Further thickness reduction of the barrier could increase the active volume fraction in 3D TFB.

In this work, we compare ultrathin 10 nm TiN films by thermal ALD and pulsed chemical vapor deposition (pCVD). The depositions are executed at 400-450 °C using titan(IV)-chloride and ammonia as reactants. The ALD film demonstrates excellent blocking capability. Only 0.03 Li per TiN formula unit are inserted exceeding 200 cycles at 3 μA/cm2 between 0.05 and 3 V vs. Li/Li+. The low specific resistivity of 115 μΩ cm allows the application as a current collector. In contrast, a partial barrier breakdown is observed for the 10 nm pCVD film. We identify that the surface quality is critical for the excellent performance of the ALD TiN. The superior surface is quantified by the lowest roughness, the highest ratio of the TiN-component, and the lowest Cl-content. Conformal deposition of TiN with thermal ALD is demonstrated in a newly designed electrochemical test chip with high aspect ratios of up to 20:1. First results of the barrier performance in 3D substrates are discussed.

10 nm TiN ALD films are an ideal candidate to enable increased energy density of integrated 3D TFB to power upcoming autonomous sensors.

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9:15am **AA2-TuM-4 Atomic Layer Deposition of Nitrogen Doped Al- and Ti-Phosphate for Li-ion Battery Applications***, **Lowie Henderick**,* Ghent University, Belgium*; H Hamed,* University of Hasselt, Belgium*; F Mattelaer, M Minjauw,* Ghent University, Belgium*; J Meersschaut,* IMEC, Belgium*; J Dendooven,* Ghent University, Belgium*; M Safari,* University of Hasselt, Belgium*; P Vereecken,* KU Leuven – University of Leuven/IMEC, Belgium*; C Detavernier,* Ghent University, Belgium

Phosphates have shown to be promising materials for Li-ion battery (LIB) applications. Their applications vary from protective coatings (Al-phosphate[1,2]) to potential cathode materials (Ti-phosphate[3]). Using ALD to tune the ionic and/or electronic conductivity through in-situ N-doping could make these materials even more interesting. In order to, for example, decrease the ionic and electronic blocking effect of the protective Al-phosphate coating, a new plasma enhanced atomic layer deposition (PE-ALD) process has been investigated. This new process is based on reports on PE-ALD of metal phosphates using a combination of trimethyl phosphate plasma (TMP*), oxygen plasma (O_2*) and a metal precursor (TMA or TTIP)[3,4].

In combining a nitrogen-containing phosphorous precursor, i.e. diethyl phosporamidate plasma (DEPA*), with nitrogen plasma (N_2*) and TMA/TTIP, a large GPC of 1.5 nm/cycle for N-doped Al-phosphate and 0.5 nm/cycle for N-doped Ti-phosphate was obtained. For both phosphates, self-limited growth is observed (figure 1, 2), and N-doping of respectively 7.9 at.% and 8.6 at.% for Al-phosphate and Ti-phosphate was found with Elastic Recoil Detection (ERD) (figure 3).

A clear effect of the nitrogen doping on the effective transversal ionic and electronic conductivities is observed (figure 4a). For both phosphates, a significant increase in the effective electronic conductivity is found. This is important, as phosphates (such as Fe-phosphate) typically suffer from poor electronic conductivity. The effective ionic conductivity shows a small increase for the Al-phosphate, but a slight decrease for Ti-phosphate. To study the possibilities of N-doped Al-phosphate in particular, a lithium nickel manganese cobalt oxide (NMC) powder was coated with (N-doped) Al-phosphate. An improved energy density at high discharge rates (w.r.t. uncoated NMC) was observed after only one deposition cycle of N-doped Al-phosphate, while the blocking effect of the undoped Al-phosphate coating (with a similar thickness as N-doped Al-phosphate) showed to hamper the battery performance at high rates (figure 4b). This shows that N-doping of phosphates with a high GPC was achieved by a new PE-ALD process, opening up opportunities for improving different types of phosphate coatings for LIB applications.

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9:45am **AA2-TuM-6 Passivation of Lithium Metal Anodes with ALD Aluminum Fluoride***, **John Hennessy**, J Jones, K Billings,* Jet Propulsion Laboratory

Lithium metal anodes are a key component of various next-generation battery technologies. However, the reactivity of the lithium surface can lead to battery cycling issues that are often associated with the formation of a solid electrolyte interphase (SEI) layer on the lithium surface. Here, we report on the use of ALD AlF_3 coatings deposited directly onto commercial lithium metal foils in order to engineer the stability of this SEI layer. ALD films are deposited at various substrate temperatures (< 175 °C) by cyclic exposure to tris(dimethylamino)aluminum and anhydrous HF. Symmetric Li/Li cells were fabricated with various electrolyte solutions in order to gauge the chemical stability of the passivated lithium surface. For example, electochemical impedance spectroscopy reveals a significant reduction in the impedance growth of ALD-coated symmetric cells fabricated with a liquid electrolyte solution of $LiPF_6$ in acetonitrile. The AlF_3-coated Li was also used to fabricate Li/S cells and more than doubled the specific capacity of test cells versus samples with unprotected Li. The increase in Li/S cell impedance during prolonged cycling was also reduced for the passivated samples, although not completely eliminated. Coated foils were also characterized with a combination of scanning electron microscopy, energy dispersive xray spectroscopy, and spectroscopic ellipsometry. Finally, progress in the development of lithium-ion conducting thin films of lithium aluminum fluoride is also presented as a building block toward solid-state battery systems.

10:15am **AA2-TuM-8 Next-Generation Li-ion Batteries Enabled by Large-Area Atmospheric-Pressure Spatial Atomic Layer Deposition***, **Mahmoud Ameen**, I Beeker, L Haverkate, B Anothumakkool, F Grob, D Hermes, N Huijssen, S Khandan Del, F Roozeboom, S Unnikrishnan,* TNO/Holst Center, Netherlands

Li-ion batteries have emerged as a key energy storage enabler, not only in portable electronic devices but also in electric vehicles and grid-storage. A combination of high energy density anodes such as Si or Li, and Ni- or Li-rich cathodes [1,2] is necessary to achieve the targeted energy density (>350 Wh/kg). However, many of such high-potential redox-chemistries lead to serious safety issues and degradation during cycling due to either oxidative or reductive instabilities [3], especially occurring at the electrode-electrolyte interface [4]. Therefore, optimizing the interfaces with chemically and mechanically-stable Li-ion conductive passivation layers is crucial for any Li-ion battery chemistry in order to mitigate the non-compatibility of the individual cell components. The interfacial stabilization layers can be formed either in-situ using electrolyte additives or ex-situ via chemical and physical methods. One option here is offered by atomic layer deposition (ALD) which is the preferred technique to achieve superior quality and 3D-conformal coatings with atomic-scale thickness precision. However, conventional vacuum-based ALD is not compatible with the mainstay high-throughput roll-to-roll battery electrode production. Here, the large-area atmospheric-pressure spatial-ALD (s-ALD) technology as established by TNO-Holst Centre several years ago can offer prime solutions for various applications including thin-film batteries [5]. A wide range of materials like metal oxides, nitrides, sulfides, and hybrid organic-inorganic materials are possible using s-ALD. In this work, we will demonstrate several s-ALD films such as Al_2O_3, TiO_2, and ZnO which are specifically tailored for dendritic Li-growth suppression, interface stabilization, and cathode degradation protection. Furthermore, we will discuss the latest results on our upscalable s-ALD grown thin film LiPON electrolyte having a Li-ion conductivity $>10^{-7}$ S/cm, low electronic conductivity ($<10^{-12}$ S/cm) and high stability against Li-metal anode during cycling. Such electrolyte is also relevant for the development of protection layers in liquid and polymer electrolyte-based Li-ion batteries, as well as for enabling thin-film planar and 3D solid-state batteries with ultra-thin electrolyte layers.

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10:30am **AA2-TuM-9 ALD Al_2O_3 and MoS_2 Coated TiO_2 Nanotube Layers as Anodes for Lithium Ion Batteries***, H Sopha,* University of Pardubice, Czech Republic*; A Tesfaye,* Ecole de Mine, France*; R Zazpe,* University of Pardubice, Czech Republic*; T Djenizian,* Ecole de Mine, France*;* ***Jan Macak****,* University of Pardubice, Czech Republic

The miniaturization of Lithium ion batteries (LIBs) as a power source to drive small devices such as smartcards, medical implants, sensors, radio-frequency identification tags etc. has been continuously developed to meet the market requirements of portable applications.[1] In this direction, 3D microbatteries have been considered to satisfy the requirements of these portable devices. Anodic TiO_2 nanotube layers (TNTs) have been recently explored as anodes for LIBs due to their high surface area, low volume expansion, short diffusion lengths for Li^+ ion transport and good capacity retention even at faster kinetics.[2,3]

Recently, various coatings produced by Atomic Layer Deposition (ALD) on electrode materials have been explored extensively in LIBs. For example, Al_2O_3 and TiO_2 coatings act as a protective layer for the suppression of the solid electrolyte interphase (SEI) in various electrode materials.[4,5] But their influence on increasing the electronic conductivity of the electrode material has not been explored in details. In addition, it is also possible to synthesize using ALD the main electrode materials, such as oxides[6] and sulphides.[7] However, high surfacearea and sufficiently conducting support would be beneficial for these ALD derived materials to support an excellent performance of the batteries. The door for various one-dimensional nanomaterials, such as TNTs, is therefore open

In this presentation, we will show ALD synthesis of Al_2O_3[8] and MoS_2[9] and their combination[10] on TNTs as new electrode material for lithium-ion batteries. We show an influence of different coating thicknesses on the battery performance, in particular on the charging and discharging capacity.

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10:45am **AA2-TuM-10 Molecular Layer Deposition for Stabilization of Electrochemical Materials***,* ***Chunmei Ban****,* University of Colorado - Boulder **INVITED**

The inherent non-passivating behavior of electrode materials in the organic lithium-ion battery electrolyte results in large irreversible capacity loss and gradual electrolyte consumption during operation. Such interaction between electrolyte and electrode becomes more pronounced for intermetallic alloy and lithium-metal anode materials and high-voltage cathode materials. When using decreased nano-size electrode materials, the chemical interaction and the formation of solid electrolyte interphase (SEI) lead to even more irreversible loss of lithium inventory. Surface modifications on both active particles and laminated electrodes—with the capability to modify the surface and interface through the control of composition, thickness and mechanical properties—would chemically or physically change the surface of electrode materials. The atomic layer deposition (ALD) technique has proven itself to be the best method to deposit continuous, conformal and pinhole-free films. Our recent work has proven ALD as an important tool in mitigating the parasitic side reactions between the electrolyte and the electrode surface, which results in the greatly improved performance of lithium-ion electrodes. Furthermore, to address the challenge of dramatic volumetric change associated with high-capacity intermetallic anodes, we have used molecular layer deposition (MLD) to modify the surface with a mechanically robust, flexible coating. Combining with the results from advanced characterization techniques, this talk will emphasize the unique chemical interaction between the electrolyte and the surface of intermetallic electrodes. Furthermore, the surface modification strategies will be introduced here and exploited, in order to dictate the interface chemistry and manipulating the chemi-physical properties of the electrode-electrolyte interphase for efficient electrochemical reactions.

ALD Applications
Room Auditorium - Session AA-TuM

ALD for Solar Energy Materials I & II

Moderators: Han-Bo-Ram Lee, Incheon National University, Wei-Min Li, Jiangsu Leadmicro Nano-Equipment Technology Ltd.

8:30am **AA-TuM-1 Atomic Layer Deposition Enabling Higher Efficiency Solar Cells***,* ***Bram Hoex****,* University of New South Wales, Australia **INVITED**

It is well known that atomic layer deposition (ALD) can synthesize materials with atomic-scale precision. In this presentation we will present some of the recent work in our research group at the University of New South Wales and show that ALD has been instrumental in improving the efficiency of both crystalline silicon as well as thin film solar cells. It will be shown that the deposition of alumina layers at both sides of a silicon solar cell can have some unexpected benefits in addition to significantly simplifying the use of batch ALD in high volume production. The ease of the controlled incorporating dopants in ALD films will be shown to be crucial in improving the properties of NiO for application in hole-selective contact for a wide range of solar cells. And finally, we will show that ALD is currently enabling world-record cadmium-free copper zinc tin sulphide (CZTS) solar cells allowing this technology to cross the important 10 % energy conversion efficiency.

9:45am **AA-TuM-6 Atomic Layer Deposition of $Zn_{1-x}Mg_xO$ and $Zn_{1-x}Mg_xO$:Al as Transparent Conducting Films for Chalcopyrite Solar Cells***,* ***Poorani Gnanasambandan****, R Leturcq, P Lunca-Popa,* Luxembourg Institute of Science and Technology, Luxembourg*; M Sood, S Siebentritt,* Université du Luxembourg, Luxembourg

We investigate atomic layer deposited aluminium-doped zinc magnesium oxide and zinc magnesium oxide films with varying Mg content as transparent conducting films and as electron extraction layers for chalcopyrite solar cells. Transparent conducting materials are quintessential part of a photovoltaic device. One of the main challenges involves the design of materials combining appropriate band alignment, conductivity and transparency, to be adapted to the absorber in the solar cells. Important parameters for optimization are reduced density of interface defects to avoid recombination, and well-controlled work function and doping. Moreover, the developed materials will require low-temperature vapor phase deposition compatible with the cell processing.

Previous studies on the impact of $Zn_{1-x}Mg_xO$:Al as transparent electrodes and Mg doped ZnO thin films for the window layer of CIGS solar cells employed co-sputtering and electrodeposition respectively [1][2][3]. With the advantage of low temperature and highly conformal thin film growth, we study ALD grown $Zn_{1-x}Mg_xO$ and $Zn_{1-x}Mg_xO$:Al (with x varying from 0.1 to 0.4). We elucidate the effect of doping on the band alignment, electrical and optical properties. We examine how the growth conditions can pave the way towards precise control of Mg content in order to adjust the bandgap and possible growth of $Zn_{1-x}Mg_xO$ film stacks with graded Mg doping. By achieving precise control of Mg content, we aim to investigate the effect of ALD grown $Zn_{1-x}Mg_xO$ films on high-bandgap solar cells based on $CuInS_2$ absorbers.

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10:00am **AA-TuM-7 Tuning Properties of ALD Oxide and Sulfide Materials for Photovoltaic Applications*, Nathanaelle Schneider,*** IPVF-CNRS, France **INVITED**

Atomic layer deposition (ALD) has unique capabilities that makes it very attractive to several applications and in particular photovoltaics (PV).[1] It allows the deposition of pinhole-free thin films, in relative soft conditions (low temperature, low vacuum level), with finely tuned properties (thickness, composition, …) and conformal on high-aspect ratio and/or large surfaces. However, such fine tuning is rarely straightforward and simplistic view of monolayer per monolayer growth is never the case. This is crucial when growing thin films with more than two elements as specific surface reactions can impact the film growth. This is even more pronounced for sulfide multinary compounds due to the higher propensity of cation exchange, greater diffusion rates and unintentional annealing of the labile sulfur.[2]

Such phenomena can be partly controlled by the right choice of precursors,[3] adapting the order of precursor introduction[4,5] or varying the number of successive growth cycles.[6] A deep understanding of the surface chemistry is also necessary and can be achieved by combining modelling (DFT calculations),[7]*in-situ* (such as quartz-crystal microbalance measurements)[2,4,5] and *ex-situ* characterisations (XPS fine profiling, …).[3,6] The aforementioned unique ALD capabilities will be illustrated by examples in PV devices such as $Cu(In,Ga)Se_2$,[6,8] silicon nanowire[5] and perovskite solar cells.[9]

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10:30am **AA-TuM-9 Solar Cells Based on Phase-Pure Sb_2S_3 by Atomic Layer Deposition Forming Planar and Coaxial Heterojunctions*, Ignacio Minguez Bacho,*** *P Büttner, F Scheler, D Döhler,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany*; C Pointer, E Young,* Lehigh University*; J Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany

Interfaces of oxides and heavier chalcogenides layers in thin-film or extremely thin absorber solar cells present defect states at the interface and often a chemical incompatibility which results in dewetting issues. Here, we establish atomic layer deposition (ALD) as a tool to overcome these limitations. ALD allows one to obtain highly pure Sb_2S_3 as light absorber layers, and we exploit this technique to generate an additional interfacial layer consisting of ZnS with thicknesses between 0.2 and 2.0 nm. This ultra-thin layer simultaneously eliminates dewetting, passivates defect states at the interface and slows down interfacial charge recombination. The ability of ALD to generate conformal coatings of porous substrates allows us to generalize the materials system from planar stacks to coaxial heterojunctions based on cylindrical nanostructures. In this system, we optimize length and layer thicknesses in dependence of the carrier diffusion lengths and the light absorption coefficient systematically. We achieve heterojunction solar devices with optimized power conversion efficiency beyond 5.0 %.

10:45am **AA-TuM-10 Metal Oxide Infilling of Quantum Dot Thin Films: Charge Separation, Stabilization, and Solar Cell Formation*, Fatemeh Hashemi,*** *R Crisp, J Alkemade, G Grimaldi, N Kirkwood, L Siebbeles, J van Ommen, A Houtepen,* Delft University of Technology, Netherlands

Colloidal semiconductor quantum dot (QD) thin films have various applications in photovoltaic devices and as light emitters. This is due to the controlled variation in their band-gap and ease of fabrication. However, these thin films suffer from instability due to their inherent inclination towards oxidative and photothermal degradation. Thus, to increase the stability of these materials for fabricating QD-based electronic devices, encapsulation or pore infilling processes are necessary. The pore infilling process has been shown to also enhance the conductivity and carrier mobility in the QD thin films. The encapsulation process should provide protection against oxidation without hindering the electron transport properties or causing sintering of the QDs. ALD is an ideal candidate for such a process as is provides excellent control over the growth in the sub-nanometer scale and results in conformal coating even in low temperatures.

We perform ALD of two different metal oxides in atmospheric pressure for the infilling and capping of QD thin films. We examine their effects on the stability and carrier mobility of the coated QD films. InP QDs are chosen because of their potential as light emitters (i.e. phosphors) across the visible spectrum. This is due to their favorable bandgap and high photoluminescence quantum yield. Furthermore, InP QDs exhibit multiple exciton generation allowing for higher solar cell efficiency than traditional materials. However, carrier mobility in QD films was too low for practical applications until now.

We compare the results of amorphous TiO_2 with crystalline ZnO films deposited with different thicknesses. The effects of the capping film thickness of QD film on stability and carrier mobility are studied with spectrophotometry and time-resolved microwave conductivity measurements. We show that the inorganic matrix reduces the size of tunnel barriers within the QD thin film hence increasing the carrier mobility through the film without causing sintering of the QDs. Furthermore, our results confirm that the stability of QD thin films is strongly improved when the inorganic ALD coating is applied. The ALD encapsulation process would open up the possibility of fabricating robust InP QD thin films for many optoelectronic devices.

11:00am **AA-TuM-11 ALD of Al_2O3 on Perovskite Solar Cells: Role of Active Interfacial Engineering***, S Ghosh, N Mahuli,* ***Shaibal Sarkar,*** Indian Institute of Technology Bombay, India

Atomic Layer Deposition of ultrathin Al_2O_3 on hybrid perovskite solar cells drew significant attention due to the considerable improvement in the overall device stability. In our laboratory, with intermittent current-voltagemeasurements, the coated devices show the value of T80>7500 hours under ambient conditions. Subsequently, these coated devices are found highly stable when measured in a cyclic manner for 7 days, replicating the real-life day-night sequences. Such *encapsulation* is found very effective as an oxygen barrier-layer and water-impermeable membrane; hence contribute to the overall stability of these devices.

In this presentation, I would like to emphasize on our experimental findings, subsequently supported by device simulation, which undoubtedly reveals that the perovskite-spiroOMeTAD interfacial band-structure play a detrimental role in initiating the degradation processes in the pristine devices (device structure). We try to provide a comprehensive insight depicting an apparently non-trivial active phenomenon resulted due to the ALD grown Al_2O_3 layer that supposedly be a passive component of the entire device stack. Favored electronic modification of the spiro-OMeTAD/perovskite interface resulted due to the Al_2O_3 ALD provides better charge extraction and lesser ionic accumulation, unlike the unencapsulated devices, and hence offers better performance stability. Our study indicates that essentially the ionic accumulation triggers the device degradation that is eventually followed by materials degradation.

ALD Fundamentals
Room Jan & Hubert Van Eyck - Session AF1-TuM
ALD Mechanisms and Modeling

Moderators: Annelies Delabie, IMEC, Michael Nolan, University College Cork

8:45am **AF1-TuM-2 Automated Design of Thermally Stable Heteroleptic Precursors by Computational Screening***, **Simon D. Elliott**, D Giesen, S Kwak, M Halls,* Schrödinger, Inc.

Ligand choice in ALD/CVD precursors is crucial for throughput, stoichiometry, impurities and process temperature. Heteroleptic precursors (containing more than one type of ligand) are one way to compromise between conflicting chemical requirements. However to date we have barely 'scratched the surface' of the vast chemical space of possible heteroleptic precursors. As an example to illustrate the magnitude of the design problem, 8,855 chemically-distinct complexes can be formed by combining four of 20 ligands around a tetravalent metal center. Clearly, an exhaustive experimental analysis is not possible. Instead we look to computational screening to narrow down the search to the most promising options. Here we present a computational approach for screening metal precursors with respect to thermal stability. The computational strategy is illustrated on the example of Zr precursors for zirconium nitride, used as a hard coating to protect industrial parts in corrosive environments.

CVD precursors should decompose unimolecularly at elevated temperature in the reactor and we therefore seek complexes with moderately low energies for homolytic bond dissociation (i.e. into a pair of radical fragments). ALD on the other hand requires the gas-phase stability of precursors to be as high as possible, as this dictates the upper temperature limit for ALD.

We first enumerate over ligands. Even a small ligand library of just six O-free, N-bearing ligands (amines, amidinates, cyano and guanidinate, with various alkyl groups) gives 6^4=1296 possible complexes, but many are symmetrically equivalent or over-coordinated, leaving 81 for optimization with density functional theory (DFT). To study thermal stability requires a second phase of enumeration, over the 1280 different bonds that can be broken in these complexes, yielding a set of radical fragments that are also computed at the DFT level. It is clear that every step in this computational workflow requires robust and efficient automation.

DFT reveals that the lowest bond dissociation energies are obtained for cleaving intact ligands from the metal. The least thermally stable complexes are found to be zirconium amides with bidentate amidinates/guanidinates, and so we predict that these would be the best CVD precursors. We observe very little steric effect when replacing methyl groups with ethyl groups. By contrast, cyano groups have a stabilizing influence, suggesting that similar electron-withdrawing groups would be useful as spectator ligands in heteroleptic precursors for ALD. On the basis of this sample system, we discuss the general requirements for chemical enumeration software and the limits faced by automation.

9:30am **AF1-TuM-5 Unravelling the Reaction Mechanisms of Trimethyl Borate for the Atomic Layer Deposition Boron- and Hydrogen-Doped Alumina Films with Non-uniform Transversal Doping Profiles***, F Mattelaer, **Véronique Cremers**, M Van Daele, M Minjauw, M Nisula,* Ghent University, Belgium*; S Elliott,* Schrödinger, Inc.*; T Sajavaara,* University of Jyväskylä, Finland*; J Dendooven, C Detavernier,* Ghent University, Belgium

Atomic layer deposition (ALD) of boron-containing films has been mainly studied for use in 2D materials, B-doping of Si and towards lithium-containing borates as solid electrolyte coatings for enhanced energy storage. A series of precursors have been studied as boron-containing precursors, including B_2H_6, BBr_3, BCl_3, $B(OEt)_3$, $B(OMe)_3$, $B(OiPr)_3$ and more complex bi-metallic molecules. Trimethyl borate ($B(OMe)^3$, or TMB) and triethyl borate ($B(OEt)_3$, or TEB) are considered as ideal candidates based on limited safety issues (not pyrophoric and limited toxicity) and high vapor pressure.

In this work, we examine TMB and triethyl borate TEB in combination with O_2 plasma as precursors for ALD of B-containing films, targeting the growth of B_2O_3. It is found that films grown from TEB contain no boron. With TMB as a boron-containing precursor, films growth was found on a SiO_2 or Al_2O_3 surface, but a rapid decrease of the growth rate to a near zero-growth mode during subsequent ALD cycles indicated surface inhibition during continued growth. DFT cluster calculations in combination with in-situ FTIR demonstrated that because of its weak Lewis acidity, the TMB molecule is found to adsorb via hydrogen-bonding to B-OH covered surfaces, without elimination of ligands, so that it is subsequently removed in the plasma pulse and does not contribute to growth. The initial growth is possible because this is not the case for adsorption of TMB on for example Al-OH sites on which TMB chemisorption is energetically more favourable and typical ligand exchange reactions are expected. Knowing this, the growth could be maintained in a mixed process, by re-activating the surface through single exposures to trimethyl aluminium (TMA) and oxygen plasma and thus resetting the surface to Al-OH.

Surprisingly, this process did not result in B_2O_3 (or Al-doped B_2O_3) films, but instead in B- and H-doped Al_2O_3 films. Moreover, rather than uniform boron doping, the Al_2O_3 films grown from this process contain a large amount of hydrogen, up to 17at%, and displayed non-uniform transversal distributions of boron and hydrogen. The depth distribution is found to rely primarily on the deposition conditions. Using in-situ FTIR, - ellipsometry and DFT, this anomalous behaviour was attributed to sub-surface reactions of the TMA with the formed B-OH films deposited. This makes the process an interesting, albeit atypical, ALD process that allows for a quasi-continuous tuning of the B-concentration in the top region of high-purity Al_2O_3 films.

ALD Fundamentals
Room Jan & Hubert Van Eyck - Session AF2-TuM
Conformality of ALD

Moderators: Riikka Puurunen, Aalto University, Finland, Myung Mo Sung, Hanyang University

10:00am **AF2-TuM-7 Role of Ions in Film Conformality and Quality during Plasma-Assisted ALD of SiO_2 and TiO_2***, **Karsten Arts**, S Deijkers,* Eindhoven University of Technology, Netherlands*; M Utrianen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland*; E Kessels, H Knoops,* Eindhoven University of Technology, Netherlands

This work discusses the impact of ions on film conformality during plasma ALD, in terms of layer thickness and material properties. Ions have been shown to improve the material quality for several plasma ALD processes,[1] yet how and to what extent this works for plasma ALD on high-aspect-ratio structures is difficult to measure and relatively unexplored. Using PillarHall™ lateral-high-aspect-ratio trench structures,[2] where only part of the growth area is exposed to ions, we show how the growth per cycle (GPC) and material properties of SiO_2 and TiO_2 are affected by the locally received ion flux. Our results reveal that ion exposure can be a key factor determining film conformality during plasma ALD of SiO_2 and TiO_2, as the ion flux is inherently anisotropic, while the reactive plasma radicals can diffuse isotropically up to aspect ratios as high as ~1000.[3]

For plasma ALD of SiO_2 using $SiH_2(NEt_2)_2$-, the GPC is affected by ions and decreases significantly when using extended ion doses. Nevertheless, when using moderate ion doses the film thickness is still very conformal. In contrast to the GPC, the material quality is only marginally affected by ions, based on an almost uniform wet etch rate of the SiO_2 film in a buffered HF solution. These results indicate that, in spite of the anisotropic ion flux, plasma ALD can provide highly conformal SiO_2 films for demanding applications.

For plasma ALD of TiO_2 using $Ti(NMe_2)_4$, we show that the GPC and material properties are more strongly affected by ions. For example, at 200 °C crystalline TiO_2 (anatase) with a high GPC and a virtually negligible wet etch rate is obtained with ion exposure, while amorphous TiO_2 with a lower GPC and a much higher wet etch rate is obtained without ion exposure.

In addition to these results, the impact of ions on the refractive index and surface morphology will be discussed, as well as the effect of ion energy and deposition temperature. On the basis of these studies, we will provide insights into the fundamental mechanisms behind the role of ions in film conformality and material quality during plasma ALD.

1. Faraz *et al.*, ACS Appl. Mater. Interfaces **10**, 13158 (2018)

2. Gao *et al.*, J. Vac. Sci. Technol. A **33**, 010601 (2015)

3. Arts *et al.*, J. Phys. Chem. C **123**, 27030 (2019)

10:45am **AF2-TuM-10 ALD Conformality: Effects of Process Parameters on the Simulated Saturation Profile***, E Verkama, **Jihong Yim**,* Aalto University, Finland*; M Ylilammi,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland

Atomic layer deposition (ALD) is widely applied in industrially and in R&D related to applications such as semiconductor processing, microelectromechanical systems, and solid heterogeneous catalysts. ALD has an unparalleled ability to grow uniform, conformal thin films on complex three-dimensional (3D) objects. Experimental and modeling works on conformality investigations have recently been reviewed [1].

This work aims to investigate through theoretical simulations how (i) (simplified) kinetic parameters related to individual ALD reactions and (ii) ALD process parameters more in general influence the saturation profile of ALD films in 3D structures. The 3D structures of interest are rectangular channels, also known as lateral high-aspect-ratio (LHAR) structures, resembling the PillarHall™ structures reported earlier by Puurunen and coworkers. The simulations are made with a Matlab implementation of the Ylilammi et al. 2018 diffusion model [2]. The simulations assume reversible single-site Langmuir adsorption as the chemisorption mechanism, with chemisorption kinetics modeled via a single "lumped" sticking coefficient.

We will present investigations on how the simulated "saturation profile" (thickness vs. distance inside the LHAR structure) or the "scaled saturation profile" (growth per cycle, GPC, vs. dimensionless distance) varies with kinetic constants and process parameters. As expected, reactant partial pressure and exposure time have a major influence on the penetration depth of the film ("50% penetration depth", $PD^{50\%}$). We will also explore the effect of the (lumped) sticking coefficient, equilibrium constant, GPC, the molar mass of the ALD reactant, ALD temperature, LHAR channel height, and total pressure on the saturation profile. An inverse correlation is found between $PD^{50\%}$ and the GPC, explained by a lower binding capacity (atoms per unit surface area) of the surface, which gives a lower GPC. With increasing process pressure, the Knudsen number decreases and the process moves from molecular flow to collisional flow. This is seen as a gradual decrease of $PD^{50\%}$ and a steepening of the slope of the leading edge of the saturation curve.

We believe that these simulations can help experimentalists to understand how different parameters are expected to affect conformality (saturation profile) of ALD processes. The simulations thereby assist one to design meaningful experiments as well as to interpret the results of those experiments. Our aim is to release the Matlab simulation code for open use.

[1] Cremers, Puurunen, Dendooven, Appl. Phys. Rev. 6 (2019) 021302

[2] Ylilammi, Ylivaara, Puurunen, J. Appl. Phys. 2018 (123) 205301

Atomic Layer Etching
Room Baekeland - Session ALE1-TuM

ALE Selectivity and Anisotropy

Moderators: Ankur Agarwal, KLA-Tencor, Sumit Agarwal, Colorado School of Mines

9:00am **ALE1-TuM-3 Highly Selective Atomic Layer Etching for Semiconductor Application**, ***Akiko Hirata,*** Sony Semiconductor Solutions Corp., Japan **INVITED**

The self-limiting process is one of the most important features of atomic layer etching (ALE). The self-limiting process refers to the highly selective etching of a modified layer over a pristine substrate. One ALE cycle consists of a surface modification step and a removal step of the modified layer. In the modification step, the binding energy in the surface reactive layer is reduced so that it is easier to remove than the bulk. For the generation of a reactive layer, chemical adsorption and chemical/physical modification are generally employed. In this study, we investigate tin-doped indium oxide (ITO) and SiN ALE, and their mechanisms, to achieve the high selectivity.

ITO is a difficult-to-etch material, since the boiling points of indium halides are very high (>700 °C). Surface modification through chemical adsorption of reactive species is difficult. Thus, surface modification by energetic hydrogen ions followed by Ar desorption was proposed. The ITO was reduced by hydrogen injection, and generated an In-rich layer on the surface. The In-rich layer of ITO could be selectively etched by controlling the incident ion energy. Thus, the self-limited etching of ITO was demonstrated.

The etch rate selectivity of ITO over a mask material is indispensable for device fabrication. We intentionally controlled the amount/incubation time of Si generated from the upper electrode, and demonstrated the highly selective cyclic etching of ITO/SiO_2. The cyclic etching by area-selective surface adsorption of Si could precisely control the etch rates of ITO and SiO_2, which resulted in an almost infinite selectivity for ITO over SiO_2.

In the case of SiN ALE, the chemical adsorption of a reactive species (CH_xF_y polymer) was employed to obtain high selectivity with SiO_2 and Si. However, the SiN ALE was easily etch-stopped, owing to the excess adsorption of polymer during cyclic etching. Thus, a sequential 3-step ALE (adsorption, desorption, and O_2 ash) was proposed. After this 3-step ALE, the SiN surface was oxidized, which resulted in a fluctuation of the etched amount. To overcome these issues, plasma-enhanced conversion ALE was proposed. First, 3-step ALE was performed for SiN ALE, and the surface SiO_2 (converted from SiN by oxidation) was generated. Subsequently, highly selective SiO_2 ALE over SiN was performed. By combining highly selective SiN and SiO_2 ALE, a stable ALE process was realized.

When we use the differences in precursor incubation time among different materials effectively, highly selective etching is expected. Thus, a database of the surface adsorption of many kinds of precursors is strongly required for future highly selective ALE processes.

9:30am **ALE1-TuM-5 Aspect-Ratio Dependence of Isotropic Thermal ALE and Mitigation Thereof*, Andreas Fischer,* *A Routzahn, T Lill,* Lam Research Corp.

Advanced memory chip manufacturing is increasingly pushing the boundary toward high aspect ratio (HAR) designs in which many layers of memory cross points are stacked on top of each other. Especially in 3D-NAND memory structures, the ability to perform isotropic etches to recess high-k oxides made of hafnia or alumina or to remove excess material beneath shaded overhangs will be a critical addition to the established suite of etch and deposition processes in chip design.

In this work, we have focused on the dependence of isotropic atomic layer etching on the aspect ratio of the structures that are being etched. Utilizing the well characterized vapor-based DMAC ligand exchange mechanism, we have investigated the dependence of lateral etch rate of this process as a function of depth in nanometer-size holes of hafnium oxide. Inside these holes, we measured the horizontal etch rates and found that it slowed to a rate of 85% at the bottom of 50:1 aspect ratio holes compared to the rate at the very top of the structures for our standard ALE process.

To overcome this issue, we established that this aspect ratio dependence could be significantly suppressed by operating the process closer to saturation in the modification as well as removal step by expanding the process step time for each of the steps.

In additional experiments we found that the use of low level, zero-bias plasma can boost the etch rate in deep structures thereby reducing the aspect ratio dependence further.

We propose a simple mechanism for explaining the dependence on step time and use of plasma.

9:45am **ALE1-TuM-6 Precise Ion Energy Control with Tailored Waveform Biasing for Atomic Layer Etching*, Tahsin Faraz,*** *Y Verstappen, M Verheijen,* Eindhoven University of Technology, Netherlands*; J Lopez, E Heijdra, W van Gennip,* Prodrive Technologies B.V., Netherlands*; E Kessels, A Mackus,* Eindhoven University of Technology, Netherlands

Anisotropic plasma ALE utilizes energetic and directional ions to remove any given material in a selective and self-limiting fashion.[1] However, high selectivity and etch control requires well-defined ion energies lying below the sputter etch threshold of the material, which serves as the upper limit of the so-called ion energy window of an anisotropic plasma ALE process.[2,3] In this contribution, we report on precise ion energy control – independent of the ion flux – using low-frequency (100 kHz) tailored bias voltage waveforms applied to a substrate in a commercial remote plasma reactor. Ion energies in such reactors are typically controlled by applying a radio-frequency (RF: 13.56 MHz) sinusoidal bias voltage waveform to the substrate undergoing plasma exposure. However, this yields ions with a broad energy distribution that leads to non-selective and continuous etching. Furthermore, the use of high frequency RF bias voltages entails electron heating mechanisms that do not allow for controlling the ion energy independent of the ion flux.[4] Precise ion energy control by applying a tailored bias voltage waveform[5,6] to a substrate undergoing plasma exposure is currently not employed in the field of ALE.

In this work, a prototype low-frequency bias voltage generator has been used to apply tailored bias waveforms consisting of a voltage pulse and a ramp. Such waveforms yielded ions having narrow energy distributions for energies upto 200 eV (measured using a retarding field energy analyzer, RFEA) in collisionless Ar plasmas. The energetic ions were used to sputter etch thin films of different materials (e.g. Si, SiO_2). Such investigations provide reliable experimental data on sputter etch thresholds of different materials that are typically determined by extrapolation of sputter yields measured at ion energies >> 100 eV to the low energy range,[7] which does not give accurate values. These thresholds serve as essential input (i.e. upper limits of ion energy windows) for designing novel anisotropic plasma

ALE chemistries. To demonstrate the feasibility of this technique in performing anisotropic plasma ALE, a conformal SiO_2 layer on a 3D trench nanostructure was etched using directional ions whose energies were enhanced to 100 eV with tailored waveform biasing.

[1] Faraz et al., *ECS J. Solid State Sci. Technol.* 4, N5023 (2015)

[2] Kanarik et al., *J. Phys. Chem. Lett.* 9, 4814 (2018)

[3] Berry et al., *J. Vac. Sci. Technol. A* 36, 01B105 (2018)

[4] Sobolewski et al., *J. Appl. Phys.* 102, (2007)

[5] S.-B. Wang and A.E. Wendt, *J. Appl. Phys.* 88, 643 (2000)

[6] Kudlacek et al., *J. Appl. Phys.* 106, (2009)

[7] *Sputtering by particle bombardment* (Behrisch & Eckstein), Springer 2007

Atomic Layer Etching
Room Baekeland - Session ALE2-TuM

ALE for GaN Devices

Moderators: Steven M. George, University of Colorado at Boulder, Nicolas Posséмé, CEA-Leti

10:00am **ALE2-TuM-7 GaN Damage Evaluation After Conventional Plasma Etching and Anisotropic Atomic Layer Etching**, ***Simon Ruel***, *P Pimenta-Barros,* CEA-Leti, France*; N Chauvet,* Lam Research, France*; F Le Roux,* CEA-Leti, France*; S Tan,* Lam Research*; F Gaucher,* Lam Research, France*; N Posseme,* CEA-Leti, France **INVITED**

GaN-based high electron-mobility transistors (HEMTs) are promising for high power device applications because of their high electric field strength, high mobility, and good thermal stability. The traditional GaN-based HEMTs is inherently normally-on because a two-dimensional electron gas (2DEG) channel is created at the AlGaN/GaN interface. As normally-off operation is desirable for commercial power applications, several structural approaches have been proposed such as recessed gate and pGaN gate. The different processing steps of GaN-based HEMTs can induce trapping effects, leading to the reduction of the 2DEG density and thus to the electrical degradation of GaN devices. In this context, plasma etching is one of the most critical step in the manufacturing of GaN devices.

In this paper, we propose to evaluate a promising Atomic Layer Etching (ALE) approach allowing to reduce or eliminate the damage compared to the conventional plasma etching.

The process investigated in this study for GaN etching consists in two steps of cyclic plasma chlorination followed by Argon or Helium bombardment. Fig 1a shows that the GaN etching is negligible after pure chlorination and pure sputtering (Ar or He plasma). GaN etching only occurs by cycling chlorination and sputtering steps, meaning that the basic concept of ALE is demonstrated for both ALE Ar and He. The etch per cycle (EPC) of ALE Ar and He is 0.5nm/cy and 1.1nm/cy respectively. Therefore, ALE He is faster than ALE Ar whereas a same bias voltage of 50V has been applied. After plasma parameters optimization, Fig 1b shows that the ideal ALE Ar and ALE He process window in term of ion energy is between [70-100V] and [50-80V] respectively. XPS analyses and roughness studies by AFM (Fig 2a and b, respectively) reveal a very similar surface state after etching with ALE or Steady only.

The plasma induced damage has also been evaluating for both ALE processes on blanket wafers and compared to the steady process. Fig 3 shows that, for a similar over etch, ALE He induces higher R_{sheet} degradation than ALE Ar. This result can be explained by deeper He ion penetration within the substrate compared to Ar ion as the He ions are lighter. While ALE Ar presents a lower R_{sheet} than the steady process, confirming a lower film damage induced by ALE process compared to the steady process.

10:30am **ALE2-TuM-9 Analysis of Ion Energy Dependence of Depth Profile of GaN by In-situ Surface Analysis***, M Hasagawa,* ***Takayoshi Tsutsumi,*** Nagoya University, Japan*; A Tanide, S Nakamura,* SCREEN Holdings Co., Ltd., Japan*; H Kondo, K Ishikawa, M Hori,* Nagoya University, Japan

In fabrication of the next-generation power electronic devices of gallium nitride (GaN), an atomic layer etching (ALE) technique with cyclic processes of ion irradiation and Cl adsorption steps has been attracted for reduction of plasma induced damage. To control surface stoichiometry of GaN in the ALE, we focus on the ion energy dependence of the depth profile of GaN at each Ar and Cl reaction step using the beam experiments with *in situ* X-ray photoelectron spectroscopy (XPS).[1,2]

The plasma beam system was used for Cl adsorption and Ar ion irradiation process. The as-cleaned surface was exposed by Cl radicals with a dosage of 10^{19} cm^{-2} generated in Cl_2 gas (flow rate 0.5 sccm) plasma by application of RF power of 400 W, while the shutter was placed in front of the sample to block the Cl ion to the surface. The Ar ion energy, that has a narrow ion energy distribution, was specified by applying a direct current (dc) voltage bias to the acceleration electrode. The one cycle consisted of these Ar ion irradiation and Cl radical exposure. To stabilize the GaN surface, five cyclic processes were carried out. Then, the GaN surface at each step was analyzed by angle-resolved *in-situ* XPS. Depth profiles of atomic concentration were estimated by the maximum entropy method.

Figure 1 show the depth profile of Ga-Ga and Ga-Cl bond distribution GaN after 5th Ar irradiation and 6th Cl adsorption process at accelerated voltages of 100 and 200 V. After Ar ion irradiation, Ar ion irradiated depth where concentration of Ga-Ga decreased by 1/e of maximum concentration is increased by Ar ion energy. After Cl radical exposure, Cl penetration depth where concentration of Ga-Cl and Ga-Cl_2 decreased by 1/e of maximum concentration is similar to Ar ion irradiated depth. This suggests that chlorinated layer thickness relates to damaged layer thickness. As a result, the etched depth would be predominantly determined by the damaged layer thickness. Namely, the etch depth is enabled to control by the ion energy in the Ar ion irradiation cycle.

[1] T. Takeuchi et al., J. Phys. D: Appl. Phys. 46, 102001 (2013).

[2] Y. Zhang et al., J. Vac. Sci. Technol. A 35, 060606 (2017).

10:45am **ALE2-TuM-10 Atomic Layer GaN Etching by HBr Neutral Beam***, S Samukawa,* ***Takahiro Sawada****, D Ohori,* Tohoku University, Japan*; K Sugawara, M Okada, K Nakata, K Inoue,* Sumitomo Electric Industries, Ltd., Japan*; D Sato, H Kurihara,* Showa Denko K.K., Japan

Refining AI/IoT techniques is absolutely essential for developing smart and sustainable societies. The amount of information in networks is becoming larger and larger as time goes on, and wireless high-speed and large-capacity data communication technologies such as 5G and beyond are key for processing big data. AlGaN/GaN high electron mobility transistors (HEMTs) are promising for both high-power and high-frequency applications because their two-dimensional electron gas (2DEG) has high saturation velocity, high mobility, and high carrier concentration with a high breakdown field. Although AlGaN/GaN HEMTs have many advantages, normally-off operation for GaN HEMTs is still a big challenge. In the gate-recess, normally-off operation is achieved by removing the barrier layer by dry etching to reduce the 2DEG concentration under the gate electrode. Thus, an atomic layer and defect-free etchings for GaN are indispensable to achieve high-frequency, high-power, and normally-off operation. In this work, we investigated atomic layer defect-free GaN etching by using Cl_2 and HBr neutral beams.

GaN etching rates and etching products on the substrate surface were investigated by using Cl_2 or HBr neutral beams with the beam acceleration bias power from 0 to 20 W. The gas flow rate and substrate temperature were fixed to 40 sccm and –20 ºC, respectively. To analyze the surface atomic layer etching reactions, we measured the Ga3d signal by X-ray photoelectron spectroscopy (XPS) and found that the surface composition ratio consisted of four kinds of peaks (Ga-Cl_3 or Ga-Br_3, Ga-O, Ga-N, and Ga metal) using Gaussian peak fitting. With the Cl_2 neutral beam, the Ga-O ratio (Ga dangling bond) increased, and the Ga-N ratio (GaN) decreased with bias power increases. The Ga-Cl3 ratio (etching product) did not significantly change, regardless of the bias power. In contrast, with the HBr neutral beam, higher Ga-N and lower Ga-O ratios could be achieved in spite of the high bias power, and the Ga-Br_3 ratio (etching product) was increased with increasing the bias power. The HBr neutral beam could make a thinner surface product layer than the Cl_2 neutral beam because the atomic size of Br is larger than that of Cl. The Cl_2 neutral beam had a five times higher etching rate than that of the HBr neutral beam at 20 W of beam acceleration bias power. These results suggest that $GaBr_3$ is a more involatile product and that the GaN surface is protected by the $GaBr_3$ layer. We found that HBr neutral beam etching could obtain more precise atomic layer level neutral beam assisted etching with the thinner and more involatile etching product layer.

Live Session
Room Live - Session LI2-TuM
Technical & Poster Sessions: Tuesday Live

Moderators: Harm C.M. Knoops, Oxford Instruments Plasma Technology, The Netherlands, Paul Poodt, Holst Centre / TNO

10:00am **LI2-TuM-7 Welcome and Introduction***, C Detavernier, J Dendooven,* Ghent University, Belgium*;* ***Paul Poodt****,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

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10:15am **LI2-TuM-8 Thermal Atomic Layer Deposition of Noble Metal Films Using Non-Oxidative Coreactants***,* ***Charles H. Winter****,* Wayne State University **INVITED**

Atomic layer deposition (ALD)[1,2] growth of noble metal (Ru, Os, Rh, Ir, Pd, Pt, Ag, Au) films is almost universally carried out by treatment of a volatile organometallic or metalorganic precursor with O_2 or ozone at temperatures of 200 °C or higher.[3] These processes lead to combustion of the organic ligands of the surface-bound metal precursors, affording a metal oxide layer, water, and CO_2. At temperatures above about 200 °C, the noble metal oxides decompose to the metals. By this general approach, thin films of Ru, Os, Rh, Ir, Pd, and Pt can be deposited. Despite the success of these existing ALD processes for noble metal films, O_2 and ozone are strong oxidants and can oxidize sensitive layers in microelectronics devices, such as W metal, TiN, and TaN.[4] Thus, combustion-based ALD processes using O_2 or ozone are unlikely to be suitable for depositions on easily oxidized substrates. Herein, we will described our efforts to develop alternative, non-oxidizing co-reactants for the thermal ALD of noble metal films. We will overview the growth of Ru metal films using (η^4-2,3-dimethylbutadiene)(tricarbonyl)ruthenium ($Ru(DMBD)(CO)_3$) with 1,1-dimethylhydrazine and several other N-based molecules.[5] With 1,1-dimethylhydrazine, an ALD window was observed from 200 to 210 °C, with a growth rate of 0.42 Å/cycle. X-ray photoelectron spectroscopy revealed >90% Ru metal in the films, with N (~7%) as the only significant contaminant. Annealing of these films under various atmospheres led to low resistivity, high purity Ru films. We will also report the thermal ALD growth of Re metal films, using Re precursors and nitrogen-based co-reactants.

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10:45am **LI2-TuM-10 Mixing It Up: Tuning Atomic Ordering in 2-D Mo1-xWxS2 Alloys by ALD***,* ***Jeff Schulpen****, E Kessels, V Vandalon, A Bol,* Eindhoven University of Technology, Netherlands

In this contribution, we show how ALD can be used to finely tune the atomic ordering of transition metal dichalcogenide alloys, while at the same time exerting excellent control over their alloy ratio. Transition metal dichalcogenides (TMDs) such as MoS2 and WS2 are promising for many applications ranging from photonics and nano-electronics to photovoltaics and catalysis. Tailoring the properties of these materials is often desired for specific applications. An effective method of enabling such tunability of these materials is by alloying multiple TMDs. Conventionally, investigations on alloys focus on how their properties change as a function of the alloy ratio, i.e. the abundance ratio of the constituents of the alloy. However, alloys also have another degree of freedom, namely their atomic ordering. This ordering can range from random to clustered, and controlling this parameter could enable additional tuning of the properties of TMD alloys.

We employ plasma-assisted ALD[1-2] to synthesize Mo1-xWxS2 films using a supercycle approach. The excellent control over the alloy achieved by this method is evidenced by XPS atomic abundance measurements and Raman spectroscopy, both of which indicate that the alloy ratio varies smoothly as a function of the relative number of MoS2 and WS2 cycles. Control over the atomic ordering of the alloys was achieved by manipulating the ordering of the ALD cycles while keeping the alloy ratio fixed. As a function of the ALD cycle ordering, systematic shifts are observed in the lattice vibration frequencies and in the exciton energies by Raman spectroscopy and visible light absorption spectroscopy, respectively. To understand these effects, density functional theory (DFT) calculations were performed on Mo1-xWxS2 structures of varying atomic ordering. Through comparison with the DFT results, we interpret our experimental results as indeed arising from the atomic-scale ordering of the alloy films. This supports the idea that ALD can be used to tune the atomic ordering of these materials, adding this parameter to the experimental toolbox for tailoring the material properties of TMDs by ALD.

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11:00am **LI2-TuM-11 Deposition of Conductive PEDOT Thin Films with EDOT and $ReCl_5$ Precursors***,* ***Saba Ghafourisaleh****, G Popov, M Leskelä, M Putkonen, M Ritala,* University of Helsinki, Finland

In this study we used the Oxidative Molecular Layer Deposition technique (oMLD) to deposit the most common conductive polymer – PEDOT. PEDOT is the polymer of ethylenedioxythiophene (EDOT, monomer) and has gained a lot of interest in solar energy and battery applications because it is stable, conductive, flexible and transparent. Here we were able to prepare PEDOT thin films by using a new inorganic oxidizing agent rhenium pentachloride ($ReCl_5$). We extensively characterized the properties of our films with XRD, EDS, SIMS and SEM.

Not many oMLD processes exist. The oMLD of polymers is based on sequential adsorption of the monomer and its polymerization that is induced by oxidation. The challenge in the oMLD of polymers is finding a suitable combination of precursors which is difficult because most organic monomers are non-volatile or unstable at high temperatures. Another challenge lies in finding an agent for oxidizing the organic monomer efficiently. The oxidizing agent should not contaminate the film with impurities, or if impurities are left in the film, they should be easily removed afterwards with post-deposition treatment.

The oxidizing agent used in this process is ReCl5 which has high thermal stability and high oxidizing ability. 3,4-Ethylenedioxythiophene EDOT is used as the organic monomer. With these precursors PEDOT films were deposited at temperatures in the 125-225 °C range. The polymer films were transparent in the visible region and showed high electrical conductivities.

XRD measurements showed that some rhenium residues were present in the polymer films and after the deposition these impurities segregated on the film surface in the form of rhenium oxychloride particulates. The PEDOT polymer is insoluble in water, whereas rhenium oxychloride is soluble. We post-treated the samples with deionized water. The post-treatment removed the contaminating rhenium impurities.

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

11:30am **LI2-TuM-13 Resistless Lithography Based on Local Surface Modification of Halogenated Amorphous Carbon***,* ***Mikhail Krishtab****,* KU Leuven/Imec, Belgium*; T Kulmala, E Cagin,* Heidelberg Instruments Nano, Switzerland*; S Armini,* Imec, Belgium*; S De Gendt,* KU Leuven/Imec, Belgium*; R Ameloot,* KU Leuven, Belgium

The fabrication of nanoscale devices involves multiple lithography steps which define the device's geometry and its performance. Electron-beam lithography and thermal scanning probe lithography (t-SPL) allow routine printing of features down to few tens of nanometers. Both techniques are based on the traditional resist process flow which relies on **bulk** modification of the sensitive layer to form an initial pattern. However, the achievement of the highest possible resolution requires application of very thin resist films thus making the successive pattern transfer particularly challenging. Inspired by the recent advances in the field of area-selective atomic-layer deposition (AS-ALD), we explored an alternative resistless approach based on local **surface** modification of an amorphous carbon film guiding the growth of a hard-mask layer.

The approach starts from plasma halogenation of a hydrogenated amorphous carbon film (a-C:H) deposited on top of a desired stack to be patterned (*Figure 1*). The carbon-halogen bonds (C-F, C-Cl) on the surface of the a-C:H prevent ALD growth of an inorganic hard-mask layer. The exposure of the halogenated a-C:H layer to a certain energy source during the appropriate lithography step (heating or e-beam) results in local breaking of the carbon-halogen bonds, which in turn enables the growth of the ALD hard-mask exclusively in the exposed areas. The formed thin hard-mask layer is then used for patterning of the a-C:H by plasma etching.

The complete patterning sequence was demonstrated using Cl_2- and CF_4-plasma treated a-C:H films and ALD TiO_2 ($TiCl_4/H_2O$) as a hard-mask deposition process. After validating the blocking capability of the 3-5 nm thick halogen-rich a-C:H surface (*Figure 2*), we studied its sensitivity to e-beam exposure (*Figure 3*) and its thermal stability (*Figure 4*). It was found that a relatively high e-beam dose was required to get a degree of surface dehalogenation sufficient for the deposition of a pinhole-free hard-mask layer. In contrast, the low decomposition temperature of the topmost halogen-containing surface groups favored t-SPL lithography. The latter appears particularly efficient when combined with an additional 405 nm laser source, exposure to which enabled fast formation of micron-size TiO_2 patterns. The final aspect of our study concerned the reduction of nucleation defects associated with imperfections of ASD TiO_2 process. The repetitive halogenation treatment and post-deposition plasma etching were tested as defect-reduction strategies.

11:45am **LI2-TuM-14 Mimicking Chitin and Chitosan Type of Functionality with Novel Thin Films Grown by Molecular Layer Deposition***, **Karina Ashurbekova**, M Knez,* CIC nanoGUNE BRTA, Spain

In a bioinspired approach, we are mimicking naturally occurring materials to fabricate hybrid antibacterial and biocompatible thin films for various applications.

In this work we will present a new process for generating chitin and chitosan type of functionality by Molecular Layer Deposition (MLD). A proposed deposition scheme of the underlying chitin-type of MLD process is presented in Fig. 1. Chitin and chitosan are prominent natural biocompatible and biodegradable polysaccharides that exhibit antimicrobial, antifungal and antiviral properties, which could find application in, for example, food packaging.

For the first time sugar molecules, such as, N-acetyl-D- mannosamine and N-acetyl-D-glucosamine, were used as precursors for MLD. Thionyl chloride was used as a chlorinating agent to bind the sugar molecules to the surface. ATR-FTIR spectra of the N-acetyl-D-Mannosamine/$SOCl_2$ MLD film show several bands that are characteristic of chitin.

Besides antimicrobial properties, packaging materials require good barrier properties for water vapor and oxygen. In order to create efficient gas diffusion barriers, various metals (Al, Ti and Zn) were grafted to the chain, creating hybrid Chitin-metal surfaces. In-situ Quartz Crystal Microbalance (QCM) studies show a linear mass increase during sequential dosing of N-acetyl-D-mannosamine and trimethylaluminum (TMA) (Fig. 2A) with a total mass gain per cycle (MGPC) of 20 ng/cm^2 (Fig. 2B).

The obtained hybrid MLD films grown at different temperatures were characterized by ATR-FTIR, X-ray reflectivity (XRR), X-ray photoelectron spectroscopy (XPS), in-situ QCM and Solid-state NMR (ssNMR).

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.

12:00pm **LI2-TuM-15 Closing Remarks & Sponsor Thank You***, C Detavernier, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; **Harm C.M. Knoops**,* Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

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ALD Applications
Room Van Rysselberghe - Session AA-TuA
ALD for Catalysis I & II

Moderators: Stacey F. Bent, Stanford University, Rong Chen, Huazhong University of Science and Technology

1:00pm **AA-TuA-1 Design of Advanced Photocatalytic Materials by Atomic Layer Deposition (ALD)**, ***Syreina Alsayegh***, *M Bechelany, F Zaviska, G Lesage,* Institut Européen des Membranes, France*; A Razzouk, J Stephan,* Lebanese University, Lebanon

Due to the increasing contamination of our natural water resources by a wide range of organic micropollutant (OMPs), there is a need for developing new energy-efficient advanced oxidation processes for the treatment of water contaminated by such refractory pollutants.

Photocatalysis has attracted much attention, due to its ability to degrade toxic organic compounds in wastewater into environmental friendly compounds such as CO_2 and water**.**

Among the various photocatalytic materials, titanium dioxide (TiO_2) has been widely used due to its high photocatalytic efficiency, high stability and low toxicity. However, fast charge recombination and the narrow absorption range in the UV spectrum; limit its photocatalytic efficiency under visible-light irradiation.

In this work TiO_2 nanofibers were synthesized by electrospinning method. In order to improve the photocatalytic activity under visible light, a developed process based on atomic layer deposition (ALD) was used to grow boron nitride (BN) and palladium (Pd) on these fibers. The morphological, structural and optical properties of all fibers were investigated by several characterization techniques such as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The influence of chemical and physical properties on the photocatalytic degradation of acetaminophen has been investigated. The results indicate that acetaminophen is stable and difficult to be photodegraded in the absence of photocatalyst. After 4h of visible light irradiation, acetaminophen has been degraded up to 90% in the presence of TiO_2-BN-Pd nanofibers, compared to only 20% degradation with pure TiO_2.

Based on these promising results, the development of ceramic nanofiltration membranes coated with these highly photocatalytic materials will be investigated. In parallel, a better understanding of the photocatalytic oxidation pathways (based on by-product analysis) coupled with toxicity tests (Vibrio Fisheri, Microtox) will be studied.

1:30pm **AA-TuA-3 Atomic Layer Deposition of Manganese Oxide Ultra-Fine Clusters on Titanium Dioxide Nanoparticles for Photocatalytic Hydrogen Production: Experiments & Simulations***,* ***Saeed Saedy****, R Verma,* Delft University of Technology, Netherlands*; S Rhatigan,* University College Cork, Ireland*; J Liu,* Delft University of Technology, Ireland*; M Nolan,* University College Cork, Ireland*; R van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) is an attractive method to synthesize advanced functional nanomaterials e.g. photocatalyst: materials that use light to drive chemical reactions. ALD enables depositing uniform nanoparticles (NPs) on the support with controlled size, shape, and morphology. We have deposited manganese oxide (MnO_x) ultra-fine clusters on titanium dioxide ($\mathrm{TiO}\text{-}_2$) NPs by means a fluidized bed ALD reactor. Bis(ethylcyclopentadienyl)manganese ($[(C_2H_5)C_5H_4]_2Mn$) and water were used for ALD of MnO_x clusters at 150°C. The microstructure and surface chemistry of ALD synthesized MnO_x/TiO_2 samples were examined using different methods including TEM, XPS, and XRD. The MnO_x/TiO_2 samples were employed as photocatalyst for solar production of H_2. In addition, we have performed first principles studies of models of MnO_x-modified TiO_2. We present detailed results on first principles modelling the metal precursor step in ALD of MnO_x on TiO_2 substrates.

TEM images of the samples revealed ultra-fine MnO_x clusters uniformly dispersed over TiO_2. Powder XRD was not able to detect any reflection corresponding to crystalline manganese oxide; indicating highly dispersed MnO_x. The surface chemistry study of ALD synthesized MnO_x/TiO_2 samples using XPS revealed that the majority of manganese exists in Mn^{2+} form. Such oxidation state could be attributed to mild synthesis temperature employed. This makes it possible to easily obtain the higher oxidation states (i.e. Mn^{3+} and Mn^{4+}) with further post-treatment of samples. In this way a good balance between different oxidation states of manganese, that are crucial for enhanced photocatalytic activity, could be obtained. Density functional theory (DFT) results show that a range of manganese oxidation states can co-exist, along with oxygen vacancies and that the modification of TiO_2 with MnO_x can enhance electron hole separation and trapping. Co-existence of Mn^{2+}, Mn^{3+}, and Mn^{4+} in heterojunction of MnO_x/TiO_2 facilitate charge separation and electron-hole trapping, resulting in superior H_2 productivity. The low temperature nature of ALD synthesis makes it possible to obtain good balance between these diverse oxidation states in final product; whilst the conventional wet chemistry methods require high temperature calcination step to remove the residues of precursors and solvent, which results in higher oxidation state of products as well as resulting in large particles.

1:45pm **AA-TuA-4 In situ Electrochemical APXPS Analysis of ALD Grown Cu Catalyst for CO_2 Reduction***, H Ali-Löytty, L Palmolahti, M Hannula,* ***Jesse Saari****,* Tampere University, Finland*; K Lahtonen,* Tampere University, Finlan*; H Wang, M Soldemo, A Nilsson,* Stockholm University, Sweden*; M Valden,* Tampere University, Finland

The grand challenge in artificial photosynthesis is to produce liquid solar fuels from water and carbon dioxide. Unfortunately, current materials solutions for a photocatalytic (PEC) solar fuel reactor lack efficiency, selectivity towards liquid fuel products, and long-term stability. Cu based catalysts are so far the most promising materials for the carbon dioxide reduction reaction (CO_2RR), whereas the selectivity of Cu catalyst towards liquid products is strongly affected by the exact chemical composition and structure. Recently, Eilert et al. suggested, based on in situ electrochemical APXPS measurements on Cu foil, that the high activity of oxide-derived copper towards CO_2RR stems from subsurface oxygen that was proposed to increase the CO binding energy and thus enhance the production of methanol and multicarbon products [1]. This contradicts the alternative hypothesis that assigns the activity to Cu_2O on the surface, albeit no copper oxide should be stable at reductive CO_2RR conditions.

In this work, ALD grown Cu oxide thin film was analyzed in situ by electrochemical APXPS at the HIPPIE beamline, MAX IV Laboratory. The results show similar oxygen species on reduced ALD Cu oxide thin film to what was assigned to subsurface oxygen in Ref. [1]. Therefore, the ALD grown Cu oxide thin film combined with ALD TiO_2 [2–4] forms a promising catalyst coating for photocathodes in solar fuel cells to produce methanol and multicarbon products from carbon dioxide, water, and sunlight.

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2:45pm **AA-TuA-8 Atmospheric-Pressure Atomic Layer Deposited Bimetallic MCu/CeO_2 Catalysts for Enhanced Removal of CO from Fuel-Cell Hydrogen by Preferential Oxidation***, E Farmani Gheshlaghi, A Irandoust,* ***Fatemeh Gashoul****, A Khodadadi, Y Mortazavi,* University of Tehran, Iran

Atomic layer deposition has recently been successfully used for uniform deposition of catalyst reactive species on supports with remarkable dispersion, intimate contact and stability. The hydrogen produced for PEM–fuel cells usually contains about 1% CO, which electrically poisons the fuel-cell. The CO can be removed at low temperatures by PROX.

Atomic layer deposition was used to deposit 2.3% Cu and either 0.3% Ni or 0.8% Ru on CeO_2 and the resulting bimetallic catalysts were used in preferential oxidation of CO in H_2-rich feed (PROX).

$Cu(acac)_2$ was reacted with CeO_2–OH groups at 210 ^oC for 75 min and the produced Hacac was monitored in a gas-cell in FTIR, followed by purging by Ar and subsequently introduction of zero-Air for oxidizing the remaining acac species at 350 ^oC for 30 min. The number of CeO_2–OH groups was determined by Grignard reaction. The self-limiting deposition of (acac)Cu-O-CeO_2 was confirmed by monitoring Hacac FTIR peak at 1626 cm^{-1}. The sharp decay of CO_2 produced in the oxidation step of remaining acac ligand was a further proof for self-limited deposition. The Catalyst average particle sizes are in the range of 8.7-13.4 nm. 2.3wt% Cu was deposited on ceria by ALD with a remarkable dispersion of 93% when 0.3wt% Ni was ALD deposited on the CuO/CeO_2 the dispersion is still very high at 84%, while the dispersion of the same $NiCu/CeO_2$ catalyst prepared by the conventional method of impregnation is much lower at 66%. $NiCu/CeO_2$ catalyst prepared by ALD reduces about 80-90 °C lower than the one prepared by impregnation, indicating higher oxygen mobility required for the PROX.

The CO conversion of catalysts in PROX is shown in Fig3 .The lowest T_{50} and T_{90}, (i.e. temperatures at 50 and 90% CO conversion, respectively) were observed for $RuCu/CeO_2$. The $NiCu/CeO_2$ catalyst prepared by ALD showed much higher activity corresponding to lower T_{50} and T_{90} than the one prepared by impregnation. This catalyst showed a bifunctional synergy of chemisorption and activation of CO on Cu species and mars van krevelen oxidation using surface bimetallic nickel-copper oxide [1, 2]. In conclusion, the $NiCu/CeO_2$ and $RuCu/CeO_2$ catalysts prepared by self-limiting ALD method showed a remarkably high dispersion and activity in PROX.

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3:30pm **AA-TuA-11 ALD Fabrication of BN Membranes: Environmental Applications***, **Catherine Marichy**,* CNRS, France*; W Hao, C Journet, V Salles,* UNiv Lyon 1, France **INVITED**

Boron nitride (BN) structures are very attractive materials with applications in various areas such as in energy[1] and environmental domains[2]. In particular, BN nanotubes (BNNT) have proven to be suited for conversion of osmotic energy. Use of nanotubes arrays or membrane would thus allow osmotic power harvesting under salinity gradients. BN nanostructures like foams and nanotubes have also revealed to be promising for water purification. ALD technique is an effective approach for surface modification and fabrication of complex nanostructured materials[3]. Recently, based on the polymer derived ceramics route, we developed a two-step ALD process[4] that enables using polymer template and fabricating various BN nanostructures.

Herein, the potential of ALD combined with PDCs for BN membranes will be discussed and exemplified. Highly stable boron nitride nanotube (BNNT) mats are fabricated, from low cost unwoven template, using the 2-step ALD of BN. The obtained membranes display high quality BNNTs, superhydrophocity and stability over a month in air and various pH conditions. Thin material containing several thousands of BN tubes, are also prepared, from a commercially available membrane. In particular, using a double inversion of a polymer membrane combining ALD and PDC vapor infiltration, good quality and large surface boron nitride membranes are successfully elaborated with fine control of the through porosity in term of shape (from annular to cylindrical pores) and size (from few tens to hundreds nanometers)[5]. The ALD fabricated BN materials are characterized in term of morphology and structure using TEM, SEM, EDS, XPS and Raman. Particular attention is given to their use and performances in water treatment.

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4:15pm **AA-TuA-14 Highly Stable and Active Catalyst for Dry Reforming of Methane via Molecular Layer Deposition Approach***, **Piyush Ingale**, C Guan, R Kraehnert, R Naumann d'Alnoncourt, A Thomas,* Technische Universität Berlin, Germany*; F Rosowski,* BASF SE, Germany

Nickel based catalysts are typically used for the production of synthesis gas by reforming reaction [1]. Dry reforming of methane (DRM) is an attractive reaction for production of synthesis gas by reduction of carbon dioxide. However, Ni nanoparticles (NPs) used in DRM reaction suffer from severe coking and sintering at high temperature which leads to decreased activity of the catalyst [2]. The challenge is to synthesize a catalyst with a high Ni loading and dispersion that is stable under reaction conditions.

Molecular Layer Deposition (MLD) is a novel technique, which is a variant of atomic layer deposition. Organic compound replaces H_2O as ALD reactant to form purely organic or hybrid inorganic-organic layers [3]. In our study, we deposited thin hybrid inorganic-organic layers of alucone on NiO/SiO_2 catalyst via alternative reaction of trimethylaluminium and ethylene glycol at 150°C in a fixed bed reactor [4]. The growth behavior of alucone layers on NiO/SiO_2 powder was studied by in-situ mass-gravimetric study. The synthesized catalytic materials were analyzed by N_2 sorption, XPS, XRD, HRTEM and XRF. The reference and MLD modified catalysts were tested for activity and stability during dry reforming of methane at different temperatures (500°C-800°C). Deactivation of a Ni/SiO_2 reference catalyst was prevented by forming a defined porous net-like over-layer by decomposition of sacrificial organic part of alucone, which prevented the sintering and detachment of Ni nanoparticles by filamentous carbon.

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4:30pm **AA-TuA-15 Using ALD to Probe Support and Promoter Effects for Syngas Conversion Catalysts***, S Nathan, A Asundi,* Stanford University*; A Hoffman, A Boubnov, S Bare,* SLAC National Accelerator Laboratory*; **Stacey F. Bent**,* Stanford University

With the intensifying global need for alternative energy and fuels, there is strong interest in the development of efficient catalysts that can drive the chemical conversion of renewable resources into useful products. One promising pathway is to catalytically convert synthesis gas (syngas, $CO + H_2$) to oxygenates. However, a commercial catalyst that converts syngas to desirable products such as ethanol and other higher oxygenates has not yet been developed due to the many kinetically favorable side reactions that shift selectivity away from the desired products. We study the conversion of syngas to synthetic liquid fuels and high-value chemicals using supported metal, heterogeneous catalysts. Two different examples will be described in which atomic layer deposition (ALD) is used to precisely-modify the catalysts to probe support and promoter effects. First, the promotion of rhodium-based catalysts, which have intrinsic selectivity towards desirable higher oxygenate production, is explored using metal oxides deposited by ALD to modify Rh nanoparticles with monolayer-precise amounts of MoO_3. We show that the promoted catalysts exhibit an increase in both activity and oxygenate selectivity relative to unpromoted Rh nanoparticles, and that this is the result of formation of a novel catalyst structure. The second system is cobalt-based catalysts. Recently, interest has risen in Co_2C catalysts for oxygenate production. We will describe how introducing a ZnO promoting overlayer on Co/SiO_2 by ALD significantly enhances oxygenate selectivity by enabling Co_2C formation during syngas reaction. By exploring several different metal oxide supports, we will show that the composition of the support surface strongly controls whether ZnO-promoted Co can transform into the catalytically-selective Co_2C. Synchrotron-based studies provide insight into the mechanisms by which the support and promoters change reactivity, while density functional theory (DFT) calculations reveal the reaction pathways on the ALD-modified catalyst surfaces. The outlook for atomic scale surface modification using ALD to synthesize and study catalytic materials will be discussed.

ALD Fundamentals
Room Jan & Hubert Van Eyck - Session AF-TuA

Characterization I & II

Moderators: Jiyoung Kim, University of Texas at Dallas, Jin-Seong Park, Hanyang University

1:15pm **AF-TuA-2 Laterally Resolved Low Energy Ion Scattering Study of Selective ALD Model Samples***, **Philipp Brüner**, T Grehl,* IONTOF GmbH, Germany*; A Mameli, F Roozeboom, P Poodt,* TNO/Holst Center, Netherlands

We present a low energy ion scattering (LEIS) study of various model samples for area-selective spatial ALD of SiO_2. The aim of the study is to assess SiO_2 selectivity and growth behavior on a number of different substrates intended as non-growth areas, including Al_2O_3, IGZO, Ta_2O_5, ZrO_2, SnO_2, and ZnO.The SiO_2 films were grown in a spatial ALD reactor, using a three-step approach consisting of successive doses of inhibitor (a carboxylic acid), silicon precursor (bis(diethylamino)silane, BDEAS) and O_2 plasma [1]. The rotary spatial ALD reactor design leads to varying dosing times of the ALD chemicals along the wafer radius, so that the different areas on the wafer are exposed to different deposition conditions [2]. Thus, laterally resolved surface analysis allows for investigating the effect of different exposure times on the selectivity on one and the same sample.

Due to the high surface sensitivity of just a single monolayer, coupled with simultaneous film thickness measurements, LEIS reveals important information about the early stages of film growth, such as surface coverage, layer closure, growth mode, and deposition rate. We show how LEIS spectra are analyzed to separate the measurement signal of the first monolayer ("surface signal") from contributions from deeper layers ("sub-surface signal"). The surface signal is evaluated to quantify the elemental composition of the outer monolayer of the sample, while the sub-surface signal contains information about elements below the surface and about film thickness.

A typical LEIS measurement probes a region of about 2x2 mm² of the sample surface. In combination with stage scanning, larger scale wafer mapping becomes possible, where small variations in film thickness and coverage across the wafer are detected with high precision. As a result, the film properties can be correlated to different exposure times of the spatial ALD process, and therefore derive optimal conditions for maximizing the selectivity.

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1:30pm **AF-TuA-3 In situ Characterization of Quantum Dot Photoluminescence during Atomic Layer Deposition: Towards Stable Cd-Free QD-Based Devices***, **Robin Petit**, N Zawacka, J Kuhs, P Smet, Z Hens, C Detavernier,* Ghent University, Belgium

Quantum dots (QD) are emerging as optically active components in an increasing number of applications including solar cells and concentrators, light-emitting diodes and lasers [1-4]. This surge is attributed to the unique benefits QD provide resulting from their size-tunable opto-electronic properties and the possibility for solution-based processing. In order to compete with the current state-of-the-art in other technologies, the stability of the QD optical performance needs to be addressed. In many cases, the QD are embedded in a host matrix which can act as a barrier, shielding the QD from their immediate environment (and vice versa) [5, 6]. One of the most promising methods used for embedding is atomic layer deposition (ALD), a vapor-based deposition technique enabling layer-by-layer growth by adopting sequential exposure to precursor materials and suitable reactants. However, the embedding of QD with ALD has been shown to also affect the QD optical performance [7]. Here, we report on a novel method to preserve the QD optical stability during the entire ALD process.

Previously, we reported on the photoluminescence (PL) stability of CdSe/CdS/ZnS core/shell/shell QD during the ALD process [8]. Due to the toxicity of Cd, the use of Cd-based QD should be avoided as much as possible. In the current study, the Cd-free $CuInS_2$/ZnS core/shell QD and InP/ZnSe core/shell QD are investigated adopting a similar approach as before [8]. Using a home-built in situ PL setup the effect of different precursors (TMA, TDMAT, DEZ), reactants (H_2O, O_3), gases (O_2, H_2O, N_2, Ar) and plasma's (O_2, H_2O, H_2) on the QD PL is evaluated, elucidating the QD PL behaviour during complete ALD cycles (Al_2O_3, TiO_2, ZnO). We demonstrate that the QD PL intensity can be maintained by incorporating an additional QD encapsulation step prior to coating with ALD. In this regard, important progress is made towards stable Cd-free QD-based devices, suitable for a growing number of applications.

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1:45pm **AF-TuA-4 Capturing the Dynamic Atomic Structure in ALD Reactions with *In situ* XANES, *ab initio* Simulations, and Machine Learning***, **Orlando Trejo**,* University of Michigan*; A Dadlani,* Norwegian University of Science and Technology, Norway*; F De La Paz, S Acharya, R Kravec,* Stanford University*; D Nordlund, R Sarangi,* SLAC National Accelerator Laboratory*; F Prinz,* Stanford University*; J Torgersen,* Norwegian University of Science and Technology, Norway*; N Dasgupta,* University of Michigan

In order to continue to improve our fundamental understanding of ALD growth mechanisms, we must build upon our model understanding of self-organization at the atomic scale. In particular, there is a need for a more detailed mechanistic understanding of the dynamic structural evolution of materials during thin-film growth. In this study, *in situ* X-ray absorption spectroscopy (XAS) measurements of the S K-edge during the growth of ZnS thin films on TiO_2 nanoparticles were collected and analyzed.[1] We built a modular ALD that can safely be used to deposit and characterize ALD of sulfide materials at the Stanford Synchrotron Radiation Lightsource. The two precursors used were H_2S and diethylzinc.

The experimental results show that sulfide and sulfate species form during the nucleation phase of ZnS on TiO_2. As the film growth proceeds, the S K-edge spectra of the *in situ* ZnS film converge to that of a representative *ex situ* ALD ZnS film. Through high-throughput screeningof *ab initio* simulations of the XAS spectra, we were able to observe the stage in the growth process during which the surface sulfur species transition into a four-fold coordination environment that resembles the bulk ZnS crystal structure. We simulated XANES spectra using the FEFF9 code and built a computational platform to enable high-throughput generation, modeling, and analysis of atomic configurations based on the simulated spectra. We used random forests and artificial neural networks to create a workflow for determining the structural changes of representative S moieties during ALD growth. The experimental and computational strategies presented in this study provide an example of how *in situ* synchrotron-based characterization can be leveraged using machine learning approaches to capture the dynamic atomic structure during thin-film synthesis.

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2:00pm **AF-TuA-5 Atomic Layer Deposition of Erbium Oxide, Erbium Fluoride and Stoichiometrically-Tunable Erbium Oxyfluoride Films***, **Neha Mahuli**, S George,* University of Colorado - Boulder

Rare earth metal oxides, metal fluorides and metal oxyfluorides have received attention as protective coatings in reactive plasma environments. Our recent work has developed the atomic layer deposition (ALD) of AlO_xF_y [1], HfO_xF_y and ZrO_xF_y oxyfluorides. This current study explored the ALD of erbium oxide (Er_2O_3), erbium fluoride (ErF_3) and erbium oxyfluoride(ErO_xF_y). Various deposition mechanisms were investigated to achieve tunable stoichiometry in ErO_xF_y films based on the HF exchange method and the nanolaminate method.

The depositions were performed at 250°C using $Er(n\text{-}BuCp)_3$ as the Er source. H_2O and HF were used as the oxygen and fluorine sources, respectively. Initially, erbium oxide and erbium fluoride ALD were investigated using *in situ* quartz crystal microbalance (QCM) measurements. The Er_2O_3 ALD cycle consisted of alternating exposures of $Er(n\text{-}BuCp)_3$ and H_2O. Both reactions exhibited self-limiting behavior versus reactant exposure. The Er_2O_3 ALD growth rate was 64 ng/(cm² cycle) or 0.7 Å/cycle. The ErF_3 ALD cycle consisted of alternating exposures of $Er(n\text{-}BuCp)_3$ and HF. Both reactions again exhibited self-limiting behavior versus reactant exposure. The ErF_3 ALD growth rate was 32 ng/(cm² cycle) or 0.4 Å/cycle (Figure 1).

Erbium oxyfluoride ALD was then conducted using the HF exchange method and the nanolaminate method. The HF exchange method is based on the thermodynamically favorable F/O exchange reaction between HF and Er_2O_3. Compositional control was obtained by varying the HF exposure time, HF pressure and the thickness of the underlying Er_2O_3 film. In the nanolaminate method, sequential deposition of Er_2O_3 ALD and ErF_3 ALD nanolayers defined each supercycle (Figure 2). Compositional control was achieved by varying the ratio of number of Er_2O_3 ALD cycles to ErF_3 ALD cycles. X-ray photoelectron spectroscopy (XPS) and Rutherford Backscattering Spectroscopy (RBS) analysis were utilized to evaluate the ErO_xF_y ALD film composition. The ErO_xF_y ALD film stoichiometry could be varied from Er_2O_3 to ErF_3 using the HF exchange method and the nanolaminate method.

[1]Neha Mahuli, Andrew S. Cavanagh and Steven M. George, "Atomic Layer Deposition of Aluminum Oxyfluoride (AlO_xF_y) Thin Films with Tunable Stoichiometry", *J. Vac. Sci. Technol. A* **38**, 022407 (2020).

2:30pm **AF-TuA-7 From the Noise: Measuring Atomic Structure in Amorphous Thin Films Grown by Atomic Layer Deposition***, **Matthias Young**,* University of Missouri-Columbia*; N Bedford,* University of New South Wales, Australia*; J Elam, A Yanguas-Gil, S Letourneau, M Coile, D Mandia, B Aoun,* Argonne National Laboratory*; S George, A Cavanagh,* University of Colorado - Boulder*; X He, A Jasim,* University of Missouri-Columbia*; Q Wyatt,* University of Missouri-Columbiai*; N Paranamana, T White,* University of Missouri-Columbia **INVITED**

The ability to successfully translate ALD coatings to applications is impaired by limited understanding of process-structure-property relationships for nanoscale ALD films, and especially by a lack of understanding of the structure of these films at an atomic or molecular level. Single-crystal materials are only rarely achieved by ALD. More often, ALD films form amorphous, polycrystalline, or defective structures. ALD process conditions such as precursor selection(s), precursor exposure(s), and reactor temperature are known to impact the properties of ALD films. The substrate also affects the properties of ALD films, especially for ultrathin film thicknesses. To date, the ALD community has had difficulty connecting the atomic-scale structure of ALD films with their performance, largely because of limited availability of techniques to determine the atomic-scale structure of ultrathin ALD films. In this talk, we summarize recent work and report new results employing high energy X-ray diffraction and electron diffraction, both coupled with pair distribution function analysis and Reverse Monte Carlo modeling, to reveal new understanding of the atomic structure of ALD films. The techniques we discuss can be applied broadly to understand the local structure of ALD films, including low-Z and amorphous films, and help tailor ALD coatings for a range of applications of emerging interest.

4:00pm **AF-TuA-13 Effects of Gas Phase Reaction Chemistry on Electronic Conductivity of ALD Grown TiO_2 Films***, **Aein Babadi**, P McIntyre,* Stanford University

In situ monitoring of gas phase composition has been used to provide a link between changes in gas phase chemistry during ALD half-cycle reactions, and the electronic conductivity and metal:oxygen ratio of the deposited TiO_2 films. Dimethylamine ($(CH_3)_2NH$), DMA was probed as the main product of both the TDMAT and water vapor half-reactions during the TDMAT/H_2O ALD process. In-plane transport characteristics of the ALD grown films demonstrated that the presence of DMA significantly increases the conductivity and transiently reduces the TiO_2 films by its reaction with surface oxygen-containing species.

In this study, we show that relatively slight variations in ALD conditions can cause large changes in the electrical conductivity of TiO_2 films. The experiments were performed in a custom-designed ALD system with a load lock to ensure a low base pressure ($<1\times10^{-3}$ Torr) of the process chamber with the aim of minimizing the potential wall reaction/contamination during the wafer load and unload sequences. A residual gas analyzer (RGA) with the mass range of 1-300 amu was integrated with the ALD reactor to achieve real-time chemical diagnostic data of the TiO_2 ALD process. An adequate pressure gradient between the process environment 5×10^{-3} Torr and the RGA region 1×10^{-6} Torr was maintained through a differentially pumped sampling system. TiO_2 films were grown using half-cycle dosing of Tetrakis(dimethylamino)titanium (TDMAT) and water vapor on both p-type silicon single crystal substrates with resistivity of 0.001-0.005 Ω.cm and fused silica with resistivity of $\rho \sim 10^{12}$ Ω.cm @ 250℃. The silicon samples were used for physical characterization while all the electrical measurements were performed on the fused silica samples. Electrical conductivity of TiO_2 films deposited on highly resistive fused silica substrates was measured using transmission line method (TLM). TLM test patterns were defined by electron beam evaporation of Pt (200 nm thickness) through a shadow mask. TLM measurement results showed an increase in resistivity as TiO_2 films are deposited with longer purge time, suggesting that DMA has the potential to reduce the TiO_2 film during the deposition. Intentional dosing of DMA, at the end of TiO_2 atomic layer deposition was used to alter the resistivity of the film by reducing the TiO_2 film transiently resulting from the reaction of DMA with surface oxygen containing species. Angle-resolved X-ray photoelectron spectroscopy was used to test for evidences of reduction of the TiO_2 films as a result of DMA exposure under ALD and ALD-like conditions. The concentration of the Ti^{3+} defect states was investigated by angle-resolved XPS (see supporting info.).

4:15pm **AF-TuA-14 *In Situ* Reflection High Energy Electron Diffraction in Atomic Layer Deposition for Monitoring the Epitaxial Transformations***, N Strandwitz, **Alexandra Howzen**,* Lehigh University

The maximum amount of thermal energy available during atomic layer deposition (ALD) is generally determined by the decomposition temperature of the precursors and also sets the maximum temperature in the "ALD window". This maximum temperature in some cases limits the structural perfection and extent of crystallization in resulting films. Intermittent annealing during the film growth in between ALD chemical exposures has been explored previously and shown to increase density and quality of ALD films.[1] However, without direct monitoring of one or more of the physical properties of the films, it can be difficult to determine the nuances of film transformation, such as crystallization temperature, surface roughening, and dependence on gas ambient.

In this work we integrate reflection high energy electron diffraction (RHEED) into a home-built ALD system to monitor structural and morphological transformations during ALD growth and thermally-induced structural transformations. RHEED is a surface sensitive diffraction technique that utilizes high energy (> 10 keV) electrons at a glancing angle, and is most commonly utilized in molecular beam epitaxy and pulsed laser deposition systems. The relatively high pressures associated with ALD are incompatible with RHEED due to filament instability and a short electron mean free path, necessitating differential pumping on the electron gun, and either 1) a short path length for electrons or 2) a pump down to high vacuum conditions. In addition to describing the system design, flow, and thermal modelling; we will show initial results of the deposition and annealing of ultrathin films (1-20 ALD cycles) focusing on transformations of polymorphic Ga_2O_3. The integration of RHEED with ALD offers a slow-motion picture of traditional epitaxial growth techniques by decoupling the deposition and crystallization steps with simultaneous monitoring of the surface structure.

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4:30pm **AF-TuA-15 In Situ Detection of the Reaction Heat Produced by ALD on High-Surface-Area Substrates***, **Benjamin Greenberg**, K Anderson, M Wolak, A Jacobs, J Wollmershauser, B Feigelson,* U.S. Naval Research Laboratory

Many ALD reactions are highly exothermic, with some likely releasing hundreds of kJ/mol per cycle. In ALD on conventional substrates (e.g., wafers), this exothermicity is typically ignored, because the deposited mass is small compared to the substrate mass. However, in the case of high-surface-area substrates such as metal-organic frameworks (MOFs) or nanopowders, the coating/substrate mass ratio can be thousands or millions of times higher, raising the possibility of nonnegligible reaction heat. To understand the potential impact of this heat on the substrate and ALD process, we measure via pyrometry the surface temperature of a static bed of low-thermal-conductivity ceramic nanopowder undergoing particle ALD (pALD). Depositing Al_2O_3 from trimethylaluminum (TMA) and water on Y_2O_3-stabilized ZrO_2 (YSZ) nanopowder with an average nanoparticle (NP) diameter of 8 nm, we observe temperature gains, ΔT, around 20 °C above the baseline. Given that the pyrometer measures only surface temperature, we propose that within the nanopowder bed—or in a hypothetical fluidized bed—the maximum local ΔT may be significantly greater than 20 °C. This proposition is supported by a calculation of individual NP temperature based on literature reaction enthalpies and sticking coefficients. To complement our investigation of NP temperature, we also acquire high-speed videos of nanopowder agitated in a rotary pALD reactor and examine how cyclical changes in surface energy influence NP motion.

Atomic Layer Etching
Room Baekeland - Session ALE1-TuA

ALE of Si-based Materials

Moderators: Thorsten Lill, Lam Research Corporation, Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation

1:00pm **ALE1-TuA-1 Realizing Selective Material Removal in Plasma-Based Atomic Layer Etching (ALE)*, Gottlieb Oehrlein,*** University of Maryland **INVITED**

In atomic layer etching (ALE) one applies iteratively sequences of cycles consisting of reactant supply and surface reaction steps to establish self-limited material removal approaching atomic scale. Since for ALE the reactant is injected only during the surface functionalization step, the surface changes continuously which has important implications for achieving materials etching selectivity. We will discuss several examples of how high materials etching selectivity in ALE may be achieved. In a first approach we describe the use of complex fluorocarbon film precursors to achieve highly selective ALE of SiO_2 over various underlayers. Additionally, reactants during the deposition step may exhibit substrate-selective deposition based on the chemical affinity of precursor gases to the substrate and nature of interfacial bonding. Combining substrate-selective deposition with a surface reaction step provides a new approach for achieving material-selective ALE, and we will describe results selective removal of HfO_2 over Si surfaces. Another material system that can be improved via ALE processing is that of maximizing the etching selectivity of a hard mask material like SiO_2 to extreme ultraviolet (EUV) photoresists in a pattern transfer process, and will be briefly reviewed.

Acknowledgements

I gratefully acknowledge the contributions and collaboration of K.-Y. Lin, A. Pranda, C. Li, D. Metzler, S. Engelmann, R. Bruce, and E. Joseph to this work, and would like to thank Semiconductor Research Corporation (Task No. 2017-NM-2726) and National Science Foundation (CBET-1134273) for funding.

1:30pm **ALE1-TuA-3 Atomic Layer Etching of SiO_2 and Si_3N_4 with Fluorocarbon, Hydrofluorocarbon, Fluoroether and Fluoroalcohol Compounds*, Yongjae Kim,*** *S Kim, H Kang, Y Lee, H Chae,* Sungkyunkwan University, Republic of Korea

Highly precise etching technologies are required to etch nanometer scale patterns and to achieve high selectivity in atomic level etching. [1-3] In this work, cyclic plasma atomic layer etching process was performed for SiO_2 and Si_3N_4 with surface modification in an inductively coupled plasma (ICP) reactor with fluorocarbon, hydrofluorocarbon, fluoroether and fluoroalcohol plasmas. Etch rate were compared at various conditions of plasma power and reaction gases. The process consists of two steps of surface modification and removal step. In the first step, fluorocarbon(FC) layers were deposited on SiO_2 and Si_3N_4 surface with fluorocarbon, hydrofluorocarbon, fluoroether, and fluoroalcohol plasmas. In the second step, the modified layers are removed with ions or radicals generated from Ar or O_2 plasmas. The etch rate was correlated with the fluorine-carbon (F1s/C1s) ratio determined from XPS peaks. Fluoroether and fluoroalcohol plasma generated FC layers having the lowest F1s/C1s ratio, and C_4F_8 plasmas produced the highest F1s/C1s ratio. Constant etch rates were observed in the bias voltage range of 55–60 V, which is identified as the ALE window. Self-limiting etch rate was confirmed with the etching process time and the etch rate could be controlled below 10 Å/cycle. High selectivities of SiO_2/Si and Si_3N_4/Si were obtained with fluoroether precursor having low F1/C1s ratio and the higher carbon on surface is attributed to the lower Si etch rate.

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Keywords: Cyclic plasma etching, Fluorocarbon polymer, Selectivity

1:45pm **ALE1-TuA-4 Strategies to Enhance the Etch Selectivity During Plasma–Assisted Atomic–Scale Etching of SiO_2 over SiN_x*, Ryan Gasvoda,*** Colorado School of Mines*; Z Zhang, E Hudson,* Lam Research Corp.*; S Agarwal,* Colorado School of Mines

Atomic layer etching (ALE) and its derivatives can provide high etch fidelity, atomic–scale precision, directionality, and high selectivity that is required for manufacturing of sub–7–nm node semiconductor devices. Specifically, plasma–assisted ALE of SiO_2 and SiN_x with ultra–high selectivity of SiO_2 to SiN_x is required in the self–aligned contact etch step. Generally, high selectivity can be achieved through manipulating the process and plasma parameters (similar to continuous etching). To further increase overall etch selectivity, we selectively functionalize the SiN_x surface with benzaldehyde prior to the start of etching. This pre–functionalization retards the net etch of SiN_x in the subsequent ALE process leading to higher SiO_2 to SiN_x etch selectivity. This etch selectivity can be reversed by selectively functionalizing the SiO_2 surface.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy in combination with *in situ* 4–wavelength ellipsometry to monitor surface reactions, film composition as well as etch per cycle during ALE. Further, the ion energy distribution (IED) in the Ar plasma activation half–cycle is characterized with a retarding field energy analyzer. We have shown previously that cyclic azasilanes can be used to selectively functionalize the SiO_2 surface from the gas phase. Figure 1 shows the infrared active region of a SiN_x (green) and SiO_2 (blue) surface exposed to benzaldehyde which selectively functionalizes the SiN_x surface with sp^2–hybridized–carbon. Figure 2 shows the infrared absorbance change for 15 sequential ALE cycles on a) bare SiN_x surface and b) benzaldehyde functionalized SiN_x. In both cases, we observe a broad increase in absorbance from ~1200 – 1800 cm^{-1} which indicates the formation and accumulation of an etch inhibiting graphitic fluorocarbon film. An etch stop is observed at cycle 13 for both SiN_x surfaces, however the net etch of SiN_x is ~20% less (~2 nm) for the benzaldehyde functionalized SiN_x than the net etch of the bare SiN_x. This shows that pre–functionalizing a SiN_x surface, selective to a SiO_2 surface, can reduce the overall SiN_x etch loss. Further, we discuss the role of maximum ion energy and IEDs in the activation step on overall etch selectivity with specific focus on non–ideal Ar plasma activation steps where the maximum ion energy is above the sputtering threshold of both SiO_2 and SiN_x.

2:00pm **ALE1-TuA-5 Cryo-ALE of SiO_2 with C_4F_8 Physisorption: Process Understanding and Enhancement*, Gaëlle Antoun,*** *T Tillocher, P Lefaucheux, R Dussart,* GREMI Université d'Orléans/CNRS, France*; A Girard, C Cardinaud,* IMN Université de Nantes/CNRS, France*; K Yamazaki,* Tokyo Electron Limited, Japan*; J Faguet, K Maekawa,* TEL Technology Center, America, LLC

Cryogenic Atomic Layer Etching (Cryo-ALE) is a different approach for ALE, proposed in order to limit drifts due to reactor wall contamination during a process. The proof of principle has been performed on SiO_2 using a fluorocarbon gas and presented in [1].In this process, C_4F_8 is injected in gas phase, and physisorbs on the cooled surface of the substrate. Then Ar plasma is initiated in order to activate the etch. However, in [1], the authors demonstrated the possibility to achieve the etching only at -120°C in their experimental conditions. The aim of this paper is to better understand the mechanisms involved in Cryo-ALE in order to enhance the process and increase the operating temperature.

In order to achieve this work, an ICP reactor has been used. An in-situ ellipsometer as well as an Electrostatic Quadrupole Mass Spectrometer (QMS) are coupled to the reactor. The ellipsometer is used in kinetic mode in order to follow the thickness variation during the process. The QMS is used to follow some species in Multiple Ion Detection (MID) mode. Tests were all performed on SiO_2 coupons glued on SiO_2 6” carrier wafers.

In addition, for surface characterization, quasi in-situ X-Ray Photoelectron Spectroscopy (XPS) measurements were also performed. The ICP reactor used here is different and the substrate is moved from the reactor to the XPS chamber with a transfer rod while keeping the substrate at low temperature.

In order to understand the mechanisms involved in Cryo-ALE, QMS tests were first performed by injecting a C_4F_8 gas flow during one minute on a cooled surface. The substrate temperature and the pressure of C_4F_8 were then varied in order to determine their influence on the surface residence time of C_4F_8. Those tests were also followed by ellipsometry in order to monitor the thickness physisorbed on the substrate surface. XPS tests in same conditions were performed and correlated with QMS results. Indeed, it has been demonstrated that decreasing temperature increases the C_4F_8 surface residence time and hence increases the concentration of fluorine at the surface.

With those data, it was possible to perform new cryo-ALE cycles by increasing the temperature to -90°C. Hence, very regular 150 cryo-ALE cycles were achieved with an etching amount of 0.13 nm/cycle.

The authors would like to thank S.Tahara for all the discussions that helped contributing to those results.

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2:30pm **ALE1-TuA-7 Interpretation of SiO_2 Atomic Layer Etching via a Simple Analytic Model***, **Youngseok Lee**, I Seong, J Lee, S Lee, C Cho,* Chungnam National University, Korea*; S Kim,* Nanotech, Korea*; S You,* Chungnam National University, Korea

We established a simple analytic model of SiO2 thickness changes during SiO_2 atomic layer etching (ALE) and analyzed our experimental data of sample thickness change trends at various ALE conditions via our model. SiO2 ALE experiments were conducted with C4F8/Ar inductively coupled plasma by admitting C4F8 gas into continuous Ar plasma for surface modification (reaction A) of the SiO_2 surface and turning the C4F8 gas off for removal of the modified surface (reaction B) by the Ar plasma ion bombardment. During that process, the thickness change of the SiO_2 samples was monitored using an in-situ multi-wavelength ellipsometer, which showed an increase of the total sample thickness including that of a fluorocarbon (CFx) film deposited on the SiO_2 surface during reaction A and a decrease during reaction B. Then, the ellipsometric results were fitted with our analytic model, which is based on the mechanism of conventional SiO_2 etching using CFx plasma that has previously been understood in detail. As a result, our model could explain several characteristic trends of the sample thickness change under different conditions, and the trends seemed to be mainly related to the deposition rate of CFx film on the SiO_2 surface. The higher CFx film deposition rate is expected to lead to more desirable ALE results. In addition to experimental data analysis, useful insights for advanced SiO_2 ALE could be achieved through the model, helping to decide the optimized ALE condition. In this presentation, physical validity of the model and SiO_2 ALE interpretation that was obtained by the model will be discussed.

Atomic Layer Etching
Room Baekeland - Session ALE2-TuA

Novel ALE Techniques and Materials

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Alok Ranjan, TEL Technology Center, America, LLC

4:30pm **ALE2-TuA-15 Novel Chemistries for Layer-by-Layer Etching of 2D Semiconductor Coatings and Organic-Inorganic Hybrid Materials***, **Anil U. Mane**, M Young, D Choudhury, S Letourneau, A Yanguas-Gil, J Elam,* Argonne National Laboratory **INVITED**

Here we report two new advances in atomic layer etching (ALEt) that extend our range of capabilities in nanoscale device fabrication. Semiconductor device manufacturing is limited by our ability to precisely deposit and remove thin film layers at the various levels of multistep device fabrication processes. Consequently, innovations in atomic layer deposition (ALD) and etching methods are essential. ALD-based methods have matured significantly and are now used extensively in semiconductor fabs. Recently, there has been an intense focus on developing ALEt methods. In particular, thermal ALEt has been shown to precisely remove ALD inorganic thin films selectively and on complex structures. These capabilities have opened new possibilities for nanoscale device design. Here, we report a new thermal etching process similar to ALEt for removing hybrid inorganic-organic layers that we call molecular layer etching (MLEt) [1]. This MLEt process uses vapor phase lithium organic salts in combination with trimethyl aluminum to perform layer-by-layer etching of molecular layer deposition (MLD) coatings. Ultra-thin layers of two dimensional (2D) transition metal dichalcogenide (TMD) semiconductors can exhibit exceptional electrical, optical, magnetic, mechanical and chemical properties. This allows the exploration of internal quantum degrees of freedom of electrons and their potential application in optoelectronic, energy, and sensor devices. Among the various 2D-TMDs, MoS_2 has shown exciting material properties and this has stimulated the exploration of a variety thin film synthesis methods such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and solution based methods. In addition, the ALD community is investigating ALD methods for MoS_2 growth [2-3]. Here we report the thermal ALEt of ALD MoS_2 thin films [4]. We believe the successful combination of both ALD and ALEt of MoS_2 and other TMDs can pave the way to control the synthesis of 2D-TMD layers over large areas. Combining ALD and ALEt will allow MoS_2 interface engineering and enable MoS_2 integration into the large-scale manufacturing of future complex device structures.

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Young et. al., https://doi.org/10.1021/acs.chemmater.9b03627

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Mane et. al., https://doi.org/10.1116/1.5003423

ALD for Manufacturing
Room Auditorium - Session AM-TuA

Spatial, Large Area and Powder ALD I & II

Moderators: Jonas Sundqvist, BALD Engineering AB, Angel Yanguas-Gil, Argonne National Lab

1:00pm **AM-TuA-1 Atomic Layer Deposition from Dissolved Precursors — 'solution ALD' or sALD***, M Barr,* Friedrich-Alexander University of Erlangen-Nürnberg, Germany*; V Koch,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany*; S Nadiri, I Kundrata, P Büttner, C Asker,* Friedrich-Alexander University of Erlangen-Nürnberg, Germany*; E Reinhardt,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany*; D Chen, P Weidler,* Karlsruhe Institute of Technology, Germany*; D Segets,* University of Duisburg-Essen, Germany*; K Fröhlich,* Institute of Electrical Engineering, SAS, Slovakia*; H Baumgart,* Old Dominion University*; E Redel,* Karlsruhe Institute of Technology, Germany*; **Julien Bachmann**,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany **INVITED**

An interdigitated geometry of the interface between semiconductors remains a Graal in the photovoltaic field. Nanocylindrical solar cells based on a coaxial p-n or p-i-n junction have been generated in a small number of materials systems only so far, mostly among the classical semiconductors. The generalization of this interface geometry to alternative semiconductors, which are expected to profit of it most, has been hampered by the lack of appropriate deposition methods suited to coating complex three-dimensional structures in a conformal manner. Atomic layer deposition (ALD) provides this capability, but is limited by the necessity to use gaseous precursors in vacuum conditions. Modern classes of semiconductors such as the hybrid perovskites are not accessible by ALD due to their ionic nature.

In this perspective, we have transferred the principles of ALD to precursors dissolved in liquid solvents. The 'solution ALD' (sALD) method can be implemented in a variety of microfluidic or slot-die processing devices. We have demonstrated that the principles of classical, gas-based ALD —self-limiting surface reactions— are reproduced in sALD. Furthermore, sALD allows the experimentalist to design new, advantageous, reactions of known semiconductors (oxides, heavier chalcogenides), or to deposit materials otherwise inaccessible to ALD altogether, such as polymers, ionic solids, and metal-organic frameworks. They may be obtained in highly pure, crystalline form at room temperature, either as planar films or as conformal coatings of porous substrates. Based on these advances, we have been able to make the first sALD-derived hybrid perovskite cells.

1:45pm **AM-TuA-4 An Atomic-Layer 3D Printer***, **Ivan Kundrata**,* ATLANT 3D Nanosystems, Denmark, Germany*; M Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark*; M Barr, S Tymek,* Friedrich-Alexander University of Erlangen-Nürnberg, Germany*; K Fröhlich,* Institute of Electrical Engineering, SAS, Slovakia*; J Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany

While 3D printing has been growing in the machining industry, with the adaptation of metal 3D printing allowing for creation of structures impossible to obtain by traditional machining, it has also been gaining traction in on the nanoscale. Despite this, only a limited number of materials have been 3D nanoprinted so far, such as electrospun nanofibers [1], and platinum and gold via electron-beam induced deposition[2]. Atomic layer deposition, uniquely among thin film deposition techniques, shares the layer by layer growth nature that universally underpins all 3D printing techniques. It also has a much broader material portfolio than other techniques.

In our contribution, we report on the design and results from a fully spatially constrained precursor delivery ALD reactor to achieve atomic-layer 3D printing. We present a full characterization of the TTIP + H_2O ALD process on the experimental prototype. Continuous flow dynamics simulations predict the experimental constraints required to achieve flow behavior between the sample and a first implementation of the spatial ALD micronozzle. A spot size of 300-450 µm is predicted for optimal precursor flow rates. Prototype testing with the TTIP + H_2O process results in a reproducible pattern generation with a line resolution of 300-350 µm at predicted flow rates. The growth per pass (GPP) depends on movement speed and precursor flow in a manner similar to classical ALD growth, and the GPP obtained in optimized conditions is similar to the GPC values reported in ALD. The temperature window, crystallinity, and film properties are compared with existing temporal and spatial ALD processes.

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2:15pm **AM-TuA-6 Reducing Precursor Cost in PE-ALD SiO_2 Processes***, **Geert Rampelberg**, V Cremers, A Werbrouck, J Dendooven, C Detavernier,* Ghent University, Belgium

Historically, thin film growth of SiO_2 has been an interesting challenge in the ALD community. Plasma-enhanced or ozone-based processes are most common since thermal ALD processes require some kind of catalytic activation.[1,2] The development of state-of-the-art Si precursors such as bis(diethylamino)silane (BDEAS) enabled the use of PE-ALD SiO_2 coatings in microelectronics, e.g. for spacer defined double patterning. The cost of these novel precursors is however high compared to traditional silicon compounds used for chemical vapor deposition and plasma polymerization, such as (3-Aminopropyl)triethoxysilane (APTES), tetraethyl orthosilicate (TEOS) and hexamethyldisilazane (HMDS). Certainly when coating large area substrates such as foils, nano- and micron-sized particles and porous materials, precursor cost can become a major fraction of the total process cost, motivating research into lower-cost precursors for SiO_2 ALD for these applications.

In this study, we investigated and compared growth characteristics of BDEAS and the three lower-cost Si precursors APTES, TEOS and HMDS during PE-ALD of SiO_2 films. Growth rates vary strongly, from around 1 Å per cycle for BDEAS down to 0.2 Å per cycle for TEOS. The conformality of all processes was evaluated using our lateral macroscopic trench structures with equivalent aspect ratio (EAR) of 22.5:1.[3,4] Whereas SiO_2 deposition from BDEAS and APTES shows excellent to medium conformality, the use of TEOS and HMDS as Si precursor does not allow to deposit SiO_2 inside our test structures. The addition of Al_2O_3 or TiO_2 subcycles to the SiO_2 deposition process leads to a remarkable growth and conformality enhancement. In view of reducing the process cost, our study focusses on the addition of low-cost titanium tetraisopropoxide (TTIP) precursor for growth of Ti-doped SiO_2 films. As a potential application example, SiO_2 coatings were deposited at room temperature onto micron sized polymer particles. Improved flowability of the powder was observed for all applied SiO_2 coatings.

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2. Ferguson, J. D. et al., ALD of SiO_2 at Room Temperature Using TEOS and H_2O with NH_3 as the Catalyst, J. Electrochem. Soc. 151, G528-G535 (2004)

3. Dendooven, J. et al., Modeling the Conformality of Atomic Layer Deposition: The Effect of Sticking Probability. , J. Electrochem. Soc. 156, P63–P67 (2009)

4. V. Cremers et al., Monte Carlo simulations of Atomic Layer Deposition on 3D large surface area structures, J. Vac. Sci. Technol. A, 35, 01B115:1-01B115:6 (2017

3:30pm **AM-TuA-11 Plasma Enhanced Spatial ALD of Metal Thin Films at Atmospheric Pressure***, **Bujamin Misimi**,* University of Wuppertal, Germany*; N Boysen,* Ruhr University Bochum, Germany*; T Hasselmann, D Theirich,* University of Wuppertal, Germany*; A Devi,* Ruhr University Bochum, Germany*; T Riedl,* University of Wuppertal, Germany

The demand for thin, highly conductive metal layers based on silver or copper has significantly increased, as these are required for various optoelectronic devices, such as solar cells and LEDs. Furthermore, thin conformal metal layers are suitable as interconnects in microelectronics. [1, 2] Plasma enhanced atomic layer deposition (PE-ALD) has been shown to be a suitable to grow thin metal layers at low temperature with the required properties. To overcome the limitations of classical vacuum-based PE-ALD, spatial atmospheric pressure plasma ALD (APP-ALD) has been introduced, and it paves the way towards high-throughput, low-cost manufacturing. [3, 4] As of yet, work on APP-ALD of metals is very limited, in part due to a lack of suitable metal precursors. In our recent work, we grown conductive Ag films by APP-ALD from a novel halogen-free Ag precursor 1,3 di-tert-butyl-imidazolin-2-ylidene silver(I) 1,1,1- trimethyl-N-(trimethylsilyl) silanaminide [(NHC)Ag(hmds)].[5] An atmospheric pressure dielectric barrier discharge with Ar/H_2 as working gas has been used. In this contribution, we introduce the APP-ALD of copper thin films from a novel, albeit structurally similar Cu precursor 1,3-di-tert-butyl-imidazolin-2-ylidene copper(I)1,1,1-trimethyl-N-(trimethylsilyl) silan-aminide [(NHC)Cu(hmds)]. All films in this study were grown at a low substrate temperature of 100 °C. Using Rutherford backscattering spectrometry, we evidence a growth rate of about 1.8×10^{14} atoms/(cm² cycle) (corresponding to an equivalent growth per cycle of 0.21 Å/cycle). We achieve percolated Cu thin films with a sheet resistance of 3.2 Ohm/sq. For comparison the analogous Ag process yields a similar growth rate of about 2.1×10^{14} atoms/(cm² cycle) and percolated Ag films with a sheet resistance of 0.9 Ω/sq (resistivity: 3.2×10^{-6} Ωcm). We will provide a comparative study of Ag and Cu grown by APP-ALD and discuss the growth characteristics depending on process parameters like substrate temperature and substrate speed. First results of integration of these APP-ALD grown metals as electrodes in perovskite solar cells will be presented.

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[3]. P. Poodt et al., J. Vac. Sci. & Technol.A 30, 01A142 (2012)

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4:00pm **AM-TuA-13 Plasma Enhanced Spatial Atomic Layer Deposition of Silicon Nitride Using Di(isopropylamino)silane and N_2 Plasma***, **Hisashi Higuchi**,* TEL Technology Center, America, LLC*; D O'Meara,* Tokyo Electron America Inc.*; S Consiglio, H Suzuki, C Wajda, G Leusink,* TEL Technology Center, America, LLC

Silicon nitride (SiN) films have been widely used for various semiconductor applications such as oxidation masks, diffusion barriers, gate dielectrics, liners, and spacers[1]. In order to maintain the constant down-scaling of transistors, a large number of SiN atomic layer deposition (ALD) processes have been developed with excellent conformality and precise thickness controllability[2]. In addition, the plasma-enhanced (PE) ALD technique has been able to lower the deposition temperature without sacrificing film quality. However, the typical SiN PEALD using dichlorosilane (SiH_2Cl_2) and ammonia (NH_3) plasma requires a relatively high deposition temperature (>350°C), which sometimes exceeds the tolerated thermal budget of some applications. Additionally, this process can be undesirable because of the detrimental effects caused by the chlorine in the precursor. Recently, SiN PEALD processes at even lower deposition temperature have been reported with halogen-free precursors such as BTBAS (bis(tert-butylamino)silane)[3], 3DMAS (tris(dimethylamino)silane)[4] and TSA (trisilylamine)[5]. In this study, DIPAS (di(isopropylamino)silane) was used for SiN PEALD in a high throughput spatial ALD chamber in contrast to the previous works which demonstrated processes in single-wafer-type chambers. SiN film deposition was confirmed at low deposition temperature (<350°C) and the film properties of the deposited film were evaluated.

An NT333™ chamber was used in a spatial ALD format, where the chamber volume is spatially separated by purge N_2 gas curtain into multiple zones: precursor area, purge area, reactant area, plasma area, and the other purge area. A quartz susceptor with five wafer capacity rotates through these areas, enabling sequential ALD with high rotation speeds and throughput. The susceptor rotation speed controls process time. Film growth was observed at the deposition temperature from 100°C to 350°C with N_2 plasma, while negligible film growth was obtained with NH_3 plasma, as reported in previous works. It was explained by Ande et al. using first-principles calculation that the surface termination of SiN_x by hydrogen-containing plasma inhibits Si precursor adsorption and results in a very low growth rate[6]. A growth per cycle (GPC) of 0.22 Å/cycle was obtained with N_2 plasma at a deposition temperature of 100°C and decreased as the deposition temperature increased (Figure 1). The film contained about 33 at. % nitrogen from XPS depth profile measurements while the nitrogen concentration at 350°C was about 41 % (Figure 2). The film deposited at 350°C showed diluted HF etch rate of 2.7 nm/min (Figure 3).

4:15pm **AM-TuA-14 Realization and *In-situ* OES Characterization of Saturated 10-100 ms Precursor Pulses in a 300 mm CCP Chamber Employing de Laval Nozzle Ring Injector for Fast ALD***, J Sundqvist,* BALD Engineering AB, Sweden*; **Abhishekkumar Thakur**, S Wege,* Plasway Technologies GmbH, Germany*; M Krug,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

ALD based self-aligned multiple patterning (SAxP) has been the key process to continued chip scaling. SAxP demands PEALD for low temperature and conformal deposition of spacers on photoresist features for the subsequent etch based pitch splitting. ALD is limited by low throughput that can be improved by raising the growth per cycle (GPC), using new ALD precursor, preforming batch ALD or fast Spatial ALD, shrinking the ALD cycle length, or omitting purge steps to attain the shortest possible ALD cycle. Today's latest and highly productive platforms facilitate very fast wafer transport in and out of the ALD chambers. Current 300 mm ALD chambers for high volume manufacturing are mainly top-down or cross-flow single wafer chambers, vertical batch furnaces, or spatial ALD chambers.

We have developed a fast PEALD technology[1], realizing individual precursor pulses saturating in the sub-100 ms range. The key feature of the technology is the highly uniform, radial injection of the precursors into the process chamber through several de Laval nozzles (patent-pending[2]). In order to in-situ study individual ALD pulses in the 10-100 ms range, we use a fast scanning (10 ms acquisition time per spectrum ranging from 200 nm to 840 nm) Optical Emission Spectrometer with a resolution in the range of 0.7 nm.

We present the results for PEALD of Al_2O_3 showing substrate surface saturation for 10 ms of TMA pulse (Fig. 1) and 100 ms of O_2 plasma pulse (Fig. 2). All processes were carried out in a 300 mm, dual-frequency (2 MHz and 60 MHz) CCP reactor in the temperature range of 30 °C to 120 °C and at <100 mTorr process pressure. The in-situ, time-resolved OES study of O_2 plasma pulse, indicating saturation of O* ($3p^5P$—>$3s^5S$) emission peak already at 50 ms pulse duration (Fig. 3, 4), suggested room for yet faster process.

Besides swift saturation, the process and the deposited films exhibited typical ALD characteristics with respect to linearity (Fig. 5), high quality with respect to film morphology (TEM, Fig. 5), low contamination (XPS, C < 1 atm%), and good conformality for applications involving structures with relaxed aspect ratios (SEM, Fig. 6). The simulation results for the gas-flow through the ring injector demonstrate highly uniform precursor distribution across the 300 mm wafer surface (Fig. 7).

References:

[1] AVS ALD/ALE 2019, Abstract Number: 658, Oral Presentation Number: AM1-WeM6, Session Title: Spatial ALD, Fast ALD, and Large-Area ALD

[2] Patent WO2017194059A1

Acknowledgment:

Thanks to Dr. Luka Kelhar, Researcher at the University of Ljubljana, Slovenia, for organizing the TEM measurements.

4:30pm **AM-TuA-15 Advanced Materials for the Next Generation: ALD a Scalable Manufacturing Process for Powders***, **Arrelaine Dameron**, S Moulton, J DuMont, D Lewis, T Procelli, R Tracy,* Forge Nano

Control of surface phenomena by powder modification via atomic layer deposition (ALD) for a spectrum of technology applications has made its way to R&D literature. But commercial adoption of ALD powder modification has been perceived as slow and too expensive to consider as a realistic commercial process. Forge Nano has patented, constructed, and demonstrated a high throughput ALD powder manufacturing capability at commercial scale and is commercializing first markets with partners. The manufacturing capability for powder modification with ALD is unlocking new potential for lower-cost integration of ALD into products. We will discuss a cross-comparison of ALD manufacturing type to product application and scaling requirements. For the first time in history, a pathway for ALD-enhanced materials to be rapidly transitioned from lab-scale demonstration to commercial presentation is available for new product development. The scaleup process addresses the stepwise progression to validate engineering and materials requirements to meet the market price demands. We will demonstrate that ALD enabled materials are the state of the art. The manufacturing of consistent materials with ALD modification is a cost-competitive level and now possible. The future of material science and product development for operation at more demanding conditions is enabled by ALD for a variety of applications.

Tutorials
Room Live - Session TU1-TuA
Tutorial Session: Tuesday Live

Moderators: Christophe Detavernier, Ghent University, Belgium, Harm C.M. Knoops, Oxford Instruments Plasma Technology, The Netherlands

1:00pm **TU1-TuA-1 Tuesday Tutorial Welcome & Sponsor Thank You***, **Christophe Detavernier**,* Ghent University, Belgium

Thank you for joining our Tutorial! We wish to thank our Sponsors for their support!

1:15pm **TU1-TuA-2 ALD Precursor Chemistry: Synthetic Routes, Purification and Evaluation of Precursors***, **Anjana Devi**,* Ruhr University Bochum, Germany **INVITED**

An open challenge for forefront research is provided by innovative strategies based on the synergic combinations of precursor chemistry and material synthesis, opening new horizons for the development of advanced functional material systems. In the case of atomic layer deposition (ALD), the important figure of merit is the precursor. High volatility, reactivity and thermal stability are the main requirements for an ALD process. But several precursors do not possess all of these characteristics. Thus, the search for alternative precursors continues to grow to overcome the drawbacks associated with the well-established or commercially available precursors in order to meet the stringent demands for modern technological applications. The reports on the design of new precursors by systematic and logical variation of the ligand sphere remains a rare occurrence in literature. Apart from identifying new and suitable precursors for ALD, it is also important that the precursors can be synthesized and scaled up to larger batches, they are non-toxic and the purity of the product is of high relevance. In this presentation, the approaches taken to synthesize different classes of precursors, their purification and the methods employed to characterize them will be discussed. The focus will be on representative precursors for metals and metal oxides and evaluating the precursor purity, volatility, thermal stability relevant for ALD applications.

2:15pm **TU1-TuA-6 Atomic Layer Engineering: Hardware Considerations for ALD System Design and Process Development***, **Neil Dasgupta**,* University of Michigan **INVITED**

As the portfolio of ALD processes chemistries continues to broaden, there is an increasing need for hardware customization to ensure process compatibility. Furthermore, the manufacturing demands for ALD continue to push for higher throughput, without sacrificing film quality or process reliability. In particular, as the form factor of ALD substrates begins to deviate from planar wafers to 3-D architectures, coupled thermal, mass transport, and chemical kinetics play an increasingly important role in ensuring optimal ALD deposition. This tutorial will describe several critical, and often under-discussed, aspects of ALD reactor hardware design and process control. The discussion will begin with a primer on vacuum system design in general – materials compatibility, fittings, o-rings/gaskets, valves, flow controllers, pumps, and metrology tools. Next, precursor delivery to the substrate will be discussed, with consideration of special challenges for solid precursors and low-vapor pressure precursor delivery. Various chamber geometries will be compared, and the coupled thermal/fluid transport behavior during vapor transport and reactivity will be described. Incorporation of in situ process metrology will be described. Finally, vacuum exhaust line design will be discussed, with an emphasis on maintaining a safe, and reproducible system.

3:15pm **TU1-TuA-10 ALD on High Aspect Ratio and Nanostructured Materials: from Fundamentals to Economics***, **Angel Yanguas-Gil**,* Argonne National Laboratory **INVITED**

The ability to conformally coat high aspect ratio and nanostructured substrates over large substrate areas is one of atomic layer deposition's enabling capabilities. From the coating of trenches and vias to the extreme case of polymer infiltration, there are numerous examples in the literature illustrating how ALD's self-limited behavior can enable new architectures and applications. In this tutorial I will focus on the fundamental aspects of the coating of high surface area materials, and in particular how the surface chemistry affects the dynamics of infiltration, scale up, and tradeoff between throughput and precursor utilization. After a brief introduction summarizing experimental approaches for both growth and characterization techniques and some conventional and extreme applications, I will explore the impact that shape, pore size, the overall microstructure of nanostructured substrates, and precursor-surface interaction have on an ideal ALD process. The impact of these parameters can be codified in a few compact expressions that help us visualize and explore the scalability of a given ALD process. I will then move on to consider how other aspects of the surface chemistry, such the presence of surface recombination or deactivation pathways, ligand-surface interactions, and non self-limited and soft-saturating components affect conformality. I will also look at the coating of nanostructured materials from a reactor scale perspective, exploring through simple models and experimental observations how precursor transport is disrupted by the presence of high surface area substrates in both cross flow and static dose configurations, two of the most common experimental approaches. I will then conclude with an overview of experimental challenges and gaps in our understanding that, if solved, could help accelerate the development of novel processes involving high aspect ratio and nanostructured substrates.

4:00pm **TU1-TuA-13 Questions & Answers***, A Devi,* Ruhr University Bochum, Germany*; N Dasgupta,* University of Michigan*; A Yanguas-Gil,* Argonne National Laboratory

Feel free to ask questions to our panel of Tutorial presenters

4:30pm **TU1-TuA-15 Session Over - View On Demand Presentations***, C Detavernier,* Ghent University, Belgium*;* ***Harm C.M. Knoops,*** Oxford Instruments Plasma Technology, The Netherlands, Netherlands

You are now welcome to view all ALD/ALE On Demand Presentations

ALD Applications
Room Arteveldeforum & Pedro de Gante - Session AA-TuP
ALD Applications Poster Session

AA-TuP-8 Stabilizing Red Fluoride LED Phosphors using Atomic Layer Deposition*, R Verstraete, H Rijckaert,* ***Geert Rampelberg,*** Ghent University, Belgium*; E Coetsee-Hugo, M Duvenhage, H Swart,* University of the Free State, South Africa*; P Smet, C Detavernier, D Poelman,* Ghent University, Belgium

Red fluoride phosphors, such as K_2SiF_6:Mn^{4+} [1-2], are now one of the key red components of white light-emitting diodes (wLEDs), e.g. in display backlighting. The $[MnF_6]^{2-}$ complexes show a narrow luminescence band at 630 nm upon blue excitation, yielding saturated red emission in a spectral region in which the human eye sensitivity is still fairly high, which is an advantage over Eu2+ doped nitride phosphors.

Despite the excellent optical properties of many fluoride phosphors, a remaining hurdle is their moisture sensitivity. Hence, surface passivation of fluoride phosphors has been an important topic in recent literature [3-5]. Conventional passivation methods are based on wet chemical processes, potentially degrading the pristine material. Moreover, in heterogeneous core-shell approaches, the fluorine terminated surface of the core shows a lack of functional sites (e.g. hydroxyl groups) inhibiting efficient bonding with typical shell materials.

In this work, the use of atomic layer deposition (ALD) for growth of Al_2O_3 and TiO_2 seed layers on fluoride phosphor particles is investigated. The coated phosphors have hydroxyl-saturated surfaces that are compatible for further bonding with hydrophobic shells. It was found that Al_2O_3 seed layers suffer from blistering, pore-formation and delamination. In contrast, conformal and uniform layers of TiO_2 could be grown. Unlike the untreated phosphor, the TiO_2 coated phosphor could easily be further treated with a hydrophobic shell [6].

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AA-TuP-9 Modulated VO_2 Phase Change Properties by Ge Doping*,* ***Guandong Bai****, K Niang, J Robertson,* University of Cambridge, UK

VO_2 shows an abrupt phase change from insulating to metallic at ~ 68 °C. Because of this metal-insulator transition (MIT) property, we can make phase change switch with VO_2. A functional random-access memory usually requires large device arrays and has a higher working temperature than 68 °C. Atomic layer deposition (ALD) has the advantage of good large area uniformity and conformality, therefore is suitable for memory applications.

To raise the $VO\text{-}_2$ transition temperature (T_{MIT}), one possible method is doping. Among various dopants that have been investigated, Mg lowers the T_{MIT} and Si shows mixed results, Ge is one of the few able to raise it[1,2,3]. ALD can perform doping by inserting dopant cycles into vanadium precursor cycles, and the doping level can be fine controlled by varying the cycle number ratio. We used a Savannah ALD 100 system to deposit amorphous Ge-doped VO_2 thin films, using tetrakis ethylmethylamino vanadium(IV) (TEMAV, heated at 105 °C) and germanium (IV) ethoxide (TEOGe, not heated) as the V and Ge precursor, respectively, and H_2O (not heated) as oxidizer. The 4-inch $Si/SiO\text{-}_2$ substrates were kept at 150 °C during deposition. We addressed the low growth rate due to the low vapour pressure of TEMAV by developing multiple pulsing method to maximize the efficiency of the vanadium dose, reaching a growth rate of 0.6 Å per cycle. The inserted Ge cycle number percentage varied from 0 to 10%. The as-deposited thin films are then crystallized by post-annealing at 450 °C in an Ar/O_2 ambient in a quartz furnace.

We analyzed the properties of Ge-doped VO_2 thin films at room temperature using spectroscopic ellipsometry (J. A. Woollam M-2000), AFM, XRD (Bruker D8 DAVINCI), Raman spectroscopy (Horiba HR800). We confirmed phase change property by checking resistivity on a Keithley 4200 parameter analyzer using a four-point probe measurement and varying the sample temperatures between 25 and 120 °C. Ellipsometry mapping shows good thickness uniformity across the 4-inch wafer. Raman spectra and XRD confirmed the +4 valency of vanadium. AFM images show a clear topography change: as the Ge doping increases, grain size decreases and roughness increased from ~2.6 nm to ~5.2nm. Electrical measurement shows a decrease of MIT on-off ratio with the increase of Ge doping, from ~ 10^3 at undoped to ~ 10^2 with high Ge doping. However, $T_{MIT\text{-}}$ increases from ~68 °C to ~78 °C, proving a modulated VO_2 phase change property by Ge doping.

[1] N. Wang, et al. Journal of Materials Chemistry C 3, 6771–6777 (2015).

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AA-TuP-11 Optical Fibers with TFBGs as Sensors*,* ***Eden Goodwin****, D Mandia, S Barry,* Carleton University, Canada

Tilted Bragg gratings in optical fibers through periodic changes to the core refractive index (RI) result in a reflection spectrum from the surface that permits interrogation of the surrounding refractive index (SRI). This sensitivity to the SRI has been used as sensor scaffold for biosensors and postulated as a mechanism exploitable for in-situ deposition sensing during ALD processes.

In order to monitor film growth in real time, two orthogonal modes of light are used: Transverse electric (TE)- and transverse magnetic (TM)-polarized. TE-polarized light creates an electric field in an azimuthal fashion that is parallel to the deposited film boundary at the fiber's surface, while TM-polarized light creates an electric field radially, resulting in a field that is perpendicular. These different modes interact with the surrounding environment in drastically different fashion. Through *in situ* analysis of these two modes, we were able to observe the insulator-to-metal transition of ALD deposited gold from 4.2-5.5nm, demonstrating an optically conductive film. This was independently confirmed by four-point probe (4PP) measurements.

We also determined the SRI sensitivity of ALD deposited gold and alumina coated films of various thicknesses. The unprecedented level of sensitivity observed in gold coated fibers hold prospects for use in biosensing applications, particularly as a tool for optical aptasensors (biosensors utilizing single strands of DNA called aptamers) offering a cost effective, label free biomolecule detection method. This presentation will discuss the fabrication of a TFBG sensor as used in detection of gold metal deposition, and further discuss a framework for biosensing using gold-tethered DNA aptamers.

AA-TuP-14 Photocatalytic Lithography with Atomic Layer Deposited TiO_2 Films to Tailor Biointerface Properties*,* ***Sofie Vandenbroucke,*** Ghent University - IMEC, Belgium*; F Mattelaer,* Ghent University, Belgium*; K Jans,* IMEC, Belgium*; C Detavernier,* Ghent University, Belgium*; T Stakenborg, R Vos,* IMEC, Belgium

Heterogeneous substrates with different functionalities are key for the production of micro- and nanostructures in various applications. For instance, the biointerface in biosensors and lab-on-a-chip devices comprise bioreceptor molecules specifically bound to the biosensor areas to enable analyte detection, while an antifouling layer is deposited onto all other parts to prevent loss of the analyte by non-specific adsorption. Patterns of self-assembled monolayers (SAMs) are often used for these purposes, but a high-throughput production process that enables patterning on a large scale is not available.

In this work, direct photocatalytic lithography is used to generate a spatial pattern of an azido-containing SAM (N_3-SAM) for the specific binding of biomolecules, and a polyethylene glycol SAM (PEG-SAM) in other areas to avoid non-specific binding. First, the degradation of N_3-SAM is monitored as a function of UV exposure time for three different thicknesses. The 10 nm and 20 nm thick ALD $TiO\text{-}_2$ films are found to remove the hydrophobic C-chains and azido groups already after 3 min of UV exposure time, while the 5 nm thick films present very limited photocatalytic activity. X-ray diffraction measurements and a wet etching procedure shows that the activity is related to the crystallinity of the material as-deposited.

Next, a biofunctional pattern is successfully created using thin ALD TiO_2 films (≤ 20 nm) that are anatase-rich as-deposited, a conventional lithography mask and a short exposure time up to 5 min to a simple 308 nm UV-lamp. The effectiveness of this approach is visualized by coupling fluorescently labelled antibodies to the patterns. A schematic illustration of the patterning procedure and the resulting patterns can be seen in figure 1. It is found that the technique is very sensitive to the exposure time. An exposure time of 3 min leads to printed features that are comparable to their actual size on the photomask, but an incomplete removal of the N_3-SAM in the exposed areas due to the influence of the soda lime glass mask on the irradiation. A longer exposure time of 5 min on the other hand, can successfully remove all N_3-SAM from the exposed areas but results in some broadening of the printed features.

The patterning technique offers the opportunity to use such TiO_2 coatings for patterning inside the microfluidic channels of a lab-on-a-chip device as ALD is known for the uniform and conformal coating in high-aspect ratio features. In addition, the technique can be implemented in a high-throughput production environment as additional processing steps are limited and short UV exposure times can be used.

AA-TuP-15 Enhanced Activity and Selectivity of $Co-Pt/\gamma-Al_2O_3$ Fischer-Tropsch Catalyst by Atomic Layer Deposited Al_2O_3 Overcoat*, **Laura Keskiväli**, P Eskelinen, N Heikkinen, M Reinikainen,* VTT Technical Research Centre of Finland, Finland*; M Putkonen,* University of Helsinki, Finland

Fischer-Tropsch synthesis is a widely used process where natural gas is converted to synthetic fuels by aid of metal catalysts, e.g. cobalt. However, leaching, sintering and coking undermine the process by decreasing the catalyst activity and selectivity. Atomic layer deposition (ALD) provides a pathway to create an overcoat to protect active sites and stabilize the particles on the support.[1,2] In our study, we used a Picosun R-200 ALD reactor with a POCA powder coating system to deposit thin Al_2O_3 overcoatings ($TMA+H_2O$, 15-40 cycles, 150 °C) on porous $Co-Pt/\gamma-Al_2O_3$ FT-catalysts. After deposition, we annealed the catalyst in N_2 at 420 °C. Catalysts were characterized by nitrogen adsorption-desorption with Brunauer-Emmet-Teller (BET), H_2-chemisorption, Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) techniques. Catalytic performance was studied using a tubular fixed-bed reactor system.

Our FT catalyst with particular Al_2O_3 coating was remarkably more active than plain catalyst without overcoat. The number of cycles and annealing had a tremendous effect on catalyst properties. The catalyst with 35 cycles of alumina showed the highest activity, up to 53%, without significant loss of selectivity towards heavier hydrocarbons (Figure 1). In addition, there was a noteworthy decrease in the olefin to paraffin ratio of light hydrocarbons. Based on our characterization, the altered catalyst properties result from the reformed surface structure of the catalyst and cobalt particle stabilization due to the annealed overcoating. The cobalt particle size decreased (XRD, chemisorption), surface area increased (BET) and roughening of the overcoated and annealed catalyst surface was detectable in the SEM images. We claim that these changes are due to the densification and a change of the composition of the overcoat, leading to a porous structure (with exposed) and new artificial active sites on the catalyst.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 768543.

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AA-TuP-23 Ferroelectricity of Ferroelectric $Hf_xZr_{1-x}O_2$/Antiferroelectric ZrO_2 Stack Structure Fabricated by Atomic Layer Deposition*, **Takashi Onaya**,* Meiji University, Japan*; T Nabatame,* National Institute for Materials Science, Japan*; Y Jung,* University of Texas at Dallas*; H Hernandez-Arriaga,* The University of Texas at Dallas*; J Mohan,* University of Texas at Dallas*; H Kim, A Khosravi,* The University of Texas at Dallas*; N Sawamoto,* Meiji University, Japan*; C Nam, E Tsai,* Brookhaven National Laboratory*; T Nagata,* National Institute for Materials Science, Japan*; R Wallace,* The University of Texas at Dallas*; J Kim,* University of Texas at Dallas*; A Ogura,* Meiji University, Japan

It has been reported that $Hf_xZr_{1-x}O_2$ (HZO) thin films show ferroelectric (FE) behavior over a wide Hf:Zr composition range, while pure HfO_2 and ZrO_2 layers generally exhibit paraelectric and antiferroelectric (AFE) behaviors, respectively. The characteristics of HZO/high-*k* stack structures, such as HZO/Al_2O_3, have been studied for the future memory device applications. [1] However, it is still not clear how the AFE-ZrO_2 film affect the ferroelectricity of HZO film when the ZrO_2 is laminated with the HZO film. In this work, we studied the ferroelectricity and crystallinity of HZO/ZrO_2 (HZ/Z) stack structure fabricated using atomic layer deposition (ALD).

The TiN/HZ/Z/TiN capacitors were fabricated as follows: An HZO film was deposited on TiN bottom-electrode by ALD at 300°C using $(Hf/Zr)[N(C_2H_5)CH_3]_4$ (Hf:Zr = 1:1) cocktail precursor and H_2O gas. The thickness of the HZO film was varied from 0 to 10 nm. Next, a 10-nm-thick ZrO_2 film was deposited at 300°C using $(C_5H_5)Zr[N(CH_3)_2]_3$ and H_2O gas. Then, TiN top-electrode was fabricated by DC sputtering. Finally, post-deposition annealing (PDA) was performed at 600°C for 1 min in a N atmosphere. The capacitors with HZO/HfO_2 (HZ/H) stacks and HZO single film were prepared as references.

For the grazing incidence X-ray diffraction (GI-XRD) patterns, the patterns of the HZ/H case showed the peaks from paraelectric monoclinic (M) phase. On the other hand, the peak from FE-orthorhombic, tetragonal, and cubic (O/T/C) phases was obtained for the HZ/Z case, while those from M phase were suppressed, indicating that the HZ/Z stacks consisted mainly of O/T/C phases. For the polarization-electric field (*P-E*) curves, the HZ/H stacks showed paraelectric properties regardless of the HZO thickness. On the other hand, the *P-E* loops of the HZ/Z stacks changed from AFE to FE behavior as the HZO thickness increased. Therefore, the remanent polarization ($2P_r$) of the HZ/Z stack gradually increased with the HZO thickness. Moreover, the HZ/Z stack with the HZO thickness of 10 nm showed the highest $2P_r$ of 14 µC/cm^2, which was higher than that (13 µC/cm^2) of TiN/HZO (10 nm)/TiN capacitor. It was reported that the pure ZrO_2 film can exhibit FE behavior. [2] Thus, these results suggest that the ZrO_2 films could exhibit FE properties as the HZO thickness increased.

In conclusion, the properties of the HZ/Z stacks changed from AFE to FE behavior as the HZO thickness increased, which indicating that the ZrO_2 film of the HZ/Z stack could exhibit FE properties.

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AA-TuP-24 Study on Optical and Electrical Properties of Zn(O,S) Films Deposited by Atomic Layer Deposition (ALD)*, N Koothan, **Yu-Hsuan Yu**, C Kei, W Cho, T Chou,* Taiwan Instrument Research Institute, Republic of China

Zn(O,S) is considered to replace CdS buffer layer in CIGS photovoltaic devices to avoid the use of toxic Cd. The efficiency of solar cells can be improved with the ideal conduction band offset(CBO), which can be optimized by adjusting the composition ratio between oxygen to sulfur. The buffer layer in CIGS requires full coverage with a pore-free, uniform layer. Therefore, ALD is adapted to deposit Zn(O,S) because it offers precise thickness control and conformal coverage.

A home-built ALD system was used to grow Zn(O,S) films, where Diethylzinc (DEZ), H_2O and H_2S were used as a metal source, oxygen source and sulfur source respectively. The ZnO ALD cycle sequence is 0.2 s DEZ, 0.1 s of H_2O separated by 10 s of N_2 purge, whereas, the ZnS ALD cycle sequence is 0.2 s DEZ, 0.1 s of H_2S separated by 10 s of N_2 purge. Fig.1 shows a supercycle in deposition progress of Zn(O,S), where m number of ZnO cycle and n number of ZnS cycles were deposited alternately. Zn(O,S) films with different ratios of m : n (ZnO:ZnS) such as 3 : 1, 5 : 1, 7 : 1 and 9 : 1 were fabricated in this study. The composition analysis of Zn(O,S) films was done by XPS. The optical and electrical properties were measured by UV-vis spectrophotometer and Hall measurement, respectively.

The Zn(O,S) films were deposited at 200°C with a growth rate of 1.6Å/cycle for ZnO and 1Å/cycle for ZnS. TEM results in Fig. 2 showed that the Zn(O,S) films can be fabricated by ALD with good conformality. Absorbance in Fig.3 shows that the absorbance of Zn(O,S) was larger than pure ZnO and ZnS within visible light wavelength.

AA-TuP-25 Atomic Layer Deposition of Highly Dispersed Manganese Oxide on Mesoporous Silicon Oxide for Selective Catalytic Reduction of Nitrogen Oxides*, **Saeed Saedy**,* Delft University of Technology, Netherlands*; D Urbanas, P Baltrėnas,* Vilnius Gediminas Technical University, Lithuania*; R van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) is a reliable method to produce catalysts in a highly controlled manner. The low temperature nature of ALD makes it possible to obtain different metal oxide nano-coatings at temperatures considerably lower than what is required to obtain the final product using conventional wet chemistry methods. Selective catalytic reduction of nitrogen oxides using ammonia (NO_x NH_3-SCR) is demonstrated as the most efficient NO_x abatement technology among different NO_x removal methods. The commercially available NH_3-SCR catalysts suffer from high temperature operational condition, i.e. 300-450°C. This requires the catalyst bed to be installed prior to desulfurization and dust removal units; this initiates catalyst deactivation by sulfur-containing compounds and dust. Manganese oxide (MnO_x) catalysts have a superior NH_3-SCR activity at temperatures lower than 250°C; the low temperature SCR activity of MnO_x catalysts is attributed to the excellent redox ability of MnO_x and the various oxidation states of manganese (Mn^{2+}, Mn^{3+} and Mn^{4+}) which are necessary to complete the NH_3-SCR reaction cycle. Since crystalline MnO_x does not contribute effectively to NH_3-SCR, the dispersion of MnO_x strongly affects the LT SCR activity. Accordingly, the conventional methods of catalysts synthesis, e.g. precipitation and impregnation, are not suitable for preparation of MnO_x-based SCR catalysts, because they often fail to achieve highly-dispersed supported nanoparticles (NPs). These methods usually require high temperature post-treatment resulting in improved crystallinity of NPs and decreased dispersion.

In this work we have employed fluidized bed ALD for deposition of highly dispersed MnO_x on mesoporous silica (m-SiO_2) aiming at low temperature NH_3-SCR catalyst. The ultra-fine MnO_x NPs were deposited on m-SiO_2 at 150°C and 1 bar. The XPS spectra of ALD-synthesized MnO_x/m-SiO_2 catalysts revealed three oxidation states of Mn^{2+}, Mn^{3+}, and Mn^{4+} in these samples. However, powder XRD was not able to detect any crystalline phases of MnO_x, suggesting that the crystalline MnO_x phase is avoided via ALD synthesis; consistently, the MnO_x NPs were scarcely observable using TEM imaging. This suggests extreme dispersion of MnO_x over m-SiO_2. The changes in surface area of support before and after ALD of MnO_x, measured using BET method, was also negligible (*ca.* 448 $m^2 \cdot g^{-1}$); this indicates that MnO_x is highly dispersed over support without pore clogging. The obtained MnO_x/m-SiO_2 with such characteristics provide a promising catalyst for low-temperature selective catalytic reduction of nitrogen oxides.

AA-TuP-26 Effect of Deposition Temperature on the Crystallinity and Polarization of Ga-doped HfO_2 Films by Atomic Layer Deposition*, **Ju-Young Jeong**, H Sohn, Y Han,* Yonsei University, Republic of Korea

Ferroelectric random access memory(FRAM) is considered as one of next gengration memoy devices due to its merits such as low power consumption and fast operation speed.[1] Recently, HfO_2 thin films with non-centrosymmetric orthorhombic phase of the space group of $P_{ca}2_1$ attracted intensive attention because of their ferroelectric property. Also, effects of doping, stress, and substrate were studied to enhance the ferroelectricity of HfO_2 films. [2] It was reported that the ferroelectric behavior of HfO_2 was affected by conditions such as deposition and post annealing temperatures in addition to alloying elements.[2]

In this study, Ga-doped HfO_2 (Ga-HfO_2)films were deposited at various temperatures, ranging from 300℃ to 340℃ . Ga-HfO_2 films were grown on bottom electrodes of TiN by atomic layer deposition with Tetrakis(ethylmethylamino)-hafnium(TEMA-Hf), Trimethyl-gallium (TMG) as precursors and ozone as the oxidant. Then, top electrodes of 15nm-thick TiN were deposited by sputtering. And the post annealing was conducted by rapid thermal annealing (RTA) in N_2 atmosphere at 600 ℃ during 20s.

Chemical composition and bonding of Ga-HfO_2 films were investigated by X-ray photoelectron spectroscopy (XPS). Structural properties were examined by Grazing Incidence X-ray diffraction (GI-XRD). The ferroelectric behaviors of Ga-HfO_2 films were measurened by P-V, PUND methods with electric pulses of 3.3 MV/cm at 50 kHz and the endurance of ferroelectric switching, in addition.

Ga concentration and the non-lattice oxygen in Ga-HfO_2 film were estimated to be 5.9 % and 17. 2 %, respectively. GI-XRD shows an increased intensty in nano-crystalline peak with increasing deposition tempreature. But the remanent polarization of Ga-HfO_2 film was decreased with increasing deposition tempreature.

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AA-TuP-27 Low Damage Remote Plasma ALD of Dielectric Layers on Graphene*, **Michael Powell,*** Oxford Instruments Plasma Technology, UK*; B Canto, M Otto, S Kataria,* AMO GmbH, Germany*; A O'Mahony, O Thomas,* Oxford Instruments Plasma Technology*; H Knoops,* Eindhoven University of Technology, Netherlands*; D Neumaier, M Lemme,* AMO GmbH, Germany*; R Sundaram,* Oxford Instruments Plasma Technology

As electronic devices become ever smaller and with the push for greater efficiency, 2-dimensional materials are becoming increasingly more desirable.[1] Amongst 2-D materials, graphene is one of the most widely researched - this is due to the extraordinary charge carrier concentration and mobility of the electrons in this material. Although graphene is excellently suited for a wide range of applications, it requires the deposition of both dielectric as well as encapsulation/barrier layers,[2] to modulate the electrical response from the graphene as well as physically protecting it from damage.

ALD is a technique that allows uniform and precise control of dielectrics, deposited by a soft/low damage route. Thermal ALD processes, unfortunately, often suffer from poor nucleation when deposited on graphene and also poor adherence of dielectric layers deposited on graphene.[3] This presents challenges, as graphene is susceptible to damage by both radicals/ions as well as high temperatures, meaning that many routes to depositing these dielectric/barrier layers can result in poor device quality.[4]

We will describe how short, low power remote plasma processing can result in high quality and conformal Al_2O_3 dielectric layers deposited on graphene surfaces with low damage, as demonstrated by ellipsometry maps and Raman spectroscopy (fig 1). We will further show that by utilising a stacked structure, where h-BN is incorporated between the graphene and alumina layers, damage is further reduced to the graphene during deposition. We will demonstrate that these layers have good electrical properties with high throughput/processing times; which is essential for scaling graphene devices for industrial processes. Furthermore, plasma processing of the dielectric layers allows thermally sensitive substrates to be used for device construction further expanding the scope for device construction.

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AA-TuP-30 Design of Li-Containing Layers with LiHMDS*, **Andreas Werbrouck**, F Mattelaer, T Dobbelaere, M Minjauw,* Ghent University, Belgium*; F Munnik, J Julin,* Helmholtz-Zentrum Dresden-Rossendorf, Germany*; J Dendooven, C Detavernier,* Ghent University, Belgium

ALD will be a key technique for solid electrolyte applications and protective films on Li-ion battery electrodes. Its conformality, uniformity and thickness control are key selling points no other technique can match. While a lot of simple oxides can be deposited for battery applications, battery performance could greatly benefit from the further development of lithium-containing processes.

Lithium hexamethyl disilyl azide (LiHDMS) is one of the few precursors suitable for the atomic layer deposition of lithium-containing layers. Earlier results with LiHMDS which are relevant for solid electrolyte applications are the growth of lithium silicate with O_3[1,2], crystalline Li_3PO_4 with trimethylphosphate (TMP)[3] and amorphous LiPON with diethyl phosphoramidate (DEPA)[4] as a coreactant. From the literature it is clear that in some cases LiHMDS exhibits a dual source behavior, incorporating lithium as well as silicon in the films, while in other processes it only deposits lithium.

We developed a new, simple ALD process to deposit lithium silicate with LiHMDS and O_2 plasma. The films were characterized with in-situ ellipsometry, ERD and XPS (figs.1 and 2). Lithium and silicon are both present in the deposited films.

With the aim of depositing a lithium silicate/phosphate, we intermixed the LiHMDS-O_2* process with TMP in an ABC/ACB way. These processes were as well self-saturating, and the stoichiometry of the resulting films was measured by XPS/ERD.

Recently we developed a new way to conduct mass spectrometry[5]. Our method allows to obtain a measurement of all masses as a function of time during a full ALD cycle (fig. 3). This way the reaction products arising in an ALD process can be fingerprinted and identified. We employed this method to the new $LiSiO_x$ process with O_2 plasma, the known Li_3PO_4 process, and the LiHMDS/O_2*/TMP and LiHMDS/TMP/O_2* process.

The composition of the films deposited with these mixed processes combined with the mass spectrometry measurements provided us with more insight in the dual-source behavior of LiHMDS and how it is affected by the preceding and succeeding precursor.

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AA-TuP-32 Resistive Switching in Titanium-Aluminum-Oxide Thin Films Grown by Atomic Layer Deposition*, **Joonas Merisalu**, T Arroval, A Kasikov, K Kukli, A Tamm, J Aarik,* University of Tartu, Estonia

Resistive switching (RS) phenomena in solid thin solid films have gained a lot of interest during the last decade offering potential for fabricating a new generation of non-volatile memory devices named resistive random access memories (RRAMs) [1].

As there are a lot of materials discovered with resistive switching properties, the explanation of RS mechanisms is complicated [2]. Intense research is going on and devoted to the modifications of the RS media, together with the interpretation of their electrical characteristics obtained from various metal-insulator-metal (MIM) structures. In the present work, electrical characteristics of RS in titanium aluminum oxide thin films are studied.

The electrically evaluated samples have MIM structure which differ from each other by the titanium-aluminum oxide multi-layer insulator film construction. All the films were deposited on Si substrate pre-covered with RuO_2 layers that acted as common bottom electrode. The insulator layers were prepared by atomic layer deposition at 350 ℃ from $TiCl_4$, $Al(CH_3)_3$ and H_2O.

The dielectric is a thin film containing layers of TiO_2 and Al_2O_3, was constructed by varying ordinarily deposited TiO_2 layers with the layers of TiO_2 which were deposited as a triple precursor process. This means that the pulse of titanium precursor was followed by aluminum precursor pulse led to the reaction chamber after a purge period and, then, the formation of oxide layer in a single cycle was completed by application of oxygen precursor, H_2O, pulse. The growth rate of reference TiO_2 layers was 0.05 nm/cycle [3]. The growth rate of TiO_2:Al_2O_3 layer was 0.15 nm/cycle [4]. The atomic ratio Al/(Al + Ti) was 0.6 [4].

The top electrodes of Pt were deposited through a shadow mask using electron beam evaporation.

Electrical characheristics were measured as voltage sweeps using Cascade Microtech EPS-150 probestation and Keithley 2636A. All studied samples showed bipolar RS properties. Clockwise bipolar RS was recognized dominantly in samples where Al_2O_3 concentration was lower. The samples that contained more Al_2O_3 tended to show signs or even full repetitive cycles of counterclockwise RS. It was also noticed that R_{on}/R_{off} ratio between low resistance state (LRS) and high resistance state (HRS) became higher when there was more Al_2O_3 present in the film.

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AA-TuP-34 New Hydrazine Based Precursors For Semiconductor Fabrication*, **Wolf Schorn**, O Briel, R Karch,* Umicore AG & Co. KG, Germany*; W Stolz,* NAsP III/V GmbH, Germany

Continuous scaling of semiconductor devices sometimes can only be achieved by introducing new materials with improved properties. CVD and ALD processes are increasingly used to meet required film conformalities of complex three-dimensional structures exhibiting specific electrical properties.

A new class of substances has proven to be a potential candidate for ALD/CVD processes, metal complexes based on the ligand *N,N'*-bisdimethylaminoacetamidine (Hbdma), whose properties combine high volatility with high reactivity. In addition, this class of ligands can be used to prepare complexes where the metal cations are solely surrounded by hydrogen and nitrogen atoms aiming at minimizing unwanted carbon impurities in deposited films.

We present various Group III complexes based on the bdma ligand, their thermal characterization, as well as first deposition tests with the complex [$Ga(bdma)H_2$]. Furthermore, Bdma is a versatile ligand which can stabilize and volatilize many metal complexes based on main group elements such as Ge or B as well as transition metals such as Ni or Fe. Herein we wish to give an outlook of further work in progress.

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AA-TuP-39 The Use of ALD Layers for Hermetic Encapsulation in the Development of a Flexible Implantable Micro Electrode for Neural Recording and Stimulation*, **David Schaubroeck**,* IMEC - Ghent University, Belgium*; C Li,* Ghent University - IMEC, Belgium*; R Verplancke, D Cuypers, M Cauwe, M Op de Beeck,* IMEC - Ghent University, Belgium

The use of electronic microsystems as medical implants gains interests due to the combination of superior device functionality with extreme miniaturization. Electronic devices are not biocompatible and will suffer from corrosion, hence a very good hermetic device encapsulation is of utmost importance. The hermetic sealing of implantable electronics requires extremely good bi-directional barrier properties against diffusion of water, ions and gases. Moreover, extremely long biostability against body fluids and biomolecules is an important requirement for the barrier materials. In this work, an ALD multilayer of AlOx and HfOx in combination with flexible polyimide is used as a flexible hermetic encapsulation of an electronic CMOS chip which serves as an implantable probe (so called hd TIME (active high-density transverse intrafascicular microelectrode) probe) for neural recording and stimulation [1]. The main part consists of a 35µm thin CMOS chips with electrodes on top encapsulated with alternating layers of spin coated polyimide (PI2611) and biocompatible ALD layers.

The total encapsulation is developed to provide excellent barrier properties. Each ALD stack (ALD-3) consists of AlOx (20 nm) capped on both sides with HfOx (8 nm) to avoid hydrolysis of AlOx. The ALD deposition temperature is 250°C. Special attention is payed to the adhesion of the ALD layers toward polyimide and vice versa. 3 to 4 PI/ALD-3 dyads are used for the total encapsulation, since long term implantation of the medical device is envisaged. Testing however is done using only a part of the total encapsulation, in order to enable to learn about the barrier properties in a reasonnable timeframe. The WVTR of a PI/ALD-3/PI film reached a value of 2.1 10^{-5} g/m^2day (38°C and 100% RH), the total encapsulation with 3 to 4 dyads will lead to WVTR's in the order of 10^{-6}g/m^2day. The same PI/ALD-3/PI film has been deposited on structured copper meanders and is exposed to PBS at 60°C for 3.5 years (equivalent to 17.5 years at 37°C) [2]. Up till now, no change in Cu resistivity has been observed proving the excellent barrier properties of the PI/ALD-3/PI film.

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AA-TuP-41 The Effect of Electrode Material and Doping Concentration on Physical and Electrical Properties by Using Thermal and Plasma-Assisted Atomic Layer Deposition in Ferroelectric Zr-doped HfO_2 Dielectrics*, P Juan,* Ming Chi University of Technology, Republic of China*; **Wen-Hao Cho,*** Taiwan Instrument Research Institute, Republic of China*; C Chen,* National Applied Research Laboratories, Republic of China*; C Kei,* Taiwan Instrument Research Institute, Republic of China

Zr-doped HfO_2 dielectric layers with TaN and/or TiN as the metal electrode for sandwich-like metal-insulator-metal capacitors were fabricated. The Zr-doped HfO_2 layers i.e., $Hf_{0.75}Zr_{0.25}O_2$, $Hf_{0.5}Zr_{0.5}O_2$, $Hf_{0.25}Zr_{0.75}O_2$ were designed by the stacking of HfO_2 and ZrO_2 thin-film using the thermal and plasma-assisted atomic deposition (ALD). The precursors used for HfO_2 and ZrO_2 depositions were TEMAHf and TEMAZr with water vaporing and oxygen ambient, respectively. The thicknesses per cycle obtained from the converged regime are 0.112 nm/ cycle for thermal and 0.117 nm/ cycle for plasma in HfO_2 films, respectively. While the thicknesses per cycle obtained are 0.111 nm/ cycle for thermal and 0.118 nm/ cycle for plasma in ZrO_2 films, respectively. Each sub-stacked layer of same atomic species was fixed to 5 cycles and the total thickness of Zr-doped HfO_2 was controlled to 20 nm. From the XRD patterns, the dielectric film is easier to be crystallized at post-annealing temperature of 450℃ for thermal than that of 600℃ for plasma. The intensity of tetragonal phase increases with increasing the doping amount of Zr for both thermal and plasma conditions. Secondary phases of TaO and $TiZrO_x$ are shown with TaN and TiN as the electrodes in thermal, but only Ti-related phase is observed in plasma scheme. The electrical properties of current-voltage and capacitance-voltage are measured and compared. A subthreshold voltage is severely shifted and the subthreshold slope is worse for samples with thermal condition. It indicated that high interface densities between dielectric film and silicon substrate is suggested and quantified by the conduction method. In a low doping concentration of Zr, the behavior of ferroelectricity is attributed to the formation of a non-centrosymmetric orthorhombic phase of space group $Pbc2_1$, which was found in the presence of TiN for plasma and TaN for thermal conditions.

AA-TuP-42 PbI_2 Growth for Solution ALD for PV Application*, **Maïssa K. S. Barr**, S Nadiri, C Asker,* Friedrich-Alexander University of Erlangen-Nürnberg, Germany*; K Forberich,* Friedrich-Alexander University of Erlangen-Nürnberg, i-MEET, Germany*; F Hoga, T Stubhan, H Egelhaaf,* ZAE Bayern - Erneuerbare Energien, Germany*; C Brabec,* Friedrich-Alexander University of Erlangen-Nürnberg, i-MEET, Germany*; J Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg, Germany

The transfer of the principles of atomic layer deposition (ALD) is possible in the liquid phase. The precursors are dissolved in a solvent and they are sequentially injected in a microfluidic chamber. This is also 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 porous structures. In the following the targeted field is photovoltaic. A great deal of interest has appeared on a new generation of material for solar cells application. Among them the perovskites are particularly interesting and the most studied one is $CH_3NH_3PbI_3$ (MAPI). The existing deposition methods such as spin coating or vapor-deposition techniques do not allow a control at the atomic level. ALD has been used to deposit PbS but it needed a two-step conversion method to obtain a perovskite [1] . Therefore, a new process based on sALD has been developed to deposit PbI_2. It allows the use of inexpensive lead salt and it is easy to process. Then, the PbI_2 can be easily converted to MAPI. The PbI_2 deposition is achieved with $Pb(NO_3)_2$ and LiI via s-ALD on large samples (up to 10 cm*10 cm). The ALD behavior is shown from the linear dependency the thickness in function of the number of cycles as well as from the saturation curves. The influence of the deposition parameters on the morphology, the crystalline structure and the chemical composition are investigated by scanning electron microscopy, atomic force microscopy, grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy. The growth of PbI_2 has been studied on different oxides with different chemical pre-treatment. Later, the obtained PbI_2 is converted to MAPI by vapor annealing. The influence of the temperature, the time and the type of gas on the conversion are investigated on the different substrates. Furthermore, the influence of the ALD parameters on the properties of the perovskite layer were studied. Thus, the Perovskite layer has been integrated into a solar cell.

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AA-TuP-43 A Combinatorial Approach to the Ferroelectric Properties in $Hf_xZr_{1-x}O_2$ Deposited by Atomic Layer Deposition*, J Mohan,* University of Texas at Dallas*; S Kim,* Kangwon National University, Republic of Korea*; H Hernandez-Arriga,* The University of Texas at Dallas*; **Yong Chan Jung**,* University of Texas at Dallas*; T Onaya,* Meiji University, Japan*; H Kim, N Kim, K Kim,* The University of Texas at Dallas*; A Ogura,* Meiji University, Japan*; R Choi,* Inha University, South Korea*; M Sung,* Hanyang University, Republic of Korea*; J Kim,* University of Texas at Dallas

The ferroelectricity and anti-ferroelectricity of doped $Hf_xZr_{1-x}O_2$ (HZO) have been extensively studied in the literature since its first report by the Muller et al [1]. The best ferroelectric properties were observed at the near 50-50 composition ratio of HfO-$_2$ and ZrO_2 in most of the reported literature, which could be attributed to the observation of the non-centrosymmetric orthorhombic phase in the polycrystal (space group $Pca2_1$) [2]. Super-cycle ALD has been commonly used as a technique to fabricate $Hf_xZr_{1-x}O_2$ with various compositions and careful study of the compositions in the near 50-50 composition is quite tedious. Hence, a combinatorial approach [3] with saturated/non-saturated Hf and Zr precursor can be used to effectively provide the relationship between small changes in composition across the wafer to the ferroelectric and dielectric properties in the film.

In this study, the ferroelectric properties of HZO was studied on MIM capacitors using Titanium Nitride electrodes HZO was deposited using TDMA-hafnium ($Hf[N(CH_3)_2]_4$), TDMA-zirconium ($Zr[N(CH_3)_2]_4$), and O_3 as the Hf-precursor, Zr-precursor and oxygen source respectively at 250°C. The precursor temperatures were set at 75°C during saturation for both Hf and Zr precursors and after reducing the precursor time to 60°C and the pulse time to 0.1s, a gradient in the HfO_2 and ZrO_2 deposition rates were observed, as shown in figure 1. Using a combination of a gradient in the HfO_2 deposition with a saturated ZrO_2 deposition and vice-versa, a composition difference across the wafer was obtained. Blanket TiN (90 nm thick) electrodes were deposited using magnetron RF sputtering before and after the HZO deposition as the electrodes. Then, rapid thermal annealing was done at 400ºC in an N_2 atmosphere for 60s to crystallize the HZO films. A conventional photolithography/etching process was used to make capacitors of different diameters. Grazing Incidence X-ray Diffraction (GIXRD) confirms that the ferroelectric orthorhombic phase is stable for HZO deposited also verified by high resolution Transmission Electron Microscopy.

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AA-TuP-46 Structure, Morphology and Mechanical Behavior of ALD TiSiN films*, **Hae Young Kim**, S Chugh, A Dhamdhere, B Nie, S Rathi, N Mukherjee,* Eugenus, Inc.

As the generation of memory devices evolve, the successful fabrication of high aspect ratio (HAR) features becomes more and more challenging. Apart from the traditional patterning, deposition and etch related issues, structural stability of these HAR structures becomes a critical parameter in determining the overall device yields. Specifically, the failure modes such as bending, cracking and toppling are commonly observed when metal films with unoptimized mechanical properties (stress, hardness and elasticity) are deposited into these HAR structures.

In the current study, we present our findings on the mechanical properties such as nano-hardness, and elasticity of the multicomponent Ti-Si-N films, an excellent alternative to TiN films. These films were grown using ALD technique on the Eugenus 300mm QXP commercial single process module, multi-wafer system. Film thickness and Si content were varied, and the Ti-Si-N films were investigated by characterization techniques such as X-ray diffraction (XRD), high resolution transmission electron spectroscopy (HRTEM), and Nanoindentation.

It was found that the Ti-Si-N films with intermediate Si% to have the highest nanohardness. The maximum nanohardness of the film was achieved as high as ≧ 20 GPa, which is two times higher than the TiN film as shown in Figure 1. Zhang *et al.*[1] also reported similar trend in the nanocomposite Ti-Si-N films. Their as-deposited films show nanocomposite structure with nano TiN grains embedded in an amorphous Si_xN_ymatrix. It was observed that TiN crystallites become very small at increased Si_xN_y content (Figure 2).[1] Thus, under mechanical loading the material only reacts by grain boundary sliding which requires more energy than deformation by dislocation movement, therefore, higher hardness is achieved. At high Si-dose, the mean grain separation becomes so wide, that cracking takes place in Si_xN_ymatrix, thereby reducing the hardness.[1]

Additionally, control of Si% in the Eugenus Ti-Si-N film enables tuning of the morphology from polycrystalline to fully amorphous with optimum resistivity; in all cases, excellent step coverage on high aspect ratio structures were obtained.

AA-TuP-61 The Influence of ALD-ZnSnO Buffer Layer Process Conditions on the Characteristics of Tin Sulfide Thin Film Solar Cells*, **Jae Yu Cho**, J Heo,* Chonnam National University, Republic of Korea

Choice of suitable *n*-type buffer layer to form favorable heterojunction is one of the promising criteria to achieve a high performance thin film solar cell (TFSC). Till date, CdS has been used as standard buffer layer for various TFSCs. However, the Cd-free alternative buffer layers are always in demand to increase environmental compatibility of such TFSCs. In this regard, atomic layer deposition (ALD) has already been proven as a potential technique to obtain conformal and ultrathin buffer layers.

In 2014, ~4.36% efficiency of SnS TFSCs with ALD-Zn(O,S) buffer layer has been reported by R. G. Gordon group, which is the best SnS TFSCs reported so far [1]. In this work, the application of ALD-ZnSnO (ZTO) buffer layer was investigated for SnS TFSCs. Initially, ZTO films were characterized for variable process conditions. Finally, the performance of the TFSCs was tested with ALD-grown ZTO buffer layers and the highest efficiency of 4.93% was achieved with the V_{OC} = 436 mV, J_{SC} = 24.0 mA/cm^2, and FF = 0.47. The detailed analysis of the influence of ALD conditions on the device performance will be presented.

AA-TuP-64 Innovative ALD Industrial Services*, **Joël Matthey**, P Steinmann, L Steinmann, B Steinmann,* Positive Coating SA, Switzerland

Positive Coating provides thin-film coating services based on magnetron sputtering and atomic layer deposition technologies. Combining the benefits of both processes, the company is mainly active in the luxury sector. Positive Coating is the pioneer that has brought ALD within the Swiss watchmaking industry as early as 2014. Heading now for diversification, Positive Coating makes its knowledge and expertise available to other industrial applications. Based on innovation and quality, it stands as a partner to develop custom-made activities related to surface engineering. New challenging applications in the medical field will be addressed. In the presentation, two patented processes will be discussed. Firstly, a unique method to produce two-tone components without organic masking. Secondly, a ultra-white coating that combines electroplating and ALD technologies. Finally, commercial applications and examples will be presented.

AA-TuP-66 Antireflection Coating on PMMA Substrates by Atomic Layer Deposition (ALD)*, **Pallabi Paul**,* Friedrich Schiller University, Germany*; K Pfeiffer,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany*; A Szeghalmi,* Friedrich Schiller University, Germany

Atomic layer deposition (ALD) is a promising chemical coating technology for growing conformal films on high aspect ratios as well as complex shaped substrates. ALD is a cyclic process, which is based on sequential and self-limiting reactions of precursors with the available functional groups on substrate surface. In contrast to conventional physical vapour deposition (PVD) methods where shadowing may occur on strongly curved surfaces leading to thickness gradient, ALD can produce uniform and conformal films on arbitrarily shaped surfaces due to the self-saturating surface reactions and precise thickness control at the nanometer range.

Thermoplastics like poly(methyl methacrylate) (PMMA) has been widely used in producing various optical components like freeform surfaces, aspheric lenses, Fresnel lenses and many other diffractive optical elements. PMMA has a high transmission in the visible spectral range, excellent hardness and high Abbe number enabling it as an important alternative to glass optics. However precision coatings on plastics are rather challenging due to the tendency of crack formation and typically low adhesion of the dielectric coatings to the polymer surface. Since the optimized process parameters on glass substrates cannot be directly transferred to plastics, an explicit polymer specific research is required to functionalize polymers.

In this work, optimization of ALD processes to develop uniform, homogeneous and dense optical thin films of Al_2O_3, TiO_2 and SiO_2 on PMMA has been carried out. Upon examining the optical properties and mechanical stability of thin films, a five-layer antireflection coating on PMMA is demonstrated. While uncoated PMMA substrates have a reflectance of nearly 8% in the visible spectral range, the reflectance of double-sided antireflection coated PMMA does not exceed 1.2% in the spectral range of 420 nm – 670 nm with a total average reflectance of only 0.7%. Microscopic analysis of the cross-hatch areas on PMMA indicates superior adhesion and excellent environmental stability of the ALD coatings. Furthermore, 3D conformal growth of ALD films has been exploited on PMMA dome ensuring identical spectral response along the entire dome surface. These investigations enable a possible route by ALD to deposit uniform, crack-free, adhesive and environmentally durable thin film layers on sensitive thermoplastics like PMMA.

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AA-TuP-68 Effect of Thermal Stability of Precursor on Electrical Properties of TiN/ZrO$_2$/TiN Capacitor*, **Younsoo Kim**, S Ryu, Y Cho,* Samsung Electronics Co., Inc., Republic of Korea*; N Yamada,* ADEKA Corporation, Japan*; J Choi, H Lim,* Samsung Electronics Co., Inc., Republic of Korea

As design rule of semiconductor device decrease continuously, various high-k materials have been evaluated including ZrO_2, HfO_2, TiO_2, and $(Ba,Sr)TiO_3$ [1-5]. Among of them, ZrO_2 is the most commonly used as a dielectric material of capacitor in DRAM (Dynamic Random Access Memory). However, it was difficult to develop high quality ZrO_2 process in 3-dimensional structure because ZrO_2 ALD (Atomic Layer Deposition) didn't show an ideal behavior.

In this study, we investigated deposition behavior of ZrO_2 ALD using 1:1 mixture (TEMAZ+EMA) of TEMAZ [Tetrakis (EthylMethylAmino)Zirconium] and EMA (EthylMethylAmine). TEMAZ+EMA showed 20^{o}C higher thermal stability and 10^{o}C higher decomposition temperature than those of TEMAZ. The thermal stability of precursors is related to the number of effective electron around the central metal. It is assumed that TEMAZ+EMA precursor is stabilized because Zr atom in the precursor is coordinated by EMA and the number of effective electron around Zr atom increase.

We compared electrical characteristics of the TiN/ZrO_2/TiN capacitor using TEMAZ and TEMAZ+EMA. The leakage current density and Schottky barrier heights were significantly improved at ZrO_2 films deposited using TEMAZ+EMA. We will present the correlation between physical properties of precursors and electrical properties of ZrO_2 films.

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AA-TuP-70 Mechanism of Leakage Variation with Aspect Ratio in ALD High-*k* ZrO$_2$ and HZO Dielectrics*, **Martin McBriarty**, R Clarke, S Barabash, K Littau,* Intermolecular

DRAM capacitors require ALD of ultrathin high-*k* dielectrics, such as ZrO_2 or $(Hf,Zr)O_2$ (HZO), throughout high aspect ratio (HAR) features. However, device performance may be compromised by trap states and other defects due to non-ideal ALD at high aspect ratios, constraining achievable capacitance. We demonstrate a simple, low-cost lateral high aspect ratio (LHAR) platform to link material properties, ALD process parameters, and device performance as a function of equivalent aspect ratio. Metal-insulator-metal capacitor (MIMcap) structures were prepared with physical vapor deposited TiN electrodes and ALD ZrO_2 or HZO dielectrics grown in the LHAR test structure using metal-organic precursors (ZyALD, ZrD-O4, TDMAHf, HfD-O4) and ozone. As expected, the ALD film thickness decreases with equivalent aspect ratio. However, we also observe intrinsic variation of the leakage performance, indicating increasingly non-ideal ALD behavior deeper in the trench. Physical characterization and kinetic modeling of the deposition process explains these trends, informing future process design to mitigate defects which worsen leakage at high aspect ratios.

AA-TuP-73 Atomic Layer Deposition Zinc-Doped Alumina and Alucone at Room Temperature for Flexible and Transparent Gas Permeation Barriers*, **Shiv Bhudia**, S Wack, N Adjeroud, J Guillot,* Luxembourg Institute of Science and Technology, Luxembourg*; D Blondin,* Met-Lux S.a.*; R Leturcq,* Luxembourg Institute of Science and Technology, Luxembourg

Gas permeation barriers are widely employed in many technological applications. From medium barrier properties (Oxygen transmission rate, OTR ≈ 1 cc m^{-2} day^{-1} bar^{-1}; Water vapour transmission rate, WVTR ≈ 1 g $m^{-2}day^{-1}$) as in the food packaging industry. To very high barrier properties (OTR ≈ 10^{-5} cc m^{-2} day^{-1} bar^{-1} ; WVTR ≈ 1 g $m^{-2}day^{-1}$) such as in flexible organic opto-electronics. Here, it is even more critical to avoid the presence of water and oxygen in the active layer.

Although, many solutions are available for high performance barriers, they typically are rigid (glass) or opaque (metal coatings) solutions, and polymeric substrates lack the capability of delivering high gas barrier properties by themselves. One promising strategy is to coat the polymeric substrate with defect free thin-films.

Atomic layer deposition (ALD) of amorphous alumina show very promising properties for passivation or encapsulation layers, in organic opto-electronics, but the deposition conditions usually require temperatures above 100 °C or highly oxidative conditions (ozone or oxygen plasma) to obtained reasonable deposition rates and high density material. A method for producing high quality alumina below 60°C, using low oxidative conditions would be highly welcome for the highly sensitive materials used in organic electronics

In this work, we propose a new process for low-temperature atomic layer deposition (ALD) of high-quality gas permeation barrier based on alumina on PET substrates. These can be employed in a multi stack structure of organic and inorganic thin-film layers for ultra-low gas permeation barrier for flexible and transparent polymeric substrates.

By incorporating up to 5 at. % Zinc as dopant during the deposition of alumina, we demonstrate the ALD of high-quality alumina at room temperature, with ALD cycles times below 1 minute. The gas barrier properties of this new material, with oxygen and water vapour transmission rate (Mocon test), show barrier properties comparable with alumina deposited at 80°C. Furthermore, the physical diffusion mechanism of a gas through a thin-film gas barrier layer is investigated; For such purpose we developed an in-house He permeation tester.

AA-TuP-74 ALD Encapsulation of QD-Polymer Composite Films for Luminescent Applications*, **Natalia Zawacka**, R Petit, J Kuhs, P Smet, C Detavernier, Z Hens,* Ghent University, Belgium

Because of their high photo-luminescence intensity, quantum dots (QDs) are a promising material for absorbing and converting light in photonic applications. However, they are very sensitive to the environmental conditions and their degradation presents major challenges. Many of the most promising technological applications of luminescence require thin films. Film deposition technology is well-established in the industry with a number of different techniques used for the manufacturing of both polymeric and inorganic thin films. From industrial point of view, the fabrication of QD-in-polymer composite films is extremely relevant. However, despite many potential advantages, the development of such composite films has been inhibited by the instability of the QDs when embedded into a polymer layer.

Here, we propose a two-layered thin film architecture and its fabrication method based on industry-compatible processing techniques. The strategic approach includes a combination of a QD-in-polymer composite film, overcoated with an additional oxide layer deposited via the ALD technique as an encapsulation layer. This assembly offers an increased stability, and provides a simple architecture for various luminescent thin film based applications.

An extensive study was undertaken where the degradation trends of QDs photoluminescence were assessed during the ALD process, investigating the influence of different precursors and gasses, as well as subsequent ageing tests in controlled ambient. We fabricated and tested a medium size (5x5cm²) device, using these highly scalable processes proving that it may represent a practical route to real-life applications of QD-based Luminescent Solar Concentrators.

AA-TuP-78 ALD-Grown Aluminum Oxide Coatings for Nuclear Applications*, **Boris Paladino**, M Vanazzi,* Italian Institute of Technology, Italy*; S Bassini, M Utili,* ENEA (Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile), Italy*; F Di Fonzo,* Italian Institute of Technology, Italy

Nuclear energy is one of the main characters in the power production field, and it is expected to experience a great development in the next future. Among the several new designs of power plant, the fusion reactor will be a substantial turning point in the energy sector. At the time being, issues related to materials compatibility persist. According to the most relevant design, fusion reactors will take the Tritium-Deuterium fusion as the reference reaction for power generation. Thus, the availability of Tritium to fuel the reactor core assumes relevant importance. The breeding process represents one of the main focus points of technological R&D activities and the inhibition of Tritium permeation is mandatory to achieve Tritium balance in the reactor chain: once Tritium is produced, an adequate permeation barrier is required to confine it. In addition, since the breeding material is the liquid eutectic alloy Pb-16Li, corrosion issues arise from the interaction of this medium with structural steels. A viable solution to mitigate the effects of both permeation and corrosion is the deposition of a protective barrier. We report on the preliminary studies about multifunctional nanoceramic Aluminium Oxide coatings grown by Atomic Layer Deposition (ALD) technique. The samples produced were initially characterized by means of SEM, AFM and XRD. The coatings are dense, compact and uniformly covering the whole substrate. From XRD analysis it is possible to understand that the deposited material is amorphous in structure, since no sharp peaks were detected. Corrosion tests in static Pb-16Li at 550°C for 2000h showed that the coating is able to protect the steel substrate mitigating the dissolutive process of the liquid medium. Finally, permeation tests with Hydrogen are still ongoing, but the preliminary results are promising. To conclude, ALD technique represents one of the few viable solutions for materials protection for the structural steels of the breeding blanket. Deeper characterization of the coating (nanoindentaion and thermal cycling) and longer corrosion tests are already planned.

AA-TuP-79 Atomic Layer Deposited Nitrogen Incorporated MoO_x Films: Electrical and Electrochemical Properties*, **Arpan Dhara**,* Ghent University, Belgium*; D Saha, S Mitra, S Sarkar,* Indian Institute of Technology Bombay, India

Oxynitrides or nitrogen incorporated transition metal oxides are rapidly gaining attention in materials research because of their tunable electrical and optical properties. They offer usage in variety of applications like photocatalysis, phosphors, electrochemical energy storage, magnetic materials etc. Primary changes in the material properties after incorporation of nitrogen occur due to the difference in electronegativity, electronic charge and polarizability between oxygen and nitrogen atoms. However, effective and homogeneous doping in the host material is a major practical issue till date. Constructive ways to increase the conductivity without significantly altering the materials chemical properties after doping are still a challenge. Usually nitrogen incorporation is carried out by annealing oxides under NH_3 or N_2/H_2 gas environment. In such circumstances the metal ions are sensitive to reduction which results in the formation of undesirable phases in the doped materials. Also the possibility of dopant inhomogeneity is a major drawback towards obtaining good quality doped materials.

In this work we report, nitrogen-incorporated amorphous molybdenum oxide (MoO_x:N) thin films synthesized by atomic layer deposition (ALD) at relatively lower temperature of 170^0C. One ALD cycle of molybdenum nitride (MoN_x) is sandwiched for nitrogen incorporation between two MoO_x layers. The concentration of nitrogen is controlled by varying the ratio of MoO_x/MoN_x layers. Quartz crystal microbalance (QCM) measurement is carried out to study the mass change after every single precursor dosed into the reactor. Secondary Ion Mass Spectra **(**SIMS) shows homogeneous distribution of nitrogen throughout the as-deposited films. Hence, uniform N-atom inclusion is adequately achieved at the reaction temperature. It is observed that conductivity of MoO_x films increase with increase in nitrogen concentration. Room temperature and low temperature electrical properties of different films are also studied in detail to understand the transport mechanism with and without nitrogen incorporation.

Both pristine and N-incorporated MoO_x layers are deposited on high surface area carbon nanotubes (CNTs) and applied as anode material in lithium ion batteries. As expected, addition of nitrogen helps to improve the electrochemical performance because of the increased ionic and electronic conductivity.

AA-TuP-82 Improvement of Thin-Film Transistor Performance in Atomic Layer Deposited SnO Film by Thermal Annealing Process*, J Lee, **Su-Hwan Choi**,* Hanyang University, Republic of Korea*; B Park,* EM Index, Republic of Korea*; J Sheng, J Park,* Hanyang University, Republic of Korea

SnO thin films was deposited by the thermal atomic layer deposition (ALD) method using N,N′-tert-butyl-1,1-dimethylethylenediamine stannylene(II) as a precursor and water as reactants. The deposited SnO thin films were thermally annealed in vacuum ambient. During thermal annealing SnO thin film transformed to SnO tetragonal from amorphous phase with the increasement of surface roughness. Also, electrical properties (carrier concentration, resistivity) could be easily controlled by employing post thermal annealing treatment, SnO showed metallic to semiconductor transition as annealing temperature increased, owing to the change of the chemical bonding state existed in SnO. The combined studies of density functional theory (DFT) calculations and experimental analyses showed different density of state (DOS) depending on the defect site and chemical bonding state, could explain the change of electrical properties. The fabricated thin film transistors (TFT) showed on/off current ratio of 1.27 x 10^3 and field effect mobility of 0.98 cm^2/Vs. The TFT bias stability were measured and SnO TFT showed good stability

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AA-TuP-87 Atomic Layer Deposition Platform in Luxembourg – Review of Emerging Applications for Sensors, MEMS, Energy Harvesters, Transparent Electronics and Coated Powder for Composites, *Noureddine Adjeroud,* Luxembourg Institute of Science and Technology, Luxembourg

The Luxembourg Institute of Science and Technology (LIST) proposes a large atomic layer deposition (ALD) platform with complementary tools for the development of new coating processes and the improvement of existing ALD processes. The platform allows processing of various types of inorganic or organic substrates, flat or 3D objects, flexible substrates and powders by FBR (Fluidized Bed Reactor) with up-scaling capabilities. The ALD platform is completed by other thin film deposition facilities (MOCVD, PVD), by cleanroom microfabrication capabilities to realize functional chips, and by a characterization platform (SEM-EDS, ellipsometry, contact angle, XRD, XPS, SIMS, AFM, UV-Vis-NIR spectrophotometry, Raman, photoluminescence, I(V), Resistivity) for quality control of the deposited thin films. This abstract is aiming to present ALD activities of our platform covering the requests and specifications from fundamental Research partners on breakthrough materials to the development and small production processing for industrial partners. A selection of ALD developments will be presented in the framework of LIST research and development projects addressing MEMS (MicroElectroMechanical Systems) and sensors (Figure 1), Energy Harvesters (Figure 2), Multilayers (Transparent Conducting Oxides and Al2O3) for transparent electronics (Figure 3), Example of Ag nano wires covered with conformal ALD ZnO film (Figure 4) and fillers' coating for composites (5).

By the means of thermal ALD and Plasma-Enhanced ALD (PEALD), we developed a library of different thin films and multilayers processes including oxides (ZnO, TiO_2, Al_2O_3, SiO_2, MgO), nitride (AlN, TiN), metals (Ag, Co, Ni) aiming both fundamental Research and applicative systems.

AA-TuP-89 Atomic Layer Deposited Films for Solar Cells Application, *Karol Frohlich,* CEMEA/Institute of Electrical Engineering, SAS, Slovakia*; M Mikolášek,* Institute of Electronics and Photonics, SUT, Slovakia*; R Subair, V Nadáždy,* Institute of Physics, SAS, Slovakia*; A Rosová, E Dobročka, M Precner,* Institute of Electrical Engineering, SAS, Slovakia*; M Jergel, E Majková,* Institute of Physics, SAS, Slovakia

Atomic layer deposition (ALD) is exceptional deposition technique because it allows for growth of high quality films on large substrates at low deposition temperatures. In our contribution ALD was employed for preparation of ZnO-based transparent conducting electrodes and for encapsulation of fabricated solar cells using Al_2O_3.

Al-doped ZnO films were used for transparent conducting electrodes. Deposition was carried out at temperatures between 150 and 250 °C on Si and quartz substrates. Diethyl zinc and trimethyl aluminium were used as precursors and water vapours as reactant. Al-doping was performed by inserting Al_2O_3 cycles in ZnO growth. Deposition of 1 Al_2O_3 layer per 7 deposited ZnO layers gave the best results. Resistivity of the Al-doped ZnO films depended on the deposition temperature and film thickness. Transition electron microscopy revealed typical columnar growth of the films with fine grained polycrystalline region close to the substrate. The films prepared at 250 °C exhibited 002 texture and for the thickness above 100 nm showed resistivity of 1 mΩcm. This corresponds to the sheet resistance of 40 Ω/square. Hall measurement revealed electron concentration of $4*10^{20}$ cm^{-3} and mobility in the range of 10-20 cm^2Vs^{-1}. Optical transmittance of the films was higher than 80% in the wavelength range between 400 and 900 nm for the thickness up to 350 nm.

Inorganic-organic hybrid perovskite solar cells suffer from poor stability in ambient atmosphere. Oxygen and moisture are believed to be reason for the solar cell degradation. To protect the cells against ambient atmosphere influence ALD prepared Al_2O_3 films were employed for encapsulation. Trimethyl aluminium was used as a precursor while water vapours were applied as reactant. Deposition of the Al_2O_3 films took place at 50°C.

Power conversion efficiency of the solar cell encapsulated by 25 nm Al_2O_3 thin film deposited using water vapours as reactant decreased to 87% while unprotected solar cell degraded below 50% of its initial value after 40 days in ambient atmosphere. Potential cause of the perovskite solar cell degradation and its link to the basic solar cell characteristics is discussed.

This study was performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by Research & Innovation Operational Programme funded by the ERDF.

AA-TuP-95 Biocompatibility of ALD Coatings on Nano- and Microstructures: Cell Viability Studies of Murine and Human Induced Stem Cell-Derived Neurons*, Robert Zierold, J Harberts, C Fendler, M Siegmund, M Schnelle, R Blick,* Universität Hamburg, Germany

Micro- and nanostructured substrates form a powerful tool for building next-generation medical devices. Especially, controlled interaction of neuronal cells—a building block of the central nerve system—with the substrate allow for sensing, stimulation, gene transfection and drug delivery paving the way for developing novel conceptual devices such as integrated solar cell nanowires for retina implants, artificial bio-computing circuits, and model systems for neurodegenerative diseases, to name a few.

One key prerequisite is the long-term biocompatibility of the surface to allow for fully functional neuronal outgrowth and cell viability. However, functional nano- and microstructured devices are often based on semiconductors or polymers which contain toxic materials. During cell culturing, cellular uptake of harmful components potentially influences the stem cell differentiation process, the neuronal outgrowth or the electrophysiological properties, and can ultimately induce the cell death.

Atomic Layer Deposition (ALD) is ideally suited to conformally coat micro- and nanostructures. Often ALD of standard oxides, such as silica, titania, and alumina, are claimed to be biocompatible; however, data reporting on cell viability are mostly missing in these studies.

Herein, we present cell viability studies on different micro- and nanostructured substrates coated by ALD with standard oxides of varying thicknesses and subsequently used for neuronal cell cultivation. The determined cell viabilities are compared to plain Petri dish control substrates and well established biocompatible parylene C coatings by chemical vapor deposition.

In detail, we investigate ALD-coated 3D-printed cavity structures and freestanding nanowire arrays for outgrowth of murine and human induced stem cell-derived neurons. We show that cell viability—utilizing a viability assay with subsequent confocal microscopy—and full electrophysiological integrity—investigated by patch-clamping of individual cells—is maintained on the micro- and nanostructures.

Our results suggest that biocompatible thin film coatings can be in fact achieved by ALD. This property in combination with the ability of conformal coating renders ALD to an economically feasible key technique for application in micro- and nanostructured lab-on-a-chip devices interfaced with human cells.

Harberts *et al.,* RSC Advances **9** (2019), 11194

Fendler e*t al.,* Advanced Biosystems **3** (2019), 1800329

AA-TuP-96 Low-Temperature PEALD of Ga_2O_3 Using TMGa and O_2 Plasma*, Ali Mahmoodinezhad, C Janowitz,* BTU Cottbus-Senftenberg, Germany*; F Naumann, P Plate, H Gargouri,* SENTECH Instruments GmbH, Germany*; K Henkel, J Flege,* BTU Cottbus-Senftenberg, Germany

Gallium oxide (Ga_2O_3), a transparent semiconducting oxide, is promising for a wide range of applications in the fields of electronics, optoelectronics, and sensors [1]. For specific applications, low deposition temperatures are required to maintain the individual material properties of subjacent layers realized in prior process steps. The use of plasma-enhanced atomic layer deposition (PEALD) on the one hand and of a gallium precursor exhibiting a high vapor pressure on the other hand facilitates the deposition at lower substrate temperatures.

Hence, in this work thin Ga_2O_3 layers were deposited by PEALD with alternating pulses of trimethylgallium (TMGa) as gallium precursor and oxygen (O_2) plasma at substrate temperatures in the range of 80 to 200 °C. The layers were prepared on silicon wafers in the SENTECH SI PEALD system [2] and subsequently characterized by spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), and electrical measurements.

In the SE measurements a linear thickness evolution with a growth rate of ~0.66 Å per cycle and an inhomogeneity of ≤ 2% across 4" wafers were found for all samples. While the refractive index of the Ga_2O_3 thin films is independent of temperature (1.86 ± 0.01 at 632.8 nm), the bandgap slightly decreases from 80°C to 200 °C (4.68 eV to 4.57 eV). Correspondingly, the permittivity of the layers determined from capacitance-voltage (C-V) measurements is constant with temperature (9.7 ± 0.2 at 10 kHz). Moreover, fixed and mobile oxide charge densities in the order of 1 to 4 × 10^{12} were deduced from C-V data. In addition, the films show electrical breakdown fields in the range of 2.2 to 2.7 MV/cm. The analysis of the chemical composition of the films by XPS revealed ideal stoichiometric gallium to oxygen ratios of 2:3 accompanied by a lowest carbon contribution of ~10% for the sample prepared at 150 °C. [3]

Furthermore, these results will be complemented by a depth profiling analysis of the layer composition based on cyclic Ar^+ ion sputtering using XPS.

The excellent materials properties are maintained even at low substrate temperatures as low as 80 °C confirming that the TMGa/O_2 PEALD process is indeed suitable for low-temperature growth.

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AA-TuP-97 ALD Coatings on Ni-Rich NMC Cathode Materials for Long Lasting, High Energy Density Batteries, *Jaime DuMont, D Lewis, M Martinez, M Herbert-Walters, S Moulton, B Hughes, A Dameron,* Forge Nano

$LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) layered oxides have become a mainstay material in Li-ion battery technology. By steadily increasing the nickel content in each generation, NMC materials have achieved impressive energy densities (~ 800 Wh kg−1) and specific capacities (~200 mAh/g) without needing to rely on complex and impractical battery chemistries. These benefits, however, come at a cost. Increasing nickel content leads to increasing structural instabilities and severe capacity fade. Extensive research on layered-structure oxides has revealed that many battery degradation mechanisms such as phase transformations, transition metal dissolution and particle cracking initiate at particle surfaces.[1,2]

In this talk, we will explore how cathode coatings by atomic layer deposition (ALD) can preserve and stabilize Ni-rich NMC surfaces, enabling increased capacity retention and high voltage utilization. Coin cell durability studies at 0.5C/1C reveal that ALD coatings can increase cycle life by up to 400% at high voltage (4.6 V). At faster C rates (4C/1C), ALD cathode coatings show decreased internal resistance growth and decreased absolute internal resistance over the lifetime of the cell. We will elaborate on these findings using results from neutron diffraction (ND), X-ray spectroscopy (XPS) and electron energy loss spectroscopy (EELS) to fully examine the mechanism by which ALD surface coatings prevent detrimental surface reactions and lengthen battery cycle life.

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AA-TuP-98 Lifetime, Selectivity, Stability, and Hydrothermal Improvements with ALD Overcoating for Hydrogenation and Dehydrogenation Catalysts, *Staci Moulton, A Dameron, T Procelli, R Tracy,* Forge Nano

While ALD has grown to be an essential and widely implemented technique in two-dimensional nanoscale device manufacturing, the innovative commercial development of applications for three-dimensional and porous materials have comparatively lagged. At Forge Nano, we recognize the criticality of enabling these ALD-assisted technologies for commercial applications, particularly in catalysis. We will demonstrate that ALD-overcoated catalysts, adding a metal-oxide top layer to a traditionally fabricated catalyst, enabled metal catalysts through targeted coating strategies for specific catalytic deactivation challenges. Our overcoat catalysts retain activity, physical stability in hydrothermal and thermal conditions, achieve improvements in selectivity, and significantly enhance lifetime. For hydrogenation of muconic acid to adipic acid, the Al_2O_3 ALD-coated catalysts retain up to two-fold activity for Pd on TiO_2 support. Second, the Pd leaching from the catalyst was reduced by four-fold on the ALD-coated catalyst. The same Pd on TiO_2 catalyst with ALD-overcoat showed significant resistance to physical restructuring under thermal treatment conditions shown both by STEM-EDS elemental mapping and activity data for uncoated and ALD-overcoated catalysts. Thermal treatment, or catalyst regeneration cycles, reduced the active catalyst surface area by over 80% for the uncoated catalyst while the ALD-overcoated catalyst retained all its active surface area over 5 regeneration cycles. The benefits of ALD for catalysis are proving to be a fertile working ground for both active materials and overcoat applications.

AA-TuP-100 Efficient and Flexible Dielectrics at Elevated Temperatures from Polymers Sandwiched with Wide Bandgap Inorganic Films Grown via Atomic Layer Deposition, *A Okyay,* Stanford University; *S Ilhom, C Wu, A Mohammad, D Shukla, Y Cao, **Necmi Biyikli**,* University of Connecticut

Flexible dielectrics with ultra-high power density are core components of electrical and electronic applications in terms of energy storage, power convertor, electrical insulating, etc. However, the drastically increased conduction current at high electric fields and elevated temperatures limited their development in applications under harsh conditions (e.g., aerospace and downhole fossil energy exploration) or systems with cutting-edge wide bandgap semiconductors, where the temperature could reach or surpass 150 °C. Reported here are flexible dielectrics based on Kapton® polyimide (PI) sandwiched with wide bandgap inorganics coated via thermal and plasma-assisted ALD, revealing greatly suppressed conduction current. Thin films of Al_2O_3 and Ga_2O_3 were separately grown on Kapton® using thermal and plasma-assisted atomic layer deposition (PA-ALD), respectively. Metal precursor and oxygen co-reactant for the process included trimethylaluminum (TMA) with DI-water in thermal, and triethylgallium (TEG) with Ar/O_2 plasma in plasma-enhanced ALD. Growth experiments were performed at 200 °C substrate temperature. The charging-discharging efficiency investigated by high electric field displacement-electric field (DE) loops was significantly improved, particularly under high electric fields and elevated temperatures. Films of varying thicknesses: 50 - 160 nm Al_2O_3 and 30 - 50 nm Ga_2O_3 were grown to study the charging-discharging efficiency. For the Al_2O_3 coating, the efficiency increased with 50 nm film when compared to 160 nm. However, the highest efficiency improvement was obtained for the plasma-assisted ALD grown Ga_2O_3 film, which possibly resulted in better blocking the charge injection in the film and thus good control of the conduction losses. Further tests will be performed to study the effect of thinner and plasma-enhanced grown Al_2O_3 on the charging-discharging efficiency enhancement of Kapton® flexible dielectrics. ALD as a facile and scalable fabrication technique would enable enormous potential in large scales of roll-to-roll processing for industrial high-power electrical cabling applications.

AA-TuP-101 On the Atomic Layer Deposition of Catalysts for Dehydrogenation of Propane with CO_2: The Study of Reaction Performance and Coke Formation, *Fatemeh Gashoul Daresibi, Y Mortazavi, A Khodadadi,* University of Tehran, Iran

Increasing the worldwide demand for propylene, inspired researchers for the study of promoted highly advanced techniques compared to the current industrial methods to fulfill the requirements of the market. Regarding this issue, CO_2-ODHP has attracted attentions due to its role in facilitation of the C-H bond activation, lowering the activation energy of the reaction as a whole and more effectively reduce the process temperature with much higher rates without the problem of deep oxidation or low selectivity.

In this study, we applied the atomic layer deposition of CrO_x/SiO_2 to enhance the performance of CO_2-ODHP reaction. Silica supported chromium oxide catalyst was synthesized by using $Cr(acac)_3$ and synthetic air as metal precursor and oxidant respectively. The support temperature was selected in the suitable range of ALD called ALD-window and the precursor dose time was 9 h. The outlet of the ALD reactor was monitored by an on-line FTIR gas cell. The loading of Cr was determined by ICP-OES. The ALD catalyst was used for the dehydrogenation of propane in presence and absence of CO_2. The oxidation step followed by stabilization of catalysts was carried out at three different temperatures, 300, 600 and 650ºC. Results reveal the higher performance of ALD catalyst in presence of CO_2 compared to direct dehydrogenation. However, in both conditions, catalyst suffers from deactivation through the time-on-stream possibly due to the structural changes during the reaction, irreversible reduction of Cr^{6+} and coke formation. The catalyst with lower oxidation and stabilization temperature, 300°C, has shown the higher reaction performance close to equilibrium conversion. The coke formation was studied with Raman spectroscopy and Temperature Programmed Oxidation (TPO) accompanied by on-line FTIR analysis. Results illustrate the presence of both graphitic and disordered carbonaceous species. The main product of the coke combustion was CO_2 with a very slight amount of CO. To find out the coke source, Ar diluted propylene was passed through the catalyst and the Raman results show a similar spectrum revealing the propylene as the main source. The adsorption-desorption isotherm and pore size distribution curves show slight structural changes after reaction. Temperature programmed reduction (TPR) over fresh and regenerated spent catalyst also shows a little decrement in reducibility of catalyst as another sign of structural changes and/or irreversible reduction of chromium (VI). To summarize, the ALD-synthesized Cr/SiO_2 catalysts show higher performance at lower oxidation temperature and in presence of CO_2 while the deactivation under reaction conditions is still an issue.

AA-TuP-103 Atomic Layer Deposited Al-doped TiO_x as Passivating Contacts on Silicon Solar Cells*, **Borong Sang,* University of New South Wales, Australia*; Z Huang,* Jiangsu Ocean University, China*; M Hossain,* University of New South Wales, Australia*; A Abdallah, Y Zakaria,* QEERI, Qatar*; B Hoex,* University of New South Wales, Australia

Atomic layer deposited (ALD) titanium dioxide (TiO_2) has been well investigated and has been reported to be an excellent electron selective contact on silicon solar cells with a high level of surface passivation; however, its poor thermal stability[1][2] limits the range of processes which can be used after the application of the TiO_2 film which is, in particular, a significant restriction for the metallization step. Aluminum (Al) doped TiO_2 is reported to effectively improve perovskite solar cell performance especially in electric properties via creating defects due to the size discrepancy between Ti and Al atoms [3]; however, ALD doping materials are yet to be thoroughly investigated applying on silicon solar cells as passivating contacts.

In this work, Al was successfully incorporated into TiO_2 layers using an ALD supercycle approach at 150 °C, showing both passivation and electrical performance of superior quality on silicon wafers. A champion effective minority carrier lifetime of 1.9 ms is obtained from Al-TiO_2/SiO_2/*n*-Si stack after 300 °C annealing while a significantly lower lifetime of 210 µs is obtained from the undoped reference. This indicates that Al incorporation increases the thermal stability of the TiO_2 layer and the passivation effects, and this is very beneficial from an application point of view. TLM measurement showed that contact resistance also reduces by introducing Al into the TiO_2 layer, which can probably be attributed to the defect states introduced by Al. Furthermore, DFT simulation results well explained the mechanisms of improved performances from experimental results. Future work will focus on fabricating solar cell devices employing this doped layer as electron selective contact to further improve the solar cell efficiency.

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AA-TuP-105 The Evolution of Temperature Monitoring in ALD*, J Paolino, **Jason Merson**,* Global Results Communications

The advancement and complexities in semiconductors are the foundation for continued technology advancements in virtually every device and machine we interact with. As semi structures become more complex, processes like Atomic Layer Deposition (ALD) are exceedingly important to ensure deposits are precise and can interconnect with the different layers. Even though these processes have been out there for people to explore, ALD has been too expensive to pursue. But now, advancements are making ALD economically feasible and the market is expected to rapidly expand within the next few years.

As ALD becomes a highly utilized deposition method, the industry should expect to see more complex structures where the measurement of temperature becomes increasingly important as a control variable. Traditionally with ALD, thermocouples have been used to monitor temperature, but these only provide an indirect measurement that requires a model to calculate the offset. This becomes problematic over time because as the thermocouple degrades the model changes making temperature readings harder to determine and unreliable. Now we are seeing a push for a better solution for measuring temperature with precision as more semiconductor manufacturers adopt ALD.

During this presentation, Advanced Energy – a global leader in highly engineered, precision power conversion, measurement and control solutions – will discuss how the industry is now moving towards the adoption of optical temperature measurement tools, such as non-contact pyrometers that can get within 2mm of a silicon wafer without causing damage or interrupting the ALD process. This will include:

- A look at the evolution of temperature reading in ALD and its challenges
- How pyrometers provide precise, non-contact temperature readings

The importance of emissivity measurement

Area Selective ALD
Room Arteveldeforum & Pedro de Gante - Session AS-TuP

Area Selective ALD Poster Session

AS-TuP-1 A Novel Cobalt Precursor for Area-Selective Deposition*, **Hiroyuki Oike**, Y Yamamoto, T Hayakawa, T Furukawa, K Tokudome,* TOSOH Corporation, Japan*; K Tada,* Sagami Chemical Research Institute, Japan

Cobalt thin films have attracted much attention for a wide variety of technological applications, such as $CoSi_2$ contacts, capping layers and liners of copper interconnects in integrated circuits.$^{1-3}$ Lately, area-selective deposition of cobalt thin films, especially by means of CVD/ALD, has been one of the hot topics in this field.

In this work, we developed a novel cobalt complex, [(2-dimethylamino-1,1-dimethylethyl)(trimethylsilyl)amino](2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt [**Co1**], as a precursor for area-selective deposition of cobalt thin films (metal-on-metal).

Co1, a deep green liquid at room temperature, has excellent physicochemical properties suitable for use in CVD/ALD processes, so its TG curve showed a single-step weight loss with almost no residue. In the DSC measurement, the exothermic peak due to thermal decomposition was observed around 210°C. The vapor pressure of **Co1** was determined to be 0.1 Torr at 88°C by the Clausius-Clapeyron plots. These results indicate that **Co1** has sufficient vapor pressure and thermal stability for CVD/ALD processes.

Area-selective behavior was examined by CVD of **Co1** with formic acid (HCO_2H) as a co-reactant at 200 °C on ruthenium, copper, platinum and SiO_2 substrate, respectively. After a deposition time of 90 min, cobalt thin films were deposited on ruthenium, copper and platinum substrates, while no cobalt thin film was formed on SiO_2 substrate. The excellent selectivity between these metal substrates and SiO_2 substrate was clearly observed. In addition, it was confirmed that the cobalt thin film on ruthenium substrate has a thickness of 33 nm and a cobalt content of 93% by XPS analysis.

We propose that **Co1** is a promising precursor for selective cobalt film deposition processes.

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AS-TuP-3 Thermally Assisted Area Selective Atomic Layer Deposition*, **Bart de Braaf**, K Storm,* Eindhoven University of Technology, The Netherlands

We explore a new method for area selective ALD by modifying the temperature profile on the substrate. The technique keeps the majority of the substrate at a low temperature, suppressing the chemical reaction, while a small, local area is heated to allow the reaction to 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 modeling. We first model the control of the temperature by various illumination protocols, and then model and simulate the nucleation and growth of spatially localized layer given an inhomogeneous temperature profile, to show that the site and the extent of nucleation can in theory be localized and controlled.

AS-TuP-5 Simple Fabrication of Patterned MOF Thin Films via Area Selective Deposition of ZnO by Spatial ALD

Chiara Crivello, *D Muñoz-Rojas,* LMGP Grenoble INP/CNRS, France*; V Nguyen,* Phenikaa University, Vietnam*; O Hassan,* Grenoble INP/CNRS, France

Metal-Organic Frameworks (MOFs) constitute a class of hybrid materials that have received a lot of attention due to their versatility in physical and mechanical properties and by the many possibilities that can be used to synthesize them. Given their particular properties and the possibilities to integrate them into devices, it has become important to synthesize MOFs as thin films. The initial methods to deposit MOF thin films were based on the same approaches used for the bulk synthesis, which involve the use of solvents and thus are not ideal for integration in nanofabrication processes [1]. More recently, solution-free approaches have been proposed based on Atomic Layer Deposition (ALD). [2] Thanks to the surface-limited, self-terminating nature of ALD reactions, the deposition of films with precise control over the thickness and with high conformity even on high-aspect-ratio or porous substrates is possible. Thus, the combination of oxide layers made by ALD with vapors of organic linkers has been reported and it is indeed a very appealing route towards achieving device integrated MOF thin films. [3]

SALD is a variation of ALD that has the advantage to be faster compared to ALD and that can work at atmospheric pressure and even in the open air. [4,5] We have also demonstrated that by adjusting the deposition parameters of our home-made SALD system we can perform area selective deposition in a direct way, i.e. without the need for patterning or masking steps [6].

In this communication, we will present the synthesis of Zeolitic Imidazolate Frameworks (ZIFs) obtained from ZnO films deposited by SALD and using less toxic ligands with respect to the classical 2-Methylimidazole. We will also demonstrate that area selective deposition of MOF thin films can be easily achieved by converting ZnO patterns deposited with our SALD.

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 801464.

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AS-TuP-7 Topographic Area Selective Deposition: A Ccomparison Between PEALD/ALE and PEALD/Sputtering Approaches

Moustapha Jaffal, *T Yeghoyan, V Pesce, A Chaker, D Sylvain, G Lefevre,* LTM-UGA, France*; R Gassilloud, N Posseme,* CEA-Leti, France*; M Bonvalot,* LTM-UGA, France*; C Vallée,* CNRS LTM, France

Multiple patterning for advanced 3D nano-electronic devices largely relies on plasma processes. For instance, conformal deposition of spacers on pitches and mandrels is carried out by Plasma Enhanced Atomic Layer Deposition (PEALD), with subsequent anisotropic plasma etching steps of top and bottom deposits, so as to keep only vertical coatings on 3D feature sidewalls. Such a technological route is well-established, although it suffers from several drawbacks, such as deposition-related trench corner accumulation, or etch-related foot formation, spacer sidewall trimming and trenching. These can be potentially avoided thanks to a so-called super-cycle approach, as developed previously by our group, whereby a complete coating of 3D structure sidewalls is achieved by multiple and alternating deposition and etch cycles [1,2].

The proof of concept for this lateral 3D structure coating by in-situ super-cycle deposition was published last year for the specific case of Ta_2O_5: super-cycles were composed of Ta_2O_5 standard PEALD steps intercalated by Ar^+ plasma sputtering steps with ions of approximately 260 eV incident kinetic energy [3]. Although this process appears to be suitable at the macroscopic scale, its transfer to the nanoscale for spacer definition with appropriate critical dimension (CD) control is not trivial, as illustrated in Figures 1 and 2. Indeed, the Ar^+ sputtering step may induce significant damages to exposed substrate surfaces, such as roughness, amorphization, redeposition or ion implantation.

In this work, we have investigated the possibility of using a so-called quasi-Atomic Layer Etching step (q-ALE) instead of an Ar^+ sputtering step, for the definition of a 3D ASD process with true nanoscale control. The q-ALE step consists in a self-limited fluorine-based passivation followed by a low-energy soft Ar^+ plasma removal of the thus-modified uppermost surface layer and can be easily performed within the same ALD reactor chamber.

The optimization of this PEALD-q-ALE super-cycle process will be presented for the topographic selective deposition on vertical surfaces only, with the objective of minimizing any drift and cross contamination. The occurrence of etch-related defects and the overall process throughput will be discussed in view of previously published results obtained from PEALD – Ar^+ sputtering processes.

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AS-TuP-10 Molecular Rearrangement of a MLD Thin Film by Electron Beam Irradiation

GeonHo Baek, *S Lee, J Lee, J Park,* Hanyang University, Republic of Korea

Recently, to increase the transistor density of logic and memory devices, the structure of device has to be technically developed and it requires the process which decreases cost of process and increases process yield with simplifying device process. Area selective deposition can be one of the methods to simplify process. Among conventional selective deposition methods, there is an electroless deposition (ELD) method which is useful for Cu metallization[1]. However, as smaller size of device is developed, the resistivity of Cu electrodes increases drastically, so the metal electrodes such as Mo, Co and Ru can be selected as a candidate for fine nano-pattern[2]. Furthermore, due to issues of particle and contamination in the ELD process, another methodology is required to fabricate defect-free nano pattern[3]. Area selective atomic layer deposition (ASALD) is a promising future technology to realize 5nm scale memory device and apply on industry. The ASALD is a key process which is one of "bottom-up" technology to reduce cost of fabrication and complement positional error alternative to conventional "top down" technology.

In this paper, the authors researched an inhibitor for the ASALD using molecular layer deposited (MLD) film annealed by electron beam irradiation (EBI). The authors studied the effect of EBI on an indicone film which is fabricated by using INCA-1 (Bis(trimethysilyl) amidodiethyl Indium) and HQ (hydroquinone) and an alucone film which is fabricated by using TMA (Trimethylaluminum) and 4MP (4-mercaptophenol). The EBI effect on MLD films was evaluated by investigating change of thickness, composition and structure. In the annealed indicone (HQ), there are only carbon and oxygen, but various elements of aluminum, carbon, oxygen and sulfur in the annealed alucone (4MP) film. The various elements act as impurity and inhibit reconstruction of graphitic carbon. The graphitic carbon of annealed indicone (HQ) film can be used for inhibitor of ASALD due to deficiency of hydroxyl group on the surface. In order to observe selectivity of the annealed indicone film, atomic layer deposition of ZnO was performed on annealed indicone / silicon line pattern and the surface of annealed indicone can inhibit 20 cycle of ALD ZnO as compared to Si surface.

AS-TuP-11 Inherent Area-Selective Atomic Layer Deposition of Ruthenium Thin Film with Novel Ru Precursor

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Ruthenium (Ru) thin films are deposited by atomic layer deposition (ALD) using novel precursor, $Ru_2\{(CH_3)_3CNCHCCH_2CH_3\}(CO)_6$ (T-Rudic), and two different co-reagents, H_2O and O_2. Ru films are deposited as 0.1 Å/cycle at 150 ^oC with H_2O and 0.8 Å/cycle at 200 ^oC with O_2. Different reaction behavior was observed between two reactants, especially film growth rate depending on growth temperature. O_2 shows only CVD growth behavior, on the other hand, H_2O co-reactant set shows ALD saturation between 150 to 200 ^oC. We find that film growth preference exists among the various substrates (Si, SiO_2, Al_2O_3, graphitic carbon) when H_2O applied at 150 ^oC. Ru film selectively grown on various substrates and except for Si substrate, nucleation delays were detected. To identify the selective deposition mechanism, density functional theory (DFT) calculation of half-reaction was progressed. Due to the difference in chemisorption energy, nucleation delay occurred on hydroxyl-terminated SiO_2 surface. Both experimental data and DFT calculation indicates that prefer growth on hydrogen-terminated surface (Si). We also infer the reaction mechanism of precursor and reactant from other precedent researches in addition to our results, remained carbonyl ligand after chemisorption of precursor reacts with H_2O by WGSR method and forms Ru film. Overall, this work shows that the ALD deposition of novel Ru precursor and its film properties, selective deposition and the reaction path of the precursor. Our study suggests that through precursor designing and selecting proper reactant ASD could be achieved using ALD technique.

AS-TuP-12 Selective Atomic Layer Deposition of Nickel on the Molybdenum Oxide Supported on γ-Al_2O_3 for Enhanced Hydrodesulphurization of Dibenzothiophene at Lower Temperatures and Pressures*, A Khodadadi, S Bahrani, Y Mortazavi,* ***Fatemeh Gashoul Daresibi,*** University of Tehran, Iran

It is believed that components such as Ni promote the hydrodesulfurization (HDS) activities of Mo- and W-based sulfide catalysts. Till now, various investigations have been done in order to understand the synergy mechanism between promoter (as Ni) and sulfided Mo(W), the structure of the active catalytic sites and HDS reaction mechanisms. Generally, the mechanism for the HDS reaction is proposed to be based on the requirement of anion vacancy for the S-containing molecule being adsorbed through S-heteroatom. In the promoted transition metal sulfides as Ni-Mo catalysts the presence of Ni promoter may accompanied the formation of anion vacancies as a result of promoter atom substitution with Mo atoms in S-Mo-S slabs of Ni-Mo-S phase which is known as the catalytic active site in the HDS catalysts. So, intimate contact of Ni and Mo species and edge decoration by the Ni promoter is believed to be necessary for formation of Ni-Mo-S active phase while the NiS_x is not reactive [1-3].

In this study, $Ni(acac)_2$ was selectively deposited on MoO_3 by atomic layer deposition (ALD) at 180 °C. The selective deposition was confirmed by monitoring Hacac as the reactive chemisorption product in the ALD reactor effluent gases using a gas cell in FTIR. There is 30 °C temperature window, at which the $Ni(acac)_2$ is selectively deposited on MoO_3 but not on γ-Al_2O_3, as shown in **Fig.1** .In this way, the determined contents of Ni (by ICP technique) showed 0.07 and 0.64 wt% deposition of Ni on MoO_3/γ-Al_2O_3 and γ-Al_2O_3, respectively during first ALD cycle for 20 minutes at 180 °C. The MoO_3, seems to catalyze the reactive chemisorption of $Ni(acac)_2$ [4]. The FTIR spectra of MoO_3/γ-Al_2O_3 and the one after reactive adsorption of $Ni(acac)_2$ shown in **Fig. 2**. confirms the successful ALD and possible formation of acac-Ni-O-MoO_x species.

3 wt% Ni on 6, 9 and 14 wt % Mo/ γ-Al_2O_3 catalysts were prepared by both S-ALD and conventional impregnation (IMP) methods and their dibenzothiophene (DBT) sulfur removal efficiencies were evaluated and presented in **Fig. 3** at 300 °C and 1 and 5 bar pressures. The S-ALD prepared catalysts show up to about 80% higher S-removal efficiency, compared to the ones prepared by IMP method.

In conclusion, the selective ALD can provide an intimate contact of Ni and Mo, which results in the formation of Ni-Mo-S reactive phase required for effective desulfurization.

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AS-TuP-13 Area Selective Atomic Layer Deposition of Molybdenum Films on Nanoscale Metal and Metal Nitride Patterns*,* ***Se-Won Lee****, M Kim,* Merck Performance Materials Ltd. Korea, Republic of Korea

Deposition of conductive metal in super-narrow lines and vias represents significant challenge for scaling semiconductor devices. Cu interconnect lines show significant increase in resistivity below 10 nm and can't be used without a barrier due to electromigration. Tungsten inherently has higher resistivity compared to copper while precursor choice is often limited to tungsten hexafluoride which also requires a relatively thick barrier film to protect dielectric layer. Molybdenum (Mo) is considered as an attractive material for future devices. Mo has almost same level of low bulk resistivity comparing to W, but it has smaller EMFP (Electron Mean Free Path), so the effective resistivity, a product of bulk resistivity and EMFP, is expected to be lower compared to W for films less than 10nm. While Mo films can be deposited by traditional CVD or ALD processes, area selective deposition of metal films can significantly reduce process steps and provide new options for device integration.

Here, we report area selective thermal ALD of Mo films on metal and metal nitride substrates using high purity molybdenum pentachloride ($MoCl_5$) and molybdenum dichloride dioxide (MoO_2Cl_2). Deposition of Mo films was investigated by thermal ALD process with hydrogen reactant gas at 350-500°C on various substrates, such as aluminum oxide, silicon oxide, titanium nitride and ruthenium metal. Both Mo precursors showed higher deposition rate on TiN substrate compared to SiO . However, MoCl showed significantly higher process selectivity toward TiN and Ru. The dependence of selectivity on process conditions, such as precursor ampoule temperature, chamber pressure and deposition temperature was investigated. Higher selectivity was attributed to MoCl ability to self-etch deposited Mo film.The films were characterized by XRF, 4-point probe, XPS, SIMS and XRD. Molybdenum films deposited from $MoCl_5$ on Ru substrate at 450°C showed no detectable chloride by XPS and << 0.01 at % by SIMS.

High resolution TEM of Mo films on patterned TiN/SiO_2 and Ru/LowK wafers shows a seamless bottom-up molybdenum fill on highly challenging structures with CD < 30 nm and feature height > 80 nm, with very minor defects on SiO_2 and LowK dielectric. Over 10 times enhancement of effective deposition rate was observed inside the features compared to blanket film. For example, selected process conditions provided 4.2 nm Mo film on blanket Ru film while the same conditions deposited over 80 nm Mo film inside of ~ 20 nm via. The result may suggest that ASD mechanism on nanoscale is different from the macroscale mechanism.

AS-TuP-14 300 mm-Wafer Characterization of Ruthenium Area-Selective Deposition in Nanoscale Line-Space and Hole Patterns*,* ***Jan-Willem Clerix****, A Delabie,* KU Leuven – University of Leuven/IMEC, Belgium*; J Hung,* Nova MI/IMEC, Belgium*; L Warad, K Shah,* Nova MI, Belgium

Area-Selective Deposition (ASD) will become more and more important for nano-electronic device fabrication. It is an approach that relies on the selective growth of materials, based on differences in precursor adsorption and diffusion on varying surfaces. The promise of both vertical and horizontal growth control, simplified production flows and elimination of edge placement errors make Area-Selective Atomic Layer Deposition (AS-ALD) an ideal technique to complement top-down patterning. Yet, unintentional island growth on the non-growth surface is a major challenge for AS-ALD, and defect mitigation strategies are being developed. Crucial to this development is the availability of characterization techniques that map selectivity and defectivity on large area substrates containing nanopatterns.

In this work, we investigate the growth rate and selectivity of Ru ASD on nanoscale TiN/SiO_2 line-space and hole patterns on 300 mm wafers. The process consists of a N,N-dimethylamino-trimethylsilane surface passivation step, (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)Ru/O_2 ALD and an O/Cl plasma defect etch; and has been used previously to create a Ru hardmask for block patterning [1]. In this work, we investigate defect mitigation strategies based on particle size control or selective etch. We therefore use a full-wafer in-line characterization approach based on Optical Critical Dimension Metrology (OCD), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). XPS provides information about both growth and non-growth patterns simultaneously without the need for cross-section imaging. Additionally, each XPS measurement probes 10^4 structures, while SEM probes ~10, which benefits XPS sensitivity. Attenuation of the Ti and Si signals is used to monitor Ru coverage on the TiN growth and SiO_2 non-growth surfaces. The Ti3s signal shows how over a 120s etch all Ru is removed from the growth surface (figure 1), not all Ru is removed from SiO_2. Our preliminary findings indicate that further optimization is needed to obtain an ASD window through etch selectivity. Alternatively, particle size control can be used when using an etch-based defect mitigation strategy.

Nanostructure Synthesis and Fabrication
Room Arteveldeforum & Pedro de Gante - Session NS-TuP

Nanostructures Synthesis and Fabrication Poster Session

NS-TuP-7 ***In situ*** **Thermal Annealing of ALD Fabricated Pt Nanoparticles and Their Stabilization via Al_2O_3 Overcoating***, E Solano,* NCD-SWEET beamline, ALBA Synchrotron Light Source, Spain*; J Dendooven, J Feng,* Ghent University, Belgium*; P Brüner,* IONTOF GmbH, Germany*;* ***Matthias Minjauw****, R Ramachandran, M Van Daele, K Van de Kerckhove, T Dobbelaere,* Ghent University, Belgium*; A Coati,* Sychrotron SOLEIL, France*; D Hermida-Merino,* ESRF European Synchrotron Radiation Facility, France*; C Detavernier,* Ghent University, Belgium

The activity and selectivity of supported Pt nanoparticles in heterogeneous catalysis depends on the particle size, shape and coverage [1]. Particle coarsening induced by the often required harsh thermal and chemical conditions during catalytic processes is undesirable since it limits the availability of catalytic sites. Large efforts and resources have been invested to prevent particle coarsening, aiming to prolong the performance and lifetime of nanocatalysts. Among the diverse approaches, particle overcoating via ALD has emerged as a promising method for coarsening prevention while enabling catalyst accessibility through pores and cracks in the overcoat [2]. However, there is a delicate balance in terms of film thickness: a thin overcoat may not be enough for particle coarsening prevention while a thick layer could totally block the surface accessibility for the catalytic application.

Here, we report an *in situ* synchrotron Grazing Incidence Small Angle X-ray Scattering (GISAXS) study on the thermal stability of supported Pt nanoparticles when overcoated with an Al_2O_3 layer deposited by means of ALD (Figure 1). As model system, we fabricated two distinct sets of samples with equivalent Pt loading but distinct particle coverage [3]. A series of different Al_2O_3 thicknesses were deposited onto the supported nanocatalysts prior to *in situ* annealing up to 850 ºC in an O_2-rich atmosphere. The real-time GISAXS patterns provided a near-continuous feed of information on the evolution of particle size and spacing during the annealing process [4]. *In situ* data demonstrated that the overcoating methodology requires isolated nanoparticles for an effective stabilization, while stabilization of the closely packed supported nanoparticles turned out to be more challenging, showing the dependence of the minimum overcoat thickness on the initial morphology. Moreover, Pt surface accessibility was evaluated by Low Energy Ion Scattering (LEIS), confirming that the amount of exposed Pt for the coated samples during the thermal treatment due to the cracks and pores formation (Figure 2). After a long isothermal annealing, the coated sample with isolated nanoparticles has a larger amount of exposed Pt surface area than an uncoated (and hence coarsened) sample, proving the efficiency of an ALD Al_2O_3 layer as stabilization tool for supported nanocatalysts.

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NS-TuP-10 Surface Functionalization and Atomic Layer Deposition of Metal Oxides on MoS_2 Surfaces, *Theodosia Gougousi*, *J Kropp, C Ataca,* University of Maryland, Baltimore County

Transition metal dichalcogenides (TMD) have been studied for device applications due to their electronic properties and their possession of a bandgap (1.8eV for single layer MoS_2). The fabrication of electronic devices requires deposition of high-quality dielectrics on the hydrophobic TMD surface and remains a challenge.

In this work we will provide examples of TiO_2 and Al_2O_3 Atomic Layer Deposition (ALD) film growth from tetrakis dimethyl amino titanium (TMDAT), trimethyl aluminum (TMA) and H_2O at 100-200°C on exfoliated and Chemical Vapor Deposition (CVD) MoS_2 flakes. We find that the initial surface condition of exfoliated MoS_2 flakes varies greatly due to residual adhesive contamination resulting in large variation in the film morphology. More controlled growth is obtained for CVD MoS_2 flakes but even in this case the surface coverage is thickness dependent for films as thick as 10 nm.

In order to alter the surface energy, seeding with inorganic and organic species have been investigated. Mercaptoethanol (ME) is a small thiol that contains a -SH functional group at one end and -OH termination at the other end. The -SH termination is expected to react with the MoS_2 surface leaving the surface -OH terminated as desired for the onset of the ALD chemistry. Atomic Force Microscopy (AFM) measurements confirm that ME treatment alone does not promote more uniform film growth. Computational studies of the ME-MoS_2 surface interaction using Density Functional Theory (DFT) reveal that ME interacts with the sulfur vacancies almost exclusively. Vacancy density is less than ~5% for as-deposited CVD MoS_2, and depositions result in non-continuous coverage for typical thermal ALD. Argon ion sputtering was used to remove Sulfur atoms from the surface and increase the vacancy density up to ~20%. AFM confirms the formation of continuous 6 nm TiO_2 films at 100°C for both ME treated and control samples. DFT calculations reveal that TDMAT can interact directly with the vacancy. However, the calculated Density of States for these defect rich surfaces contain gap states that are undesirable for high quality devices. Treatment of defect rich surfaces with ME results in the removal of the gap states which is expected to result in good electrical properties.

$HAuCl_4$ solutions have been also used to seed the surface with -Cl terminal species to initiate film growth. XPS data confirm both the presence of Au on the surface and absence of residual chlorine. AFM shows only partial surface coverage for films as thick as 6 nm. A distinct difference in the film morphology is obtained though as a result of this treatment indicating that the film growth mechanism has been altered.

NS-TuP-11 Comparison of Growth Characteristics and Nanoparticle Formation by O_2 or H_2 Reactant Gas in Pt ALD, *Tatsuya Nakazawa*, *D Kim, T Nam, J Park, H Kim,* Yonsei University, Republic of Korea

The utilization of platinum nanoparticles has already been commercialized in catalysts, Pharmaceutical applications, and device fabrication. The size control of nanoparticles is significant for obtaining the desired properties of nanoparticles, for example, catalytic ability, interaction with pharmacological agents, quantum effect. Therefore, we focused on an atomic layer deposition (ALD) process that controls particle size by self-limiting growth. Thus, the conformal growth can be caused in each initial particle on the substrate; it is expected that the particle size and the cycle number is in a linear relationship.

Lee *et al.* reported that DDAP (Dimethyl(N,N–Dimethyl-3-Butene-1-Amine–N) Platinum) is a candidate precursor for Pt ALD with O_2 reactant. [1] DDAP is a promising precursor to prepare the Pt film because of its high vapor pressure and low decomposition temperature. Additionally, the high purity of the deposited platinum by DDAP precursor is expected to be applied in the semiconductor industry. However, PtO_x generated in an oxidizing atmosphere has a high diffusion coefficient. It is an advantageous effect forming a uniform thin film having, but it is difficult to control the size and dispersibility of nanoparticles. Several studies of Pt ALD have been reported to prepare Pt nanoparticles using H_2 reactants as well as O_2 reactants. [2][3] O_2 and H_2 reactants have different reaction mechanisms, which may affect growth characteristics and chemical composition of Pt deposition. In this study, we first compared the Pt ALD using DDAP with O_2 and H_2 as reactants for application to the Pt nanoparticle preparation process. The film thickness, surface morphology, and nanoparticle distributions were measured by FE-SEM (Field Emission Scanning Electron Microscopy) and image analysis. Moreover, chemical composition and chemical states were determined by XPS (X-ray Photoelectron Spectroscopy). We will discuss the differences in the reaction mechanism from each growth characteristic and chemical analysis. Based on these results, size-controlled nanoparticle production studies with Pt ALD using DDAP were conducted. Also, we clarified the relationship between particle size and cycle number and growth temperature in the preparation of nanoparticles using DDAP. We have found that the conditions for nanoparticle formation are entirely different depending on the ligand gases. Therefore, we will talk about the mechanism of growth when O_2 or H_2 is used as reactant gases.

Reference

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Live Session
Room Live - Session LI3-WeM
Technical & Poster Sessions: Wednesday Live

Moderators: Christophe Detavernier, Ghent University, Belgium, Jean-François de Marneffe, IMEC

10:00am **LI3-WeM-7 Welcome & Introduction***, **Christophe Detavernier**, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

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10:15am **LI3-WeM-8 Surface Reactions Between Metals and Diketone induced by Gas Cluster Ion Bombardments***, **Noriaki Toyoda**, K Uematsu,* University of Hyogo, Japan **INVITED**

Gas cluster ion beams (GCIB) are aggregates of several thousands of gaseous atoms or molecules. Since the thousands of low-energy (several eV) atoms bombard a surface at the same time and the same position, the bombarded area experiences transient high-temperature and high-pressure conditions, which enhance sputtering of atoms or molecules. By using these characteristics, GCIB is now widely used for surface analysis tools in XPS or SIMS system. In recent years, we are investigating the feasibility of GCIB as energetic ions to enhance the surface reactions between adsorbed molecules and target atoms. We have reported ALE process using GCIB for transition metals (Cu and Ni) with diketone (acetylacetone and hexafluoroacetone). We separated each etching step as following; (1) adsorption of diketone molecules on metal oxide, (2) evacuation of residual vapor, (3) irradiation of O_2-GCIB to remove metal oxide. By using 5 keV O_2-GCIB (~ 2eV/molecules), thin layer of nickel oxide with adsorbed acetylacetone is removed. There is no physical sputtering at this energy region, which realizes self-limiting ALE process. From in-situ XPS study, Ni oxide with adsorbed diketone molecules can be removed by Ar-GCIB irradiation. It means that other oxidation method can be used to form metal oxide, and Ar-GCIB can be used for the removal steps. In this talk, we will report surface reactions between metals and diketone induced by gas cluster ion bombardments, and etching characteristics of various metals using GCIB irradiation and diketone.

10:45am **LI3-WeM-10 ALE 2020 Best Student Paper Award Talk: Isotropic Plasma ALE of Al_2O_3 using SF_6 Plasma and TMA***, **Nicholas Chittock**, M Vos, A Mackus,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands

Isotropic ALE is typically achieved using thermal chemistries, while plasma ALE processes are generally anisotropic in nature due to directional ions generated by the plasma. In this work, a plasma ALE process for isotropic etching of Al_2O_3 is introduced which involves SF_6 plasma exposure and TMA dosing. This process demonstrates that a fluorine containing plasma can serve as a viable co-reactant for ALE, and that plasmas can also be utilized for isotropic ALE.

From Fourier transform infrared spectroscopy (FTIR) analysis it was deduced that the SF_6 plasma step eliminates surface methyl groups while also fluorinating the surface. This fluorinated region is then removed by dosing TMA, similar to the pathway for the thermal HF/TMA ALE process.[1-5] A decrease in the Al-O IR absorbance peak for increasing ALE cycles indicates that the process is effective for etching Al_2O_3.

Self-limiting ALE behavior of this etch process was confirmed by measuring saturation curves for SF_6 plasma exposure and TMA dosing using in-situ spectroscopic ellipsometry, yielding an etch per cycle (EPC) of 3.1 Å/cycle at a substrate temperature of 260 ˚C. Higher EPC values than previously observed in the literature for thermal ALE of Al_2O_3 were obtained over the investigated substrate temperature range of 155 – 285 ˚C.[1-5] Furthermore a significant EPC of 0.83 Å/cycle was already achievable at the low substrate temperature of 185 ˚C. Performing multiple doses of only one half-cycle does not lead to observable etching of either Al_2O_3 or HfO_2 surfaces, while the complete ALE cycle was effective for etching both materials, thereby demonstrating the synergy of the ALE process. The measured EPC of HfO_2 ALE is 1.1 Å/cycle using the SF_6 plasma TMA process, which is higher than previously reported for a similar thermal HF/TMA process.[6] The isotropic nature of the plasma ALE process was demonstrated by transmission electron microscopy (TEM) analysis of 3D trench structures, with the Al_2O_3 thickness on Si trench structures being analyzed before and after etching. This work highlights that the use of plasmas allows for extension of the operating space for isotropic ALE by offering lower temperatures, higher EPC values and alternative plasma co-reactants.

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11:15am **LI3-WeM-12 Monolayer Lithography: Exploiting Inhibition Contrast from the Extreme Ultraviolet Irradiation of Organic Monolayers for Area Selective Depositions***, **Rudy Wojtecki**,* IBM Research - Almaden **INVITED**

The enablement and miniaturization of technologies, such as electronic devices, are largely dependent on patterning materials. For instance, polymer resists can be used to create a broad range of desired feature geometries that continue to extend the capabilities of nanoscale fabrication at a remarkable rate. The 7nm technology node, which is reliant on extreme ultraviolet exposures exposures, may still rely on chemically amplified resists (CARs) from previous technology nodes. However, at critical dimensions (CDs) and below, CARs reveal increasingly difficult challenges to achieve the resolution and line edge roughness demanded by future technology generations. These include: the low absorbance of organic polymeric materials can lead to low aerial image contrast and may require higher dose exposures that reduce throughput. An alternative bottom-up approach to patterning using an organic monolayer and subsequent area selective deposition technique that can be tuned to a positive or negative-tone image generation. The method of aerial image generation in monolayer lithography takes advantage of two processes that can be used to build contrast in image development as the sensitivity of the organic itself is not alone sufficient for high contrast imaging: (i) removal of a desired organic material after exposure and (ii) a post exposure area selective deposition. These organic materials exhibit a non-linear relationship in a subsequent area selective deposition (ASD) image development step using atomic layer deposition (ALD), a key component for the development of a high-resolution system. This approach provides a method that utilizes the thinnest possible organic material and a pattern development step that produces an effective etch mask for pattern transfer.

11:45am **LI3-WeM-14 Super-Conformal ALD of Metallic Mo Films by Simultaneous Deposition and Etch***, **Jean-Sebastien Lehn**,* EMD Performance Materials*; C Dezelah,* ASM, Finland*; J Woodruff, R Kanjolia, D Moser, T Polson,* EMD Performance Materials

Super-conformal ALD processes, where more material is deposited at the bottom of a narrow trench or via versus its top, are needed for future generations of micro-electronic devices. Standard conformal ALD processes are unable to fill a via/trench without leaving a hollow seam. Using a conformal ALD process to fill re-entrant features, where the opening is narrower compared to the features' bottom, will lead to a void. These defects result in performance and reliability problems.

Recently disclosed super-conformal ALD processes require additional steps compared to the normal ALD sequence. A bottom-up deposition process had been developed for copper, relying on catalytical iodine atoms.[1] The addition of a nitrogen-plasma based inhibiting step,[2] or of etching steps,[3] had been demonstrated as pathways to bottom-up growth. These approaches, however, lengthen the deposition process, and may lead to increased impurities.

A new simple ALD process to deposit molybdenum films only at the bottom of vias is presented here.[4] It uses only two precursors, $MoCl_5$ and CHD (2-methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene), a strong reducing agent active at low temperatures where H_2 is inactive. This process does not require a catalyst, a growth inhibitor, or an additional etchant. This is possible as $MoCl_5$ quickly deposits a monolayer of $MoCl_x$ while it slowly etches Molybdenum (Scheme in Figure 1). The etched Molybdenum species can also be re-deposited on available sites. The ratio between the etch and the deposition depends on the gas phase concentration of chemical species. Increasing the $MoCl_5$ dose leads to a slowly-increasing deposition rate and a rapidly-increasing etch rate; therefore the Molybdenum deposition rate shows a maximum when the $MoCl_5$ dose is varied (Fig. 2a).

When depositing Molybdenum inside vias, chemical species' concentrations vary with the depth within the via. It is therefore possible to deposit Molybdenum only at the bottom of vias – a super-conformal process (mechanism shown in Fig. 2b). Fig. 2c shows SEM/EDS of vias with Molybdenum deposited only at the bottom of vias. Molybdenum can also be selectively deposited between substrates (the deposition/etch ratio is substrate-dependent during the nucleation phase). Characterization of films grown with this new ALD process will be shared.

* EMD Performance Materials is a business of Merck KGaA, Darmstadt, Germany.

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12:15pm **LI3-WeM-16 Process Optimization in Atomic Layer Deposition Using Machine Learning**, *A Yanguas-Gil, S Letourneau, A Mane, N Paulson, A Lancaster,* ***Jeffrey W. Elam,*** Argonne National Laboratory

Process development and process optimization are ubiquitous, resource-intensive tasks in thin film research and development. The goal of these activities is to find the set of process parameters (e.g. temperature, pressure, and flow) that maximize film quality at minimal cost. Typically, this is accomplished by coating a substrate (e.g. a silicon wafer) under a given set of conditions, measuring the film properties ex situ, and adjusting the conditions to improve the film quality. This activity can consume significant time and resources, especially if an additional goal is to achieve uniform films across a large substrate. Process development can be accelerated and economized using in situ measurements. For instance, quartz crystal microbalance (QCM) measurements can be employed to monitor film thickness in real time as the deposition conditions are varied. However, this still requires the careful attention of a skilled operator to make informed choices based on experience and intuition. An alternative strategy is to use machine learning (ML) to analyze the QCM data in real time and adjust the growth conditions based on an algorithm. To explore this possibility, we used ML to optimize the atomic layer deposition (ALD) of Al_2O_3 with trimethyl aluminum (TMA) and H_2O in a viscous-flow tubular reactor using in situ QCM measurements. We initially developed the ML code using simulated QCM data generated by a 1-D model of ALD transport and reaction. This allowed us to tailor the algorithm to ensure saturation of the TMA and H_2O ALD reactions and to converge efficiently on the optimal dose and purge times. We examined several ML algorithms including Bayesian optimization, physics-inspired optimization, and random optimization. An additional benefit of these simulations was that we could explore the effects of non-ideal behavior such as a CVD component to the surface reactions and strong interaction between the reaction products and the surface. Next, we interfaced the ML code to our ALD system and allowed the algorithm to optimize the TMA and H_2O timings. We observed rapid convergence, as predicted by our simulations, and found that the ML algorithm was capable of adapting to variations in the initial conditions such as the precursor partial pressures and the carrier gas flow rate. We are now building an array of QCM sensors to measure the thickness simultaneously at 10 locations along our flow tube, and we hope to report on ML opimization of thickness and uniformity using this array.

12:30pm **LI3-WeM-17 ALD/ALE Student Awards, Closing Remarks, & Sponsor Thank You**, *C Detavernier, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*;* ***Jean-François de Marneffe,*** IMEC, Belgium

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ALD Applications
Room Van Rysselberghe - Session AA-WeM
ALD for Semiconductor Applications I

Moderators: Adrien LaVoie, Lam Research Corp., Mike McSwiney, Intel, USA

11:15am **AA-WeM-3 Atomic Layer Epitaxy of GaN Directly on 4H-SiC using Ga–N Bonded Precursors***, P Rouf, N O'Brien, R Samii,* ***Henrik Pedersen,*** Linköping University, Sweden

Gallium nitride (GaN) is a key material in high electron mobility transistors (HEMT) based on the group 13-nitrides. These structures are routinely made by CVD at high temperatures (1000 °C) using trimethylgallium (TMG) and NH_3. These high deposition temperatures hinder the exploration of GaN films on temperature sensitive materials such as InN, which is highly desirable to integrate into HEMTs due to its high electron mobility. ALD is a low temperature alternative that could be used to deposit high quality GaN. GaN has previously been explored by ALD using trimethylgallium (TMG) or triethylgallium (TEG) together with N_2/H_2 plasma [1], NH_3 plasma [1] and thermal NH_3. However, these GaN films were found to be non-stochiometric and show high amounts of C and O impurities, which is undesirable in materials to be used in electronics.

Herein, we report on two alternative Ga precursors: tris(dimethylamido)gallium(III) **1** and tris(1,3-diisopropyltriazenide)gallium(III) **2** and their use in ALD in combination with NH_3 plasma to deposit GaN. These two precursors possess Ga–N bonds instead of Ga–C bonds like TMG and TEG. As the Ga–C bond is stronger than the Ga–N due to its more covalent nature of the bond, precursors with Ga–N bonds could potentially have a more favourable surface chemistry with lower impurity levels. Both **1** and **2** show self-limiting deposition behaviour for GaN growth. Precursor **1**saturates after 4s and 6s of NH_3 plasma exposure, with 10s purge between to give a growth rate of 1.4 Å/cycle. The growth remains constant at 1.4 Å/cycle between 130-250 ˚C. GaN growth from **2** shows a growth rate of 0.3 Å/cycle which is constant between 300-350 ˚C.

GaN deposition directly 4H-SiC (0001) using these ALD processes grew with the epitaxial relationships of GaN(0002)úúSiC (0002) and GaN (10-13) úú SiC (10-12). This set these ALD processes apart from traditional MOCVD of GaN as the later requires an AlN buffer layer for epitaxial growth of GaN on SiC.

The composition of the films was measured with RBS/ERDA. Precursor **1** gave GaN films with 45.7 at.% Ga, 47.2 at.% N, 3.1 at.% O, 2.8 at.% C, 1.2 at.% H, giving a Ga/N = 0.97. GaN grown from **2** has 48.8 at.% Ga and 46.4 at% N giving a Ga/N = 1.05. GaN from **2** contained 3 at.% O, 1.8 at.% H and no detectable carbon. Absorption measurements show the optical bandgap of the GaN to be 3.42 eV, which is close to the theatrical value of 3.4 eV. Fermi level measurements with XPS show that the fermi level is closer to the conduction band then the valence band, making the GaN film unintentionally n-type doped.

[1] Ozgit-Akgun, C. et al. *J. Mater. Chem. C* **2014**, *2* (12), 2123–2136.

Area Selective ALD
Room Baekeland - Session AS-WeM
Selective ALD I

Moderators: Dennis Hausmann, Lam Research, Hanjin Lim, Samsung Electronics Co., Inc.

10:45am **AS-WeM-1 Promixity Effect of Selective Co ALD on the Nanoscale***,* ***Michael Breeden****, S Wolf, A Anurag, V Wang,* University of California San Diego*; D Moser, R Kanjolia, M Moinpour, J Woodruff,* EMD Performance Materials*; A Kummel,* University of California San Diego*; M Li, M Bakir,* Georgia Institute of Technology

The use of selective-area Co ALD is desired both for bottom-up fill of Co in interconnect and vias, as well as in forming connections between stacked dies in packaging. The cobalt ALD process using $Co(DAD)_2$ and formic acid (HCOOH) or tertiary-butyl amine (TBA) is known to have nearly infinite selectivity (>1000 cycles) on metal vs. insulator (SiO_2 or low-k SiCOH) planar surfaces [1,2]. However, when the spacing between the metal and insulator regions is less than 100 nm, there can be a reduction in selectivity under identical ALD conditions, due to the diffusion of molecularly-adsorbed metal precursor from reactive to non-reactive surfaces [3].

In this report, Co ALD was performed using $Co(DAD)_2$ + TBA at 180°C on 85 nm wide Cu stripes on SiO_2, as well as on suspended Cu stripes with a 200 nm spacing between the Cu growth surfaces. The planar structure of these stripes enables top-down scanning electron microscopy (SEM) imagery and x-ray photoelectron spectroscopy (XPS) quantification to be used to monitor the presence of unwanted Co nuclei on insulator (SEM) and the growth rate on Co (XPS). To control precursor dose, multiple precursor pulses were employed in each cycle to limit the maximum pressure when dosed through a turbomolecular pump to minimize background contamination. XPS is performed without breaking vacuum to prevent oxidation of Co. The Cu stripes were tested for open- or short-circuit connection between surfaces due to Co ALD growth. Finally, cross-sectional transmission electron microscopy of the alternating strips was performed.

Four strategies have been found to improve Co ALD selectivity: adding a passivant to remove insulator defect sites, increasing the purge time, decreasing the precursor dose, and periodic annealing at 260°C in vacuum. SEM of the striped pattern with a longer purge time shows decreased unwanted nucleation; while the periodically annealed stripe pattern shows a removal of all unwanted nuclei on SiO_2, along with a densified film and edge buildup of Co. This is consistent with reabsorption of the Co nuclei from the insulator surface to the growth surface in a low-temperature nanoscale reflow process. It is possible the low temperature nanoscale reflow process would enable further scaling of the diffusion barriers to SiCOH. For packaging, this low temperature ALD process has the potential to induced selective Cu bump bonding as shown by the results on the suspended Cu stripes.

1. M. Kerrigan, et al. J. Chem. Phys, 2017 **146**, pp. 052813.
2. S. Wolf, et al. Appl. Surf. Sci., 2019, **510**, pp. 144804
3. F. Grillo, et. al. ALD Conference Proceeding, Seattle, WA 2019

11:00am **AS-WeM-2 Cobalt Electron-Enhanced Atomic Layer Deposition (EE-ALD) Using High Electron Flux Hollow Cathode Plasma Electron Source (HC-PES): Rapid Growth and Bottom-Up Fill***,* ***Zachary Sobell****, A Cavanagh,* University of Colorado - Boulder*; S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) facilitates low temperature ALD using an electron beam that can remove surface species by electron stimulated desorption. Previous work has demonstrated BN [1] and Co [2] EE-ALD using an electron gun. Higher electron fluxes by a factor of > 3000 can be produced by a hollow cathode plasma electron source (HC-PES). In addition, the HC-PES is more resistant to chemicals and has significantly faster ON/OFF times. This HC-PES has been used to grow Co films with area selectivity using cobalt tricarbonyl nitrosyl [CTN, $Co(CO)_3NO$] exposures together with electron exposures.

Rapid Co EE-ALD is observed with cycles times of ~40 s/cycle. In situ ellipsometry measurements reveal that nucleation is rapid on the native oxide of silicon wafers (Figure 1). Co EE-ALD displays growth rates of ~2.5 Å/cycle over an area of > 4 cm^2. The uniform film thickness over this area also argues that the electron exposures are able to obtain saturation behavior by desorbing all the ligands from the adsorbed CTN species. The high electron fluxes have also led to new growth phenomena. At small electron exposures <0.05 C/cm^2, normal “ALD like” Co growth is observed versus sequential CTN and electron exposures. At higher electron fluxes >0.1 C/cm^2, the Co growth enters a new regime where the growth can continue for many precursor doses following only one electron exposure. Co film thickness as large as 1000 Å have been grown using multiple CTN exposures following only one electron exposure.

The directionality of the electrons is also useful for area selective EE-ALD. Because the electron flux is normal to the surface, the horizontal surfaces are exposed to higher electron fluxes than the vertical surfaces. Consequently, EE-ALD on vias should occur primarily from the bottom up. Co EE-ALD films were grown on high aspect vias and then examined using transmission electron microscopy (TEM). Co EE-ALD was performed using 45 CTN/electron cycles with electron energy at 140 eV and electron exposure at 10 mA for 10 s. For the vias with an aspect ratio of ~4, the TEM images revealed a film thickness of ~5 nm on the sidewall (Figure 2) and ~30 nm on the bottom (Figure 3). The six times larger deposition on the bottom could facilitate bottom-up fill of the via.

[1] J.K. Sprenger et al., “Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Boron Nitride Thin Films at Room Temperature and 100°C”, *J. Phys. Chem. C***122**, 9455 (2018).

[2] Z.C. Sobell et al., "Growth of Cobalt Films at Room Temperature Using Sequential Exposures of Cobalt Tricarbonyl Nitrosyl and Low Energy Electrons", *J. Vac. Sci. Technol. A***37**, 060906 (2019).

11:15am **AS-WeM-3 Probing the Selectivity of Area-Selective Spatial ALD + Etch-Back Supercycles for SiO_2 by Low Energy Ion Scattering***, **Alfredo Mameli**,* TNO/Holst Center, Netherlands*; P Brüner,* IONTOF GmbH, Germany*; F Roozeboom,* TNO/Holst Center, Netherlands*; T Grehl,* IONTOF GmbH, Germany*; P Poodt,* TNO/Holst Center, Netherlands

Area-selective ALD interleaved with etch-back steps in a supercycle fashion has recently been reported as very effective in achieving high selectivity. Such supercycles can result in lower defectivity on the non-growth area and thicker layers on the growth area, as compared to solely area-selective ALD.[1, 2] The complementarity of deposition and etching techniques can therefore offer great potential for reaching the ultimate requirements in advanced device manufacturing.

Here we use low energy ion scattering (LEIS) to probe the selectivity of the first supercycle, consisting of plasma-enhanced selective spatial-ALD of SiO_2 and conventional CF_4-based reactive ion etching (RIE). Given its extreme sensitivity to the top monolayer(s) of a thin film, LEIS can reliably quantify the selectivity and defectivity on the non-growth areas in terms of surface coverage and derived thickness.

For the selective spatial ALD a three-step approach was adopted,[3] consisting of successive inhibitor, silicon precursor (BDEAS) and O_2 plasma exposures. Silicon wafers (growth area) with large ZnO patterns (non-growth area) were used as substrates. After 20 spatial ALD cycles, no silicon was detected on the non-growth area by LEIS (detection limit 2 % SiO_2 surface coverage), implying excellent process selectivity. The selectivity is however gradually lost by increasing the number of ALD cycles up to 110. On the non-growth area, the SiO_2 layers now had an averaged thickness of 3.5 nm as measured by spectroscopic ellipsometry (SE) and corroborated by LEIS measurements (86% Si surface coverage). At the same time on the growth area, a SiO_2 thickness of 11 nm was measured. In order to correct for the selectivity loss, a 3 seconds RIE step was applied, which restored the Si coverage and reduced the SiO_2 thickness on top of the non-growth area back to zero, as demonstrated by LEIS. Concurrently, 8 nm thick SiO_2 was left on the growth area.

The data presented in this work demonstrate the effectiveness of combining selective spatial ALD + etch-back corrections to achieve extreme SiO_2 selectivity while retaining high deposition rates. Furthermore, we will discuss how LEIS can provide useful information on selectivity as well as defect formation on the non-growth area. Finally, we have extended the plasma-enhanced selective spatial ALD of SiO_2 to other non-growth areas.

[1] R. Vallat et al., *JVSTA*, 35, 01B104 (2017).

[2] S. K. Song et al., *Chem. Mater*. 31 4793-4804 (2019).

[3] A. Mameli et al., *ACS Nano*, 11, 9303-9311 (2017).

Emerging Materials
Room Jan & Hubert Van Eyck - Session EM-WeM
Organic and Organic-Inorganic Hybrid Materials I

Moderators: Steven M. George, University of Colorado at Boulder, Mato Knez, CIC nanoGUNE

11:00am **EM-WeM-2 Vapor-Phase Synthesis and Surface Area Analysis of ZIF-8 Metal Organic Framework (MOF) on Fibrous Substrates via Atomic Layer Deposition***, R Nye, S Smith, **Nicholas M. Carroll**, G Parsons,* North Carolina State University

Solvent-free synthesis methods for metal-organic frameworks (MOFs) will help expand their applications in catalysts, gas adsorption, and sensors. Unfortunately, methods of using atomic layer deposition on silicon wafers to convert a metal oxide to MOF prevent surface area measurements, which are critical in the aforementioned applications. In this work, we describe low-temperature formation of zeolitic imidazolate framework (ZIF-8) MOF on high-surface area polypropylene polymer fiber substrates via vapor-directed conversion of ALD ZnO. The resulting MOF-fiber structures are highly stable and withstand robust mechanical deformation, demonstrating excellent MOF adhesion to the polymer fiber surface. Moreover, for the first time, our synthesis approach enables direct gas adsorption analysis of vapor-derived MOFs, including determination of net surface area by Brunauer-Emmett-Teller (BET) analysis. To form the MOF-fiber structure, approximately 10 nm of zinc oxide is deposited at 90°C via ALD on nonwoven polypropylene fiber mats. The coated mats are then placed into a loosely sealed vessel containing 2-methylimidazole powder and heated at 100-135 C for 1-24 hours, enabling volatilization of the 2-methylimidazole and reaction with the solid ZnO to form ZIF-8 crystals. During the process, the pressure in the vessel is maintained at atmospheric pressure. The formation of ZIF-8 is confirmed by XRD, and SEM shows crystals of ~100-300 nm on the fiber surface. BET analysis on the MOF-coated fiber mats demonstrated surface area values of 400 m^2/g (fiber+MOF). Using the mass of MOF determined by sample weight before and after MOF growth, the surface area of the ZIF-8 on the fibers in 1500 m^2/g ZIF-8, which is comparable to ~1300 m^2/g expected for ZIF-8 powder, indicating good quality of synthesized MOF. To the best of our knowledge, this is the first report of surface area measurements on solvent-free MOFs. By tuning deposition and conversion parameters, the crystallinity and surface area of the ZIF-8 can be controlled. This MOF formation on fibers enables applications and measurements not otherwise available, such as incorporation into protective garments. Additionally, successful vapor-phase MOF synthesis opens the doors for selective deposition of MOFs for use in sensing and electronic applications.

11:30am **EM-WeM-4 Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Mechanisms of Inorganic Entrapment and Structure-Property Implications***, **Mark Losego**,* Georgia Institute of Technology **INVITED**

Vapor phase infiltration (VPI) transforms polymers into organic-inorganic hybrid materials by infusing the polymer with inorganic constituents from the gas phase. Hybrid materials synthesized with VPI have been demonstrated for numerous applications ranging from energy harvesting to filtration media to photolithographic hard masks. The infiltration process consists of three basic steps: (1) sorption of the gaseous precursor molecule into the polymer, (2) diffusion of the precursor throughout the polymer, and (3) "entrapment" of that precursor within the polymer. This talk will focus on this final step: "entrapment". The mechanism of entrapment informs both how to design an infiltration process and the final chemical structure of the hybrid material. Processes for entrapment can largely be understood by the energy landscape for precursor binding and reaction with the polymer. Most important to understand is the depth of the energy well for the bound state and the activation energy for the reaction pathway. These energetics determine whether a precursor is easily entrapped and whether the final hybrid has unbound or chemically bound inorganic constituents. In this talk, we will show evidence from our lab for infiltrated materials where the inorganic constituents are homogeneously distributed throughout the hybrid material but are chemically unbound to the organic – creating an interpenetrating, unbound organic-inorganic bicontinuous network. Similarly, we will show how increasing reaction temperature can increase the probability for chemical reactions and covalent bond formation. Subsequently, we will show how these different chemical states lead to differences in material properties including solubility, glass transition, thermal expansion, and interfacial adhesion strength.

Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS-WeM
2D Nanomaterials by ALD I

Moderators: Tae Joo Park, Hanyang University, Virginia Wheeler, U.S. Naval Research Laboratory

10:45am **NS-WeM-1 Exploring ALD 2D Chalcogenides Beyond MoS_2***, **Miika Mattinen**,* University of Helsinki, Finland **INVITED**

Two-dimensional (2D) materials have rapidly emerged as promising materials for a range of applications from microelectronics to sensing as well as energy storage and production. Deposition of 2D materials as high-quality films of controlled thickness on large, temperature-sensitive, and complexly shaped substrates is one of the main challenges hindering industrial applications. ALD can fulfill these requirements, but unlocking the full potential of ALD of 2D materials requires careful examination of precursor chemistry, nucleation, substrates, film characteristics, and device performance.

Much of the ALD research on 2D transition metal dichalcogenides (TMDCs) has focused on semiconducting MoS_2. Lately, some of the efforts have shifted to other 2D semiconductors, which may offer improved charge carrier characteristics (e.g. WS_2 and WSe_2) and lower processing temperatures (SnS_2), for example. So far, little attention has been given to ALD of metallic TMDCs (e.g. NbS_2 and TaS_2), which may be used to complement 2D semiconductors in devices or by themselves in energy storage and production. Furthermore, ALD of selenide and telluride TMDCs is still in its infancy.

Deposition of these “new” 2D chalcogenides by ALD is no simple feat. This talk focuses on finding precursors for a range of 2D chalcogenides from MoS_2 to other semiconductors including HfS_2, SnS_2, WS_2, and ZrS_2 as well as my recent efforts towards metallic sulfide TMDCs. Precursor challenges related to reactivity, thermal stability, and etching reactions will be considered. I will cover some challenges and opportunities related to selenide and telluride TMDCs. I am also going to discuss the stability of the deposited films and deposition of protective layers.

The anisotropic, layered crystal structure of 2D materials affects their growth. The morphology of the grown films in turn affects their properties and performance in applications. The effect of the substrate on morphology, continuity, and crystallinity of 2D films will be discussed through the following three examples. First, the growth of crystalline TMDC films often leads to rough morphology. By depositing amorphous films that are crystallized after deposition, smooth crystalline SnS_2 and WS_2 films can be obtained. Second, deposition of thin and continuous TMDC films is challenging. It will be shown that thinner continuous SnS_2 films can be deposited on sapphire compared to silicon. Third, methods to improve the quality of the films deposited at low temperatures are desired. To this end, I will discuss van der Waals epitaxial growth of 2D chalcogenides.

11:30am **NS-WeM-4 Growth of Wafer-Scale Monolayer MoS_2 using Adsorbate-Controlled Atomic Layer Deposition**, *D Kim,* ***Jae Chan Park****, W Kim,* Hanyang University, Republic of Korea*; J Park, B Shong,* Hongik University, Republic of Korea*; J Ahn, T Park,* Hanyang University, Republic of Korea

Monolayer transition-metal dichalcogenide compounds with two-dimensional (2D) layered structures have attracted considerable attention because of their potential applicability as next-generation active materials for versatile electronic and optoelectronic devices. For industrial application of these materials, a reliable method for well-controlled large-area growth of high-quality material at the wafer scale should be developed. Atomic layer deposition (ALD) of 2D materials has been widely studied for realizing atomically flat monolayer films, but it has limitations regarding the implementation of a perfect monolayer owing to its deposition characteristics.

In this work, we propose a novel chemical route for the deposition of a monolayer MoS_2 film with large-area uniformity at wafer scale using ALD. First, by modulating the precursor injection step, the amount of adsorbed precursor in one cycle can be precisely controlled in a range exceeding the limitation imposed by “typical” ALD reaction. Utilizing such process, we successfully realized (for the first time) a uniform and complete monolayer MoS_2 film using ALD at the wafer scale. The monolayer MoS_2 film exhibited excellent uniformity at the wafer scale, and the luminescence quantum efficiency of a monolayer MoS_2 film deposited via the newly-proposed ALD method was approximately 9 times greater than that of the film formed via conventional ALD. These results indicate that our method can be employed for obtaining complete single layers of various materials or developing high-quality monolayer-scale 2D materials using ALD.

ALD Applications
Room Van Rysselberghe - Session AA-WeA
ALD for Semiconductor Applications II & III

Moderators: Scott B. Clendenning, Intel Corp., Charles Dezelah, ASM

1:00pm **AA-WeA-1 Study of ALD HfO_2-Based High-k for GaN Power Devices and Ferroelectric Devices***, **Toshihide Nabatame**,* National Institute for Materials Science, Japan*; T Onaya,* Meiji University, Japan*; E Maeda, M Hirose,* Shibaura Institute of Technology, Japan*; Y Irokawa,* National Institute for Materials Science, Japan*; K Shiozaki,* Nagoya University, Japan*; Y Koide,* National Institute for Materials Science, Japan **INVITED**

Recently, HfO_2-based high-k materials have been investigated as dielectric for GaN power devices and ferroelectric devices. These HfO_2-based high-k thin films were deposited by plasma-enhanced atomic layer deposition (PE-ALD) using O_2 plasma.

In GaN power device, gate dielectric is required that they have more stable amorphous structure at 800 °C, relatively high dielectric constant (k) value (>10) and high breakdown electric field (> 8 MV/cm). For these reasons, we have been investigated Hf-rich $HfSiO_x$ as gate dielectric [1, 2]. To fabricate $HfSiO_x$ films, the HfO_2/SiO_2 laminate was initially deposited by PE-ALD with tetrakis(dimethylamino)hafnium (TDMAHf) and Tris(dimethylamino)silane (TDMAS) precursors [1]. Understanding the SiO_2 growth mechanism on HfO_2 layer is an important in terms of the design of the $HfSiO_x$ formation. The growth per cycle (GPC) values of PE-ALD-SiO_2 layer on HfO_2 underlayer was 4 times larger than that on SiO_2 underlayer because of the different adsorption of TDMAS precursor on the surface of Si-O and Hf-O which has the difference of electronegativity. Using the GPC of PE-ALD-SiO_2 layer on HfO_2 underlayer, we could design Hf-rich $HfSiO_x$ ($Hf_{0.57}Si_{0.43}O_x$) films by controlling ALD cycle of each HfO_2 and SiO_2 layer. The $Hf_{0.57}Si_{0.43}O_x$ dielectric of n-GaN capacitors exhibited superior characteristics such as an amorphous structure after annealing at 800°C, high k value of 13.5, a small flatband voltage shift (-0.36 V), a high breakdown electric field (8.6 MV/cm).

FeRAM and FeFET application with ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) films is required low temperature fabrication process. To achieve this requirement, we have been investigated characteristics of HZO films fabricated by PE-ALD at 300°C and post-metallizaiton annealing at 300–400°C [3, 4]. As-grown HZO film, which deposited by PE-ALD using TDMAHfZr (Hf:Zr = 1:1) cocktail precursor and O_2 plasma, had nanocrystalline structure with ferroelectric orthorhombic, tetragonal, and cubic phases. TiN/HZO/TiN capacitors showed excellent remanent polarization (2*Pr*) and k values of 34 μC/cm^2 and 39, respectively, after PMA at 300–400°C.

We conclude that ALD process including specific technique such as laminate formation due to different absorption of precursor and direct complex oxides formation using cocktail precursor is suitable for various electric devices.

This work was in part supported by MEXT GaN R&D project.

[1] T. Nabatame et al., Appl. Phys. Express 12, 011009 (2019).

[2] E. Maeda et al., Microelectron. Eng. 216, 111036 (2019).

[3] T. Onaya et al., Microelectron. Eng. 215, 111013 (2019).

[4] T. Onaya et al., APL Mater. 7, 061107 (2019).

1:30pm **AA-WeA-3 The Effect of Oxygen Source on Ferroelectricity of Atomic Layer Deposited $Hf_{0.5}Zr_{0.5}O_2$ Thin Film***, **Yong Chan Jung**, J Mohan,* University of Texas at Dallas*; H Kim, H Hernandez-Arriga,* The University of Texas at Dallas*; T Onaya,* Meiji University, Japan*; K Kim, N Kim,* The University of Texas at Dallas*; S Kim,* Kangwon National University, Republic of Korea*; A Ogura,* Meiji University, Japan*; R Choi,* Inha University, South Korea*; J Ahn,* Hanyang University, Republic of Korea*; J Kim,* University of Texas at Dallas

Recently, ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films have caught great interest for non-volatile memory and field-effect transistor applications, due to their high scalability and compatibility with CMOS process.[1] In our previous work, we achieved a low thermal budget process (400 °C) under large tensile strain (about 3-5 GPa) using TiN top and bottom electrodes.[2] The HZO films using the TiN electrodes can prevent degradation of the ferroelectric properties from hydrogen incorporation owing to the TiN electrodes can act as a barrier layer against hydrogen diffusion. However, during the deposition of HZO film using atomic layer deposition (ALD), the choice of oxygen source can affect the residue in the deposited film. When hydrogen-related substances are used as the oxygen source, the ferroelectric properties can be altered by the residues remaining in the HZO film.

Therefore, in this study, we investigated the effects of the oxygen source, especially O_3, H_2O, and Deuterium oxide (D_2O) on the ferroelectric properties of the ALD-HZO films. The HZO films with Hf:Zr ratio of 1:1 were deposited on the TiN bottom electrode by ALD using TDMA-Hf and TDMA-Zr as the precursors of Hf and Zr, while O_3, H_2O, or D_2O as the oxidant. After the TiN top electrode was deposited, rapid thermal annealing was done, and metal-insulator-metal capacitors were fabricated using a Pd/Au hard mask and wet etch process.

Regardless of the oxidant, the HZO films exhibited the formation of a non-centrosymmetric orthorhombic phase which is origin of the ferroelectricity.[3] However, it was confirmed that the ferroelectricity of the HZO film deposited with the source related to hydrogen such as H_2O and D_2O, is worse than the HZO film deposited with O_3. From the polarization-electric field curves, the remnant polarization ($2P_r$) of O_3-, H_2O-, and D_2O-based HZO devices was 47, 38, and 34 μC/cm^2, respectively. Whereas, the H_2O- and D_2O-based HZO devices exhibited higher leakage current than that of O_3-based device. We suspected that the degradation of $2P_r$ and the leakage property is caused by more hydrogen incorporation in the HZO film when H_2O and D_2O oxidants are used. The result implies that the use of O_3 as the oxygen source is advantageous for improving ferroelectric properties of the ALD-HZO films.

This work is supported by the National Research Foundation of Korea (NRF) grant (No. NRF-2019R1F1A1059972), Brain Pool Program (No. 2019H1D3A2A01101691), and the Fostering Global Talents for Innovative Growth Program (No. P0008750).

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[2] S.J. Kim, et al., Appl. Phys. Lett. **111**, 242901 (2017).

[3] S.J. Kim, et al., JOM **71**, 246 (2019).

1:45pm **AA-WeA-4 Deposition of Inherently Ferroelectric Films by ALD Using ZrD-04 and HfD-04***, **Vijay K. Narasimhan**,* Intermolecular, Inc.*; J Lehn,* EMD Performance Materials*; K Littau,* Intermolecular*; J Woodruff, R Kanjolia,* EMD Performance Materials

ALD HfO_2- and ZrO_2-based ferroelectrics enable novel, CMOS-compatible devices for both logic and memory[1]. Although the most stable bulk crystal structure of these materials is a monoclinic phase, this phase does not support ferroelectricity. Other polymorphs (for example, some orthorhombic and rhombohedral phases) have the symmetry required to support ferroelectric switching behavior, while still others (for example, a tetragonal phase) can be anti-ferroelectric[2]. In many hafnium oxide and zirconium oxide ALD processes, the thin films are amorphous as deposited. Therefore, obtaining a desired ferroelectric phase depends not only on the deposition conditions of the film itself, but also on the choice of capping interfaces[3] and annealing conditions[4] after deposition.

Here, we demonstrate a pathway to achieving phase control in zirconia and hafnia ALD films that does not depend on capping or post-deposition annealing. We use the advanced metallocene precursors $(MeCp)_2Zr(OMe)Me$ and $(MeCp)_2Hf(OMe)Me$ (commonly known as ZrD-04 and HfD-04, respectively). These precursors have an ALD window that can extend to near or above the crystallization temperature of zirconia and hafnia thin films[5]. Using GIXRD, we examine the phase of films deposited with different reactants (i.e. water and ozone), growth temperatures, and thicknesses. We show that, for ZrO_2 in particular, the as-deposited films are crystalline across a wide process space and that the films are phase-stable after subsequent thermal processing. We extend previously published results[6] to elucidate a processing window where the non-ferroelectric monoclinic phase can be substantially suppressed. We use the results from the unit film studies of ZrO_2 and HfO_2 to create a blended ZrO_2/HfO_2 film that is inherently ferroelectric, demonstrating strong remanent polarization with no explicit post-deposition cap and annealing. These results provide a pathway to developing ferroelectric devices in which the electrodes and thermal processing conditions of the entire stack can be optimized independently with minimal effects on the ferroelectric layer.

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2:00pm **AA-WeA-5 Ferroelectricity of 300°C Low Temperature Fabricated $Hf_xZr_{1-x}O_2$ Thin Films by Plasma-Enhanced Atomic Layer Deposition using Hf/Zr Cocktail Precursor**, ***Takashi Onaya,*** Meiji University, Japan*; T Nabatame,* National Institute for Materials Science, Japan*; Y Jung,* University of Texas at Dallas*; H Hernandez-Arriaga,* The University of Texas at Dallas*; J Mohan,* University of Texas at Dallas*; H Kim, A Khosravi,* The University of Texas at Dallas*; N Sawamoto,* Meiji University, Japan*; C Nam, E Tsai,* Brookhaven National Laboratory*; T Nagata,* National Institute for Materials Science, Japan*; R Wallace,* The University of Texas at Dallas*; J Kim,* University of Texas at Dallas*; A Ogura,* Meiji University, Japan

Recently, low temperature fabrication process for ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) films has attracted a lot of attention for use in future device application, such as FeRAM and FeFET. The amorphous HZO films deposited by thermal atomic layer deposition (TH-ALD) using H_2O or O_3 as an oxidant gas were generally employed, then, an annealing process at > 400°C with TiN top- and bottom-electrodes (TE- and BE-TiN) was performed to obtain ferroelectric orthorhombic (O) phase due to inducing tensile stress from TiN to the HZO film. [1] On the other hand, we focused on plasma-enhanced ALD (PE-ALD) using O_2 plasma, because the as-grown HZO film had nanocrystalline structure with O, tetragonal, and cubic (O/T/C) phases. In this work, we studied the ferroelectricity and crystallinity of PE-ALD HZO films using a low temperature annealing process at 300–400°C.

The TiN/HZO/TiN capacitors were fabricated as follows: A 10-nm-thick HZO film was deposited on BE-TiN by PE-ALD at 300°C using $(Hf/Zr)[N(C_2H_5)CH_3]_4$ (Hf:Zr = 1:1) cocktail precursor and O_2 plasma. TE-TiN was then fabricated by DC sputtering. Finally, post-metallization annealing (PMA) was performed at 300–400°C for 1 min in a N_2 atmosphere. Pulse write/read measurement was employed to obtain the remanent polarization (P_{sw}) and dielectric constant (k). [1] The crystallinity was analyzed using synchrotron wide-angle X-ray scattering (WAXS) at NSLS-II, Brookhaven National Laboratory.

The PE-ALD HZO film after PMA at 300°C clearly showed ferroelectricity with P_{sw} of 28 μC/cm^2 and exhibited high k of 41, while the HfO_2-based films with stable ferroelectricity using a lower process temperature below 400°C have not been reported. The P_{sw} of PE-ALD HZO films increased with PMA temperature. For synchrotron WAXS patterns of PE-ALD HZO films, the peaks originating from O/T/C phases were clearly observed while those from the paraelectric monoclinic (M) phase were suppressed using a low temperature PMA process even at 300°C, leading to the stable ferroelectricity. This might be because nanocrystal grains with O/T/C phases in the as-grown HZO film play an important role as nuclei for the crystal growth of the HZO film during PMA process, while the as-grown HZO film deposited using TH-ALD typically have an amorphous structure. In addition, the phase transformation from C-phase to O/T-phases was observed as PMA temperature increased, resulted in high P_{sw}.

In conclusion, PE-ALD and a low temperature PMA process at 300°C are promising methods for the fabrication of ferroelectric HZO films with superior P_{sw}.

This work was partially supported by JSPS KAKENHI (JP18J22998).

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2:15pm **AA-WeA-6 Atomic Layer Deposition of GeS Film for 3D Cross-Point Memory Scaling*, Myoungsub Kim,*** *Y Kim, I Sohn, H Kim,* Yonsei University, Republic of Korea

Recently, the emergence of storage class memory (SCM) in the memory hierarchy has attracted attention as a new role for improving the performance of computing systems [1]. The 3D cross-point (X-point) memory using chalcogenide amorphous materials as ovonic threshold switching (OTS) selectors, is the most powerful product for SCM and already requires future scaling research. The X-point memory of today`s planar 3D structure is expected to change to a vertical 3D X-point structure, as in the history of NAND flash, so it is necessary to study chalcogenide ALD for OTS application.

We present ALD study of GeS thin film motivated by the expectation of lower off-current for device scaling and larger array implementations because it is known to have higher optical bandgap than GeTe and GeSe films, recently published in ALD studies [2][3]. The ALD GeS amorphous film synthesis using commercially available $GeCl_4$ precursor and H_2S reactant was minutely investigated on RF plasma, temperature effect and interesting non-conventional saturation growth behavior. GeS films were identified quantitative composition and impurities level through auger electron spectroscopy (AES) depth profile analysis, and the tunable Ge and S composition ratio results were obtained by controlling the deposition temperature and plasma power. And excellent thermal stability of GeS amorphous film up to 600℃ was confirmed using in situ heating X-ray diffraction (XRD). In addition, atomic layer deposited GeS film was confirmed the good conformality in the vertical 3D patterned wafer using focused ion beam transmission electron microscopy (FIB-TEM).

Finally, the devices fabricated using ALD GeS were studied the scaling effect of OTS electrical characteristics on the decrease of GeS film thickness from 30nm to 5nm and the decrease of bottom electrode contact size from 80nm to 40nm. The achievement of a novel binary GeS ALD study for OTS selector will contribute to the development of 3D X-point memory scaling in the future.

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3:00pm **AA-WeA-9 Atomic Layer Annealing of AlN to Template The Growth of High Thermal Conductivity Heat Spreader Films**, *S Ueda, A McLeod,* University of California, San Diego*; M Chen, C Perez, E Pop,* Stanford University*; D Alvarez,* RASIRC*;* ***Andrew Kummel,*** University of California, San Diego **INVITED**

The low-temperature (<400 ^{o}C) deposition of polycrystalline AlN films is demonstrated by atomic layer annealing (ALA) which is a variant of ALD that utilizes a third pulse of ions in addition to the usual metal and co-reactant pulses [1]. As transistor size continues to decrease, it becomes a significant challenge to remove the heat generated during the operation of microelectronic circuits. The use of electrically conductive heat spreaders complicates 3D integration in VLSI CMOS or stack memory devices and induces parasitic losses in RF MMICs. Crystalline AlN has a thermal conductivity close to that of Cu and is a good electrical insulator making it an ideal heat spreader material.

Using trimethyl aluminum (TMA) and the highly reactive nitrogen-containing precursor hydrazine (N_2H_4), AlN can be deposited at 200 ^{o}C [2]; however, these films are amorphous and would have low thermal conductivity due to phonon scattering. Using tris(dimethylamido) aluminum (TDMAA) or tris(diethylamido) aluminum (TDEAA) with N_2H_4 or NH_3 at temperatures >350 ^{o}C, polycrystalline films can be deposited in a purely thermal process; however, the reported grain sizes are small (<5 nm) or there is a mixture of polycrystalline and amorphous phases [3-4]. ALA has been used to deposit crystalline films such as AlN [1,5] and GaN [6] at low temperature, but a nitrogen-containing plasma was used.

In the present study of AlN ALA, two metal precursors (TMA and TDMAA) were compared using anhydrous N_2H_4 as a co-reactant and argon ions with tuned energy for the third pulse. High-quality AlN films are deposited with large grain size and low C/O contamination which can then be used as a templating layer for further high-speed AlN film growth.

The deposition of high quality, stress controlled AlN films deposited by ALA are successfully used as templates for thicker heat spreading layers deposited via sputtering and polycrystalline sputtered AlN films with near-record thermal conductivities of ~70 Wm^{-1}K^{-1} were obtained for sub-0.5 micron thick films.

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Research was sponsored by ASCENT-JUMP-SRC-DARPA and the TDMAA was donated by EMD.

3:30pm **AA-WeA-11 Precision Defect Engineering of Metal/Insulator/Metal (MIM) Diodes Using Localized ALD Transition Metal Impurities*, Konner Holden*,** *Y Qi, J Conley, Jr.,* Oregon State University

Thin film MIM tunnel diodes are finding increased interest for high-speed applications such as THz detection and energy harvesting. Asymmetry of current density vs. field (J-$\mathcal{E}$) ($f_{asym}= J^-/J^+$) in MIM diodes is typically achieved through the metal electrode work function difference ($\Delta\Phi_M$). Using ALD to form an asymmetric nanolaminate insulator tunnel barrier enables MIIM diodes that exhibit enhanced low voltage performance due to "step tunneling" in which electrons under one polarity tunnel through only the wider gap insulator instead of both.[1] Replacing the narrow E_G insulator with one containing *intrinsic defects*, further improves low $\mathcal{E}$ performance via "defect-enhanced direct tunneling" (Fig. 1).[2,3] Here, we investigate the impact of intentionally introduced *extrinsicdefects* by using ALD to place Ni at precise locations in an ALD Al_2O_3 MIM tunnel barrier.

ALD of Al_2O_3 on TiN bottom electrodes was performed at 200 °C using TMA and H_2O. Five samples were prepared in which a baseline 100 ALD cycle Al_2O_3 sequence (10 nm thick) was interrupted by two ALD cycles of $Ni(^{tBu2}DAD)_2$ and O_3, after either 25, 50, 75, or every 25 cycles of Al_2O_3 (Fig. 1). Al was then evaporated through a shadow mask. As-deposited MIM devices were tested with bias applied to the Al top electrode.

DC J-$\mathcal{E}$ sweeps of the 100 ALD cycle Al_2O_3-only device show Fowler-Nordheim tunneling (FNT) at high $\mathcal{E}$, with $f_{asym}> 1$ due to $\Delta\Phi_M \approx 0.2$ eV (Fig. 2). The addition of Ni cycles in all cases leads to an increase in J at low $\mathcal{E}$, suggesting defect-related conduction. At high $\mathcal{E}$, however, J of all Ni containing devices is lower than the baseline 100 c device, suggesting suppression of FNT. The 25/2/75 and 75/2/25 ($Al_2O_3/NiO/Al_2O_3$) devices show reversed polarity asymmetry to the 100 c device, while the symmetrically doped 50/2/50 and 25/(2/25)x3 devices are roughly symmetric. The reduction in J at large negative $\mathcal{E}$, f_{asym} reversal, and reduced J-$\mathcal{E}$ slope for the Ni devices suggest the presence of negative charge in the Al_2O_3. Internal photoemission (IPE) spectroscopy reveals modified metal/insulator barrier heights and MIM and MOS CV sweeps (Fig. 3) show positive shifts in $V(C_{min})$ and V_{FB}, respectively, for all Ni devices. Taken together, these results suggest negative charge in the Al_2O_3 associated with the ALD Ni impurities.

The asymmetry reversal demonstrates the potential of ALD for precision defect engineering of MIM tunnel devices. J-$\mathcal{E}$, *C*-V, temp-*IV*, frequency-*CV*, IPE, TEM crosscuts, and annealing will be presented.

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3:45pm **AA-WeA-12 Two-Dimensional Electron Gas at the Interface of an Atomic-Layer-Deposited Binary Oxides Ultrathin (< 5 nm) Film Heterostructures***, T Park,* ***Ji Hyeon Choi,*** *T Seok, Y Liu,* Hanyang University, Republic of Korea*; J Jang,* Korea Basic Science Institute, Republic of Korea*; S Lee,* Ajou University, Republic of Korea*; D Cho,* Chonbuk National University, Republic of Korea

Recently, two-dimensional electron gas (2DEG) has attracted great attention due to its presence at various heteroepitaxial perovskite oxide interfaces. Typically, epitaxial $LaAlO_3$/single-crystal $SrTiO_3$ (LAO/STO) heterostructure shows high density of electrons (~10^{13}-10^{14} cm^{-2}) confined at the oxide interface, where the density is about ~100 times higher than that of a typical semiconductor interface (~10^{11}-10^{12} cm^{-2}).[1] Creation of 2DEG is conventionally defined on the basis of discontinuity in polarity linked with the difference in the charge of the atomic layers. Simply, it can be described as half an electron being transferred to the interface to avoid the potential divergence, 'polar catastrophe'.[2] Another mechanism is associated with the generation of oxygen vacancies (V_o) at the surface of the STO layer during LAO or Al_2O_3 layer deposition, acting as electron donor for the 2DEG formation. It provides an opportunity for 2DEG realization for various oxide heterostructures and fabrication processes. Recently, we reported V_o generation mechanism-based 2DEG formation process using atomic-layer-deposited (ALD) ultrathin (~10 nm) binary metal oxide heterostructure. 2DEG layer can be formed at the interface of Al_2O_3/TiO_2 heterostructure on a thermally oxidized SiO_2/Si substrate at a low temperature (< 300 ℃) without any epitaxial layer.[3] The Al_2O_3/TiO_2 heterostructure has comparable electrical properties with typical LAO/STO epitaxial 2DEG system at room temperature (sheet carrier density, n_{sh}= ~10^{14} cm^{-2}, electron mobility, μ_n= ~4 $cm^2V^{-1}s^{-1}$). An *in-situ* resistance measurement directly demonstrated that the resistance of the oxide heterostructure interface dropped significantly with the injection of trimethylaluminum (TMA) molecules, indicating that V_o were formed on the TiO_2 surface during the TMA pulse in the ALD of the Al_2O_3 film, such that they provide electron donor states to generate free electrons at the interface of the ultrathin Al_2O_3/TiO_2 heterostructure.[4] In this work, we demonstrate improved field-effect transistors (FETs) using ultrathin Al_2O_3/TiO_2 heterostructure 2DEG system with a high on-current (I_{on} > ~12 A/m), low off-current (I_{off} ~10^{-8} A/m), high on/off current ratio (I_{on}/I_{off} > ~10^8), and low subthreshold swing (SS ~100 mV/dec.), which outperforms the oxide heterostructure-based FETs reported so far. Ultrathin (~7 nm) TiO_2 bottom layer is easy to fully depleted, allowing an extremely low I_{off} and low SS with maintaining high I_{on}*via* 2DEG channel with a high carrier density at the interface. The heterostructures with the other ultrathin oxide combinations (< 5 nm) were also studied.

Area Selective ALD

Room Baekeland - Session AS-WeA

Selective ALD II & III

Moderators: Adrie Mackus, Eindhoven University, Netherlands, Christophe Vallée, LTM/CNRS-UJF, France

1:00pm **AS-WeA-1 Area-Selective Atomic Layer Deposition of 2D WS_2 Nanolayers using Inhibitor Molecules*, Shashank Balasubramanyam*,** *M Merkx,* Eindhoven University of Technology, Netherlands*; M Verheijen,* Eurofins Materials Science Netherlands B.V., Netherlands*; E Kessels, A Mackus, A Bol,* Eindhoven University of Technology, Netherlands

Due to the continued downscaling of device dimensions, ultra-thin two dimensional (2D) semiconductors like WS_2 are considered as promising materials for future applications in nanoelectronics. At these nanoscale regimes, device fabrication with precise patterning of critical features is challenging using current top-down processing techniques. In this regard, area-selective atomic layer deposition (AS-ALD) has emerged as a promising technique for bottom-up processing to address the complexities of nanopatterning.[1] To date, AS-ALD of metals and dielectrics have been successfully demonstrated.[1] However, AS-ALD of 2D materials has remained elusive. In this contribution, we demonstrate area-selective deposition of 2D WS_2 nanolayers by using a three-step (*ABC-type*) plasma-enhanced ALD process.

AS-ALD of WS_2 was achieved by using acetylacetone (Hacac) inhibitor (A), bis(tertbutylimido)-bis(dimethylamido)-tungsten precursor (B), and H_2S plasma (C) pulses at a low deposition temperature of 250 °C. This process resulted in immediate growth on: (1) SiO_2 (commonly used substrate for the growth of 2D TMD layers), (2) 2D TMDs such as MoS_2, NbS_2, and TiS_2 and (3) metal oxides such as MoO_3, Nb_2O_5 and WO_3 while effectively blocking growth on Al_2O_3 and HfO_2 surfaces, as determined from *in situ* spectroscopic ellipsometry and *ex situ* X-ray photoelectron spectroscopy measurements. The surface chemistry of this selective process was analysed by *in-situ* Fourier transform infrared spectroscopy. The analyses revealed that the inhibitor adsorbed on the non-growth surfaces (Al_2O_3), blocking precursor adsorption, while little or no inhibitor adsorption was detected on the growth surface (SiO_2) where WS_2 was readily deposited. As WS_2 grows readily on several TMD surfaces, our process can be also used to selectively grow 2D TMD vertical heterostructures (*e.g.* WS_2 on MoS_2) in presence ofthe non-growth areas (*i.e.,* Al_2O_3 and HfO_2).

To improve the crystallinity, the AS-ALD WS_2 films were annealed at temperatures within the thermal budget of industrial semiconductor processing (≤ 450°C). The annealed films exhibited sharp Raman peaks, which is a fingerprint of highly crystalline WS_2. Furthermore, Raman line scans over the patterns showed very sharp peak intensity transitions at the SiO_2-Al_2O_3 interface which confirmed that annealing had no impact on selectivity.

To summarize, this work pioneered the combination of two key avenues in atomic-scale processing: area-selective growth and ALD of 2D materials. It is expected that the results of this work will lay the foundation for area-selective ALD of other 2D materials.

Reference:

[1] Mackus *et al.*, *Chem. Mater.***31,** 2–12 (2019).

1:15pm **AS-WeA-2 Kinetic Modeling of Ru Area-Selective Atomic Layer Deposition on Nanopatterns*, Jan-Willem Clerix,*** KU Leuven, Imec, Belgium*; E Alonso Marques,* KU Leuven, Imec, TU Delft*; J Soethoudt,* KU Leuven, Imec, Belgium*; F Grillo,* ETH Zurich, Switzerland*; G Pourtois,* Imec, Belgium*; R van Ommen,* Delft University of Technology, Netherlands*; A Delabie,* Imec, Belgium

Area-Selective Deposition (ASD) is emerging as a promising bottom-up approach for nano-electronic device fabrication. However, unintentional growth on the non-growth area is a major challenge during ASD by atomic layer deposition (ALD). In addition, processes at the interface between growth and non-growth areas remain poorly understood. Insight into the growth mechanisms during ALD on nanoscale patterns can contribute to the development of ASD processes.

First, we investigate the mechanism of (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)Ru/O_2 (EBECHRu) ALD on different blanket non-growth surfaces by experimentally parametrized mean field and kinetic Monte Carlo models (KMC) [1]. We compare two hydrophobic methyl-terminated surfaces: SiO_2-$Si(CH_3)_3$ and organosilicate glass (OSG). The extent of growth inhibition during Ru ALD differs for these two cases. We identify a growth mechanism that describes the Ru areal density, surface coverage and particle size distribution and their evolution during ALD. Ru nanoparticles initially grow mainly by surface diffusion and aggregation. Precursor adsorption on the Ru nanoparticles occurs only when they reach a critical diameter of 0.85 nm, as smaller particles do not catalyze O_2 dissociation. The initial precursor adsorption is faster on SiO_2-$Si(CH_3)_3$ and the diffusion length of Ru adatoms and nanoparticles is larger. This explains the higher Ru content and larger particle size for a given number of cycles (Figure 1).

Informed by such insights, we use KMC simulations to study the impact of surface diffusion near the interface between growth and non-growth areas. We use the model parameters as determined for Ru ALD on blanket substrates and assume the growth area to act as sink for Ru nanoparticles. The simulations indicate a depletion zone with low nanoparticle density on the non-growth surface near the interface with the growth area (Figure 2).

We conclude that the interface between growth and non-growth areas plays an important role during ASD, and that the growth mechanisms critically depend on the surface properties and functionalization.

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1:30pm **AS-WeA-3 Area-Selective Atomic Layer Deposition on Chemically Similar Materials*, Tzu-Ling Liu,*** *S Bent,* Stanford University

Traditional top-down semiconductor fabrication processes are facing more challenges as a result of the scaling down of devices. Multiple processing steps not only increase the process complexity and cost but also introduce more process errors, such as with two-dimensional overlay and edge placement. Area-selective atomic layer deposition (AS-ALD), which allows direct deposition of materials on desired regions, is considered to be one promising solution and has been attracting more attention recently. One common way to selectively inhibit ALD growth on specific regions is to use self-assembled monolayers (SAMs), which form spontaneously on specific surfaces, depending on the reactivity of the SAM headgroup with substrates.

Despite the apparent simplicity of using SAMs as inhibitors for AS-ALD, the approach requires the starting substrate to have materials with sufficiently different chemical properties to allow selective SAM adsorption. This can present challenges when the desired substrate pattern has chemically similar materials present on the surface at the same time, such as dielectric/dielectric systems. Hence, it is important to expand selective deposition to more general systems. In this study, we describe new area selective ALD systems in which the above challenge is addressed. We have performed area selective ALD on chemically similar materials by selective deposition of alkylsilane and phosphonic acid SAMs on different dielectric surfaces. By taking advantage of the distinct reactivity of SAMs on various surfaces, we can choose SAMs that pack differently, affecting the ALD blocking ability. We show that a relatively well-packed SAM which is able to block ALD can be formed on Al_2O_3, HfO_2, TiO_2 and TaN substrates, while a poor SAM is formed on SiO_2 surfaces, after optimization of the SAM deposition. Selectivities greater than 90% are reached for 50 cycles ZnO ALD on SAM-treated Al_2O_3, TiO_2 and TaN compared to the SAM-treated SiO_2 surface, while a selectivity above 90% can be achieved for HfO_2 versus SiO_2 after 25 cycles ZnO ALD. In addition to MO_x/SiO_2, more general selectivity in MO_x/MO_x systems is also studied and we demonstrate AS-ALD in the Al_2O_3/HfO_2 system where Al_2O_3 is the non-growth surface. With our strategy, we demonstrate the ability to perform AS-ALD on patterns with chemically similar materials such as TaN/SiO_2, Al_2O_3/SiO_2 and Al_2O_3/HfO_2. This study gives insight into achieving more general selectivity and opens up the possibility for new applications in next generation electronic devices.

1:45pm **AS-WeA-4 Area-Selective Atomic Layer Deposition Al_2O_3 using a Small Thiol Inhibitor and Effects of Precursor Size*, H Lee, Bonwook Gu,*** Incheon National University, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) is attracting increasing interest because of its ability to enable both continued dimensional scaling and accurate pattern placement for next-generation nanoelectronics. Self-assembled monolayers (SAM) have been used as inhibitor to change the surface property in AS-ALD. The conventional SAMs, however, were relatively long and big in the range of 2~3 nm, so they are not suit for AS-ALD in few nanometer scale 3D patterns. In this work, we investigated ethanethiol (ET) for a small size inhibitor of AS-ALD on metal substrates, Co and Cu. We used two Al precursors with different molecular size, trimethyl-aluminum (TMA) and dimethyl-aluminum-isopropoxide (DMAI) for blocking property, with H_2O counter reactant. ET was selectively absorbed on Cu and Co, but not on SiO_2 and showed better inhibition property against ALD Al_2O_3 using DMAI than that using TMA. In order to investigate the different blocking property of ET to TMA and DMAI, we calculated the adsorption kinetics and dynamics of Al precursors on Cu and Co surfaces inhibited by ET using density-functional theory (DFT) and realized physical adsorption behavior based steric hindrance using Monte-Carlo (MC) simulation. DFT results showed that DMAI forms dimers during adsorption on surfaces, and TMA preferably reacts even on the CH_3-terminted ET surfaces. Consistently, the steric hindrance simulation by MC showed a reasonable difference in Al precursor adsorptions on ET-inhibited Co and Cu surfaces. From the results and knowledge, we could extend the degree of freedom to obtain better AS-ALD property to selection of ALD precursors, and it could be applied to other AS-ALD materials systems.

3:15pm **AS-WeA-10 Effect of Copper Surface Condition on Passivation Characteristics for Applications to Area Selective Atomic Layer Deposition*, Su Min Hwang,*** University of Texas at Dallas*; H Kim, J Kim,* The University of Texas at Dallas*; Y Jung,* University of Texas at Dallas*; L Pena, K Tan, J Veyan,* The University of Texas at Dallas*; D Alvarez, J Spiegelman,* RASIRC*; K Sharma, P Lemaire, D Hausmann,* Lam Research Corp.*; J Kim,* University of Texas at Dallas

Recently, area-selective atomic layer deposition (AS-ALD) by locally passivating the copper surface has garnered attention by reducing the number of processing steps as well as by alleviating key challenges associated with lithography and layer alignment at the sub-5 nm node.[1–3] However, despite the enormous scientific effort in recent years, lack of surface science during cleaning and passivation of Cu surfaces impede the development of AS-ALD. Specifically, the effect of the copper surface on the quality of passivation materials, such as self-assembled monolayers (SAMs) has been rarely reported.

Herein, electroplated Cu films were treated using glacial acetic acid (CH_3COOH) and anhydrous N_2H_4, respectively.[4] After cleaning, the Cu samples were immersed in a 1 mM solution of octadecanethiols (ODTs) in ethanol for 20 h. To elucidate the surface chemistry and stability of ODTs, the passivated Cu samples were loaded into an *in-situ* reflectance absorption infrared spectroscopy (RAIRS) system equipped with an ALD chamber, then ALD of AlO_x process was performed using TMA and H_2O at 120 ^oC. During surface cleaning, CH_3COOH removes surface adventitious contaminants (e.g., $–CH_x$, $–CO_3$, and –OH), and most importantly, reduces the surface oxide (Cu_2O) to metallic copper by forming copper acetate as an intermediate material. In the *ex-situ* XPS and RAIRS, the SAMs on the CH_3COOH-treated Cu sample gives poor selectivity of ALD-AlO_x compared to the SAMs on the as-is Cu and N_2H_4-treated Cu, respectively. It implies that the residual copper acetate on the surface can affect the chemisorption of ODTs during passivation, eventually attributing a relatively lower surface coverage, poor thermal stability of ODTs, and poor selectivity during ALD process. To circumvent the issue, the effect of post-treatment after surface cleaning with CH_3COOH was investigated. Vacuum treatment of the sample under the UHV condition (~10^{-8} Torr) can partially reduce the copper acetate by forming $-CH_x$ and -OH species. However, a post-annealing at 75 ^oC effectively removes the copper acetate and residual contaminants on the surface, which can improve not only ODTs quality in the passivation process but also the increase of nucleation delay during the consecutive ALD process. The detailed experimental results will be presented.

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3:30pm **AS-WeA-11 Top and Bottom Ta_2O_5 Topographical Selective Deposition on 3D structures by Plasma Enhanced Atomic Layer Deposition***, **Taguhi Yeghoyan**, V Pesce, M Jaffal,* LTM-UGA, France*; R Gassilloud, N Posseme,* CEA-Leti, France*; M Bonvalot, C Vallée,* LTM-UGA, France

Advanced nanoelectronics technologies, e.g. FinFETs or DRAM deep trench capacitors, are made of active 3D objects. This 3D structuration of matter increases integration complexity, adding multiple nanopatterning steps that affect the fabrication cost. Part of the patterning cost could be reduced if thin films could be selectively deposited on specific surfaces of the 3D structures, like pillars or trenches. Such Topographical Selective Deposition (TSD) processes can be achieved using an anisotropic deposition technique based on a standard Plasma Enhanced Atomic Layer Deposition (PEALD) coupled with directional plasma ion bombardment that induces a local modification of material properties [1].

Recent reports of TSD on 3D structures have two main objectives. The first objective is to deposit thin films only on sidewalls of 3D structures, for which several methods have been already reported, including pre-growth surface deactivation [2], post-growth in-situ plasma etching or ex-situ wet etching processes [1,3]. The second objective is to deposit thin films only on horizontal (top and bottom) surfaces of 3D structures, for which process routes have been scarcely reported and remain challenging [4,5]. R. A Ovanesyan *et al*. used a three-step ALD process composed of two conventional thermal steps, followed by a subsequent N_2 plasma step in order to reduce carbon contamination in the top and bottom SiN_x deposit, hence, densifying it. The obtained film was then wet etched to achieve the desired top and bottom topography [4].

In this work, we present an original approach leading to only top and bottom Ta_2O_5 densification, based on a standard two-step PEALD cycle, followed by a post-growth wet etching step with an effective selectivity of 10 to 1. As evidenced from SEM imaging, as-grown Ta_2O_5 thin films deposited on 3D trenches (aspect ratio 13:1) show approximately 70% conformity from bottom to top and middle to top, whereas post-growth wet etched structures do not exhibit any vertical coating while maintaining initial bottom to top conformity. We think that the methodology established here could be easily extended to most PEALD deposited materials.

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Emerging Materials
Room Jan & Hubert Van Eyck - Session EM-WeA

Organic and Organic-Inorganic Hybrid Materials II & III

Moderators: Tero Pilvi, Picosun Oy, Ganesh Sundaram, Veeco-CNT

1:15pm **EM-WeA-2 Enhanced Stretchability in Inorganic-Organic Alucone Thin Films Deposited from Long-Chain Organic Precursors***, **Janne-Petteri Niemelä**, N Rohbeck, J Michler, I Utke,* Empa, Switzerland

Molecular layer deposited (MLD) hybrid inorganic-organic materials ("metalcones") have recently received increasing attention, largely due to their potential for applications demanding mechanical stretchability/flexibility.[1,2] Alucones (Al-based hybrids) are among the most studied metalcones owing to e.g. their promising performance as an electrode-electrolyte interface layer in Si-nanoparticle based batteries, where the charging/discharging cycles involve huge volumetric changes up to 300 %.[3] The research on mechanical (and battery) properties of metalcones is limited to the materials based on short-chain organic precursors,[4] while increasing the precursor chain length is an unexplored but rational route for enhancing mechanical performance of the metalcone thin films.

In this work we deposited alucone thin films using trimethyl aluminum (TMA) as the Al metal precursor, and 1,2-ethanediol (EG), 1,6-hexanediol (HD) and 1,10-decanediol (DD) as the organic precursors. The TMA/HD and TMA/DD processes were studied at 130 °C: they exhibit MLD-type behavior with self-saturating surface reactions, and linear film growth (studied up to 150-200 nm) with the growth-per-cycle values of 0.32 and 0.37 nm, respectively. Mechanical stretchability was studied via tensile testing coupled with in-situ optical microscopy for 100-nm alucone films deposited on the stretchable polyimide substrates. The critical strain for fracture was enhanced up to around 9 % for the alucone films deposited via the TMA/DD process. This value is more than an order-of-magnitude higher than the value for purely inorganic Al_2O_3 and represents a factor-of-four increase in comparison to the EG-based alucone material (the state-of-the-art for the metalcones). The 9-% critical strain translates to critical volume expansion of 300 % for (battery-relevant)[3] around 3-nm coating thickness on a nanoparticle surface (assuming a spherical particle and inverse-square-root thickness extrapolation for the critical strain), and to 0.25-mm critical bending radius on the 50-µm substrate. The film structure is moreover studied via the XRR, FTIR and SEM techniques, while the mechanical properties are further analyzed via nanoindentation.

The present results highlight that the potential of the MLD technique can be further enhanced by exploring a wider space of larger/longer/complex organic precursor molecules instead of the conventionally used small molecules.

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1:45pm **EM-WeA-4 Self-Terminating Molecular Layer Deposition of Polyurea and Growth Rejuvenation via Precursor Linking Group Selection***, **Rachel A. Nye**, G Parsons,* North Carolina State University

Molecular layer deposition (MLD) has recently been explored due to the vast tunability of film properties and growth conditions. Polyurea coupling by MLD commonly proceeds by reacting molecules with diisocyanate functional groups (such as p-phenylene diisocyanate, PDIC) with other molecules containing diamine functional groups (such as ethylenediamine, ED). Under steady-growth conditions at 60°C, the PDIC/ED sequence typically leads to continuous film growth of ~0.41 nm/cycle. Recently, we discovered a modified polyurea MLD reaction that shows a growth trend very different from commonly reported processes. Specifically, we find that using 1,6-hexanediisocyanate, HDIC, in place of PDIC, causes a significantly lower film growth rate: less than 0.1 nm/cycle even at temperatures as low as 40°C.

Additionally, the low growth rate obtained from the HDIC/ED reaction continues to decrease with increasing cycle number. This significant change in polyurea growth rate is achieved simply by varying the organic linker groups, while maintaining the same urea coupling chemistry. Interestingly, the low growth rate of the flexible HDIC/ED can be increased by incorporating the aromatic PDIC compound into the overall polymer structure. Thus, the self-terminating and rejuvenating growth of aliphatic polyurea can be controlled with aromatic composition. The entirely flexible HDIC/ED polymer is very difficult to grow to a thick film, but incorporating small amounts of benzene enable deposition of a much thicker film without significantly affecting film properties. These trends are likely due to high frequency of double reactions for the entirely aliphatic HDIC and ED precursors. The rigid benzene ring in the PDIC precursor then seems to promote a more rigid structure that reduces the number of site-terminating reactions and enhances growth. This self-limiting and rejuvenating growth is of potential interest for the field of area selective deposition. Additionally, the ability to modulate polymer growth rates with the incorporation of benzene rings has significant implications to the development of new precursors and polymer thin film properties.

3:00pm **EM-WeA-9 Vapor-Phase Infiltration Synthesis of Organic-Inorganic Hybrid Nanocomposite Resists for Next-Generation Nanolithography***, N Tiwale,* Brookhaven National Laboratory*; A Subramanian,* Stony Brook University*; K Kisslinger, G Freychet, M Lu,* Brookhaven National Laboratory*; J Kim,* University of Texas at Dallas*; A Stein, **Chang-Yong Nam**,* Brookhaven National Laboratory

Vapor-phase infiltration (VPI), a material hybridization technique derived from atomic layer deposition, can generate molecular-scale organic-inorganic nanocomposites with uniquely enhanced material properties by utilizing the infiltration and binding of gaseous organometallic precursors within organic media. In this study, we report the application of VPI on developing new organic-inorganic hybrid polymer resists for the next-generation nanolithography. Hybrid resists are emerging as an effective way of addressing stringent process requirements for aggressive down-scaling of semiconducting devices. However, hybrid resists generally require complex chemical synthesis while being predominantly negative-tone with high exposure dose requirement. For positive-tone processes and high-aspect-ratio pattern transfer, resist choices are limited to costly non-hybrid alternatives, whose etch resistance is still inferior compared with hybrid resists. Here, demonstrated is a novel hybrid positive-tone resist platform utilizing simple *ex-situ* VPI of inorganic components into standard resist materials. A model system based on poly(methyl methacrylate) (PMMA) thin film hybridized with AlO_x has been demonstrated for electron-beam lithography patterning, featuring fully controllable critical exposure dose, contrast, and etch resistance. The hybrid resist not only achieves exposure contrast as high as ~30, a six-fold enhancement over standard PMMA, but also enables Si nanostructures with resolution down to ~30 nm and aspect ratio up to ~17, owing to extremely high Si etch selectivity far exceeding those in known commercial positive-tone resist systems. Interrogation of the effect of varying etching protocols on etch rate reveals a surprisingly high enhancement of chemical etch resistance over the physical one with increasing amount of infiltration, which we attribute to the strong chemical biding between infiltrating Al precursor, trimethylaluminum (TMA), and carbonyl group in PMMA. Also briefly discussed is the electron-beam-induced exposure mechanism (i.e., change in solubility) in the hybrid resist probed by synchrotron X-ray absorption spectroscopy as well as other hybrid resist systems being developed for extreme ultraviolet (EUV) lithography application, where the infiltrated inorganic elements can potentially improve not the etch resistance but also EUV sensitivity and other resist performance parameters. The easy implementabilility, combined with versatile *ex-situ* control of resist characteristics, makes this hybrid resist synthesis approach uniquely suited for addressing the resist performance required for advanced next-generation nanolithography techniques.

3:45pm **EM-WeA-12 Synthesis of SiAlCO Polymer Derived Ceramics (PDC) Thin Films using Molecular Layer Deposition***, **Kristina Ashurbekova,*** Dagestan State University, Russian Federation*; E Modin, A Chuvilin, M Knez,* CIC nanoGUNE BRTA, Spain*; I Abdulagatov,* Dagestan State University, Russian Federation

Organosilicon PDC materials and its derivatives have gained interest for various important applications such as electrode material for lithium-ion batteries, ultra-high temperature composites and others [1]. Conventionally, PDC coatings are prepared by wet-chemical dip, spin, thermal-spray coating or by plasma-assisted chemical vapor deposition (CVD), followed by high temperature pyrolysis [2].

In this work, molecular layer deposited (MLD) hybrid organic-inorganic films serve as precursors for a synthesis of SiAlCO PDC composite coatings. Alumina-polysiloxane films were grown using 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V_4D_4) and trimethylaluminum (TMA) (Supplemental Figure 1). The deposition was conducted at temperatures between 120 and 220ºC. An *in-situ* quartz crystal microbalance (QCM) study showed linear mass increase with the number of MLD cycles with the highest growth rate of 24 ng/cm^2/cycle occurring at 180ºC. QCM measurements revealed a self-limiting surface chemistry of the MLD process. FTIR analysis of deposited films showed vibrational features characteristic of organosilicon polymers: $Si\text{-}CH_3$, Si-O-Si, $Si\text{-}CH{=}CH_2$ and Si-O-Al peaks (Supplemental Figure 2).

Upon growth of the film, cross-linking is needed to increase the mass yield during the polymer-to-ceramic transformation. Cross-linking was achieved at 200ºC by introducing a third precursor, di-tert-butyl peroxide (TBP), into the MLD process, following a V_4D_4/TBP/TMA sequence. The thus obtained films were pyrolyzed at 900ºC in an Ar atmosphere. XRR, XRD, Raman, HRTEM, and EDX were applied for characterization of the films. After pyrolysis, the composite thin film remained amorphous. The final film contained Si, Al, O, and C uniformly distributed throughout the film. Raman spectroscopy showed presence of graphitic carbon within the film. This MLD-derived SiAlCO thin film is expected to have exceptional high temperature stability, creep, and corrosion resistance.

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Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS1-WeA

2D Nanomaterials by ALD II

Moderators: Jeffrey W. Elam, Argonne National Laboratory, Hyungjun Kim, Yonsei University, Korea

1:00pm **NS1-WeA-1 Atomistic Simulation of ALD of 2D Transition-Metal Dichalcogenides***, **Mahdi Shirazi**, E Kessels, A Bol,* Eindhoven University of Technology, Netherlands **INVITED**

Extensive research has been done during the last decade to unravel the remarkable electronic properties [1], [2] of two dimensional transition-metal dichalcogenides (2D-TMDs) in the monolayer regime. In spite of their astounding electrical properties, these material systems are not ready yet for replacing Si based materials for future nanometer-sized electronic devices. One key challenge is the integration of these materials in bottom-up processes at low temperature (usually < 500 °C) into the semiconductor manufacturing flow. Horizontal growth at wafer scale with a large grain size (typically 1x1 µm^2) is required for nano-electronic devices [3]. The cyclic process of atomic layer deposition (ALD) [4] with tight control over the chemical reactions shows promise as such a bottom-up process. The chemical reactions of ALD are self-limiting and are designed to proceed only at the surface. In this contribution, we have employed density functional theory (DFT) to provide fundamental insight into the reaction mechanisms of the MoS_2 growth. We have studied the deposition of MoS_2 that is initiated by the exposure of metal precursor $Mo(NMe_2)_2(NtBu)_2$ ($C_{12}H_{30}N_4Mo$) to the SiO_2 surface and then followed by exposure of H_2S/H_2 as co-reagent in the second pulse [5]. In this so-called hetero-deposition, the involved chemical reactions during ALD lead to the formation of a buffer layer at the surface of SiO_2 [6]. After formation of this buffer layer, ALD enters into the steady-growth regime (also called homo-deposition). In the steady growth regime, vertically or horizontally aligned MoS_2 structures grow in a layer-by-layer fashion. The calculated reaction energies and activation energies indicate that the reaction kinetics in the hetero-deposition are slower than reaction kinetics in homo-deposition. Artificial intelligence is used to generate an efficient interatomic potential using the calculated energies and forces of configurations obtained by DFT. The generated interatomic potential will be used for larger scale simulations to provide further fundamental insight into the deposition of MoS_2 by ALD.

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1:45pm **NS1-WeA-4 ALD of $MoSe_2$ using New Precursors***, **Raul Zazpe**,* University of Pardubice, Czech Republic*; R Krumpolec,* Brno University of Technology, Czech Republic*; J Charvot, L Hromadko, H Shopa, M Motola, M Krbal, F Bures, J Macak,* University of Pardubice, Czech Republic

2D semiconductor transition metal dichalcogenides (TMDs) have attracted considerable attention due to their layered structure, suitable band gap for visible light absorption, high carrier mobility, electrochemically active unsaturated edges and relatively good stability against photocorrosion [1]. Recently, 2D $MoSe_2$ has been gaining considerable interest due to its higher electrical conductivity as compared to MoS_2, its wider inter-layer distance (~0.65 nm), narrow bandgap (1.33–1.72 eV), high resistance to photo-corrosion, high surface area layer, electrochemically active unsaturated Se-edges and close to zero Gibbs free energy edges for hydrogen adsorption.These properties are promising for different applications of $MoSe_2$ including hydrogen evolution [2], photocatalysis [3] and Li-ion batteries [4]. However, their low light absorption efficiency, recombination issues of the photogenerated electron–hole pairs and slow charge transfer of the intrinsic semiconducting 2H-phase are a handicap. An efficient strategy to surpass those intrinsic limitations are hybrid nanostructures using conducting supporting materials. In this regard, anodic TiO_2 nanotubes (TNTs) are excellent photoactive supporting material providing a high surface area, unique directionality for the charge separation, and highly effective charge collection. [5] Accordingly, we present anodic TiO_2

nanotubes homogenously decorated with $MoSe_2$ nanosheets by atomic layer deposition (ALD). In parallel, we address the current scarcity of convenient ALD Se precursors by the synthesis a set of new selenium precursors - alkysilyl $(R_3Si)_2Se$ and alkytin $(R_3Sn)_2Se$, and cyclic silylselenides compounds. Those Se precursors were extensicely characterized and their reliability as ALD Se precursors explored [6,7]. Several compounds exhibited promising results to be convenient ALD Se precursor as will be presented in the presentation. The synthesis of the $MoSe_2$ nanosheets and their composites with TiO_2 NTs, their physical and electrochemical characterization, and encouraging results in electrochemical characterization, hydrogen evolution reaction (HER) and photocatalysis will be presented and discussed.

2:00pm **NS1-WeA-5 Low Temperature Creation of Layered-MoS_2 Thin Films on Large Area High Aspect Ratio Substrates**, ***Anil Mane**, D Choudhury, S Letourneau, J Elam,* Argonne National Laboratory

Thin layers of two dimensional (2D) materials mainly transition metal dichalcogenides (TMDs) and more specifically ultra-thin layered-MoS_2 semiconductor possess exceptional properties such as electrical, optical, magnetic, mechanical and chemical properties. This allows the exploration of internal quantum degrees of freedom of electrons and their potential for use in semiconductor microelectronics, optoelectronic, energy, and sensor and detector applications. These exciting results are being achieved mostly by using exfoliation of flecks from bulk MoS_2 crystal. However, the biggest challenge in realizing TMDs full potential has been the lack of scalable material synthesis methods for such films with high uniformity, conformality and interfacing with other materials such as oxides, metals and its process compatibility.

Among the various thin film deposition methods, atomic layer deposition (ALD) offers the best combination of precisely controlled layer-by-layer thin film growth at low temperature with very high conformality on complex substrates. Here we will present the growth of layered-MoS_2 thin films. To grow high quality layered–MoS_2 thin films, we have developed an ALD-based two step processing approach [1]: firstly the growth of well controlled ultra-thin layer of Mo metal using ALD followed by the sulfurization of the ALD Mo layer at various temperatures. This two-steps processing results in high quality layered-MoS_2 thin films on large substrates. For the Mo ALD process we used molybdenum hexafluoride (MoF_6) and Si_2H_6 precursors. We used in-situ QCM measurements to study interfacial and nucleation effects in the formation of continuous ultra-thin metal layer of Mo. The composition of both the ALD Mo and the layered MoS_2 layers was determined by X-ray photoelectron spectroscopy (XPS). Further, cross-sectional transmission electron microscopy (TEM) was performed to confirm the formation of layered MoS_2 on high aspect ratio trenches and Raman analysis to verify the signature of E^1_{2g} blue shift and A_{1g} red shift in the MoS_2 structure. In this presentation we will discuss the details of the two-step thin film growth process for creating layered MoS_2 layers via ALD Mo and subsequent sulfurization as well as the properties of the MoS_2 films.

[1] Anil Mane, Devika Choudhury, Steven Letourneau, Jeffrey Elam, (US patent application submitted 2018)

2:15pm **NS1-WeA-6 Gas Sensing Characteristics of $Mo_xW_{1-x}S_2$ Synthesized by Atomic Layer Deposition**, ***Inkyu Sohn**, Y Kim, M Lee, J Park, H Kim,* Yonsei University, Republic of Korea

Two-dimensional Transition metal dichalcogenide (2D TMDC) have been attracted great attention as gas sensing materials with high sensitivity in room temperature. [1] Because of this characteristic, 2D TMDC gas sensor could overcome the oxide-based semiconductor which need heating for gas sensing. Therefore, various 2D TMDC gas sensor studies have been ongoing. Recently, it has been shown that the gas sensor property could be improved through the changing the composition in $WS_{2x}Se_{2-2x}$ alloy. [2]

Here we report a synthesis method of $Mo_xW_{1-x}S_2$ alloys for gas sensor by atomic layer deposition. Layer controlled 2D MoS_2 and WS_2 were synthesized with $Mo(CO)_6$, $W(CO)_6$ and H_2S as precursors and reactant. For the first time, we systematically modulate the composition of $Mo_xW_{1-x}S_2$ alloys by changing the configuration of low-temperature ALD super-cycles. AFM and Raman spectroscopy results of $Mo_xW_{1-x}S_2$ alloys demonstrate that the thickness of alloy is accurately controlled by ALD. Also XPS results confirmed that composition of alloy is precisely controlled by ALD super-cycles. Furthermore, gas sensors fabricated by $Mo_xW_{1-x}S_2$ alloys were evaluated for NO_2 gas. It showed response time and recovery characteristics of $Mo_xW_{1-x}S_2$ alloy gas sensor is dramatically enhanced.

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Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS2-WeA

Nanomaterials by ALD - Nanoparticles and ALD on Polymers

Moderators: Jeffrey W. Elam, Argonne National Laboratory, Hyungjun Kim, Yonsei University, Korea

3:00pm **NS2-WeA-9 Visualizing the Nucleation of ALD on Polymers**, ***Laura Astoreca**,* Ghent University - IMEC, Belgium*; P Esbah Tabaei,* Ghent University, Belgium*; D Schaubroeck, M Oop de Beeck,* Ghent University - IMEC, Belgium*; R Morent,* Ghent University, Belgium*; H De Smet,* Ghent University - IMEC, Belgium*; N De Geyter,* Ghent University, Belgium

Polyimides are vastly used in the microelectronics industry as they can withstand the conditions of many processes due to their mechanical robustness, and thermal and chemical stability. A specific polyimide (PI 2611) has been used as packaging material for flexible implantable medical devices and electrodes due to its relatively good water barrier properties and biocompatibility. Yet, it cannot provide the necessary hermeticity for long term implantation. Therefore, this PI can be combined with metal oxide ALD layers (SiOx, AlOx, TiOx or HfOx) to develop ultra-hermetic barriers (WVTR = 10^{-6} g/cm²day). To characterize the interaction between the PI and the ALD layers it is fundamental to understand the nucleation of the ALD layer on the polymer. These are commonly studied by quartz microbalance, ellipsometry, FTIR, or XPS, all of which provide valuable information but do not allow visualizing the nucleation behavior during the initial stages of ALD growth until full closure of a layer on polymers. In this contribution, a new qualitative method to study this is proposed and applied to the Al_2O_3 and HfO_2 ALD deposition on PI. The deposited metal oxide acts as a hard mask during PI reactive ion etching (RIE). This results in local features of the deposited ALD being visible in FEG SEM images. The samples were also analyzed by XPS to verify the Al or Hf content present on the surface. The proposed method produces repeatable results, and by increasing the exposure time of the RIE it was confirmed that the deposited Al_2O_3 or HfO_2 was not damaged by the etching step. As expected, the images taken and the XPS results showed a faster nucleation and growth of a fully closed layer of the AlOx compared to HfOx. In both cases an island-coalescence type of nucleation and growth was observed. First, islands were formed on the surface of PI, growing into filamentous structures that progressively coalesced into meshes, which became denser until eventually a closed layer was formed. The Al or Hf content measured by XPS presented an equivalent increase behavior. The content of Al or Hf was low and constant at the beginning, corresponding to the island stage. It progressively increased as the mesh structures were formed and became denser until it stabilized at a constant value. Herein, a qualitative method to visualize the nucleation and growth of a full ALD layer on polymers was introduced. It is not presented as an alternative to the available techniques but rather as a complementary tool.

3:30pm **NS2-WeA-11 Pt-Doped In_2O_3 Thin Films: Control of the Chemical State and Structure via ALD**, ***Ranjith K. Ramachandran**, M Filez,* Ghent University, Belgium*; E Solano,* Ghent University, Belgium, Spain*; H Poelman, M Minjauw, M Van Daele, J Feng,* Ghent University, Belgium*; A La Porta, T Altantzis,* University of Antwerp, Belgium*; E Fonda,* Synchrotron SOLEIL, SAMBA Beamline, France*; A Coati, Y Garreau,* Sychrotron SOLEIL, France*; S Bals,* University of Antwerp, Belgium*; G Marin, C Detavernier, J Dendooven,* Ghent University, Belgium

It is well known that noble metal addition to metal oxides improves the electronic properties of the oxides. Depending on the targeted application of the resulting material, another mode of addition is demanded. While noble-metal doped semiconducting metal oxides show improved catalytic and gas sensing properties, metallic nanoparticles (NPs) embedded in metal oxides are used as charge storage materials in single-electron memory devices. In any case, accurate tuning of the dopant level/NP's size is crucial to achieve an optimal performance.

Here, a novel atomic layer deposition (ALD)-based method for doping Pt into In_2O_3 is demonstrated.[1] We combine alternating exposures of Pt and In_2O_3 ALD processes in a single "supercycle" followed by supercycle repetition leading to multilayered nanocomposites (**Figure 1**). The resulting samples of Pt embedded in an In_2O_3 matrix are characterized chemically and structurally using a variety of X-ray-based techniques, such as X-ray fluorescence (XRF), X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), grazing-incidence small-angle X-ray scattering (GISAXS), and high-angle annular dark-field scanning transmission electron microscopy

(HAADF-STEM), combined with energy dispersive X-ray spectroscopy (EDXS).

The proposed method enables controlled doping of Pt/PtO_x species inside the In_2O_3 matrix with the ability to fine-tune their chemical and structural properties. For example **Figure 2** shows the results from a series of samples (samples B1 – B6) where the number of Pt ALD cycles was varied from 1 to 30 while keeping the number of In_2O_3 cycles at 30. XAS and XRD shows that a few Pt ALD cycles lead to the formation of oxidized Pt species due to their highly dispersed nature. GISAXS and HAAD-STEM, combined with EDXS, show that Pt is evenly distributed in the In_2O_3 matrix without the formation of clusters. For a larger number of Pt ALD cycles, the oxidation state gradually evolves toward fully metallic, and metallic Pt clusters are obtained within the In_2O_3 matrix.

In addition to giving valuable information on the dopant distribution and its chemical state, which provides strategies for fine-tuning the properties of doped metal oxides, this approach allows characterization of the nucleation stages of metal ALD processes by freezing those states through embedding and stacking them multiple times. This allows the use of XAS and other techniques to study even a single-metal ALD cycle, without the need for the use of high-surface-area supports.

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3:45pm **NS2-WeA-12 Study of Tuning Size, Coverage and Shape of Pd Nanoparticles Using Atomic Layer Deposition Through X-ray Based In-situ Characterization***, **Ji-Yu Feng**,* Ghent University, Belgium*; E Solano,* NCD-SWEET beamline, ALBA Synchrotron Light Source, Spain*; R Ramachandran, M Minjauw, M Van Daele,* Ghent University, Belgium*; D Hermida-Merino,* ESRF European Synchrotron Radiation Facility, France*; A Coati,* Synchrotron SOLEIL, France*; C Detavernier, J Dendooven,* Ghent University, Belgium

Atomic-level control of the morphology of supported nanoparticles (NPs) is of great importance in heterogeneous catalysis, because the catalytic performance is closely related to the size, interparticle distance and shape of the NPs. On this aspect of uniformity and precise control, ALD has proven to be a promising synthetic method for catalytic applications, where several studies have focused on the relationship between processes and NPs morphology evolution. Synchrotron-based in situ X-ray fluorescence (XRF) and grazing incident small-angle scattering (GISAXS) experiments can offer insights in the NP morphology evolution during the nucleation stages of ALD processes.[1]

In this work, we study the evolution in Palladium (Pd) NP morphology during plasma-enhanced ALD using in situ XRF and GISAXS. Firstly, the role of the co-reactant choice is investigated by comparing Pd NP growth by ALD processes using $Pd(hfac)_2$ as precursor and different plasma sequences as co-reactants (H_2* and H_2*+O_2*) on Al_2O_3 substrates. Different from the process with only H_2* as coreactant, an additional O_2* step leads to an increase in initial nucleation density, which is explained by a cleaning effect of O radicals towards poisoning surface species from the reaction between the hfac ligands and the surface. Moreover, O_2* induces enhanced mobility of Pd atoms and/or particles, thus resulting in a more dynamic coalescence during further growth, as observed from the continuous increase in center-to-center distance. The 2D GISAXS patterns also reveal that the H_2* and O_2* exposures have a different impact on the particles' shape and wetting behavior. As a result, a clear difference in Pd particles morphology for both studied processes is observed at higher loadings: worm-like structure for the H_2* process vs. isolated particles for the H_2*+O_2* process. Secondly, to further tune the initial nucleation density, trimethylaluminum (TMA) exposures are introduced during the first ALD cycles of the $Pd(hfac)_2$/H_2* process to clear the surface blocking species.[2] XRF-GISAXS shows TMA exposures in the early ALD cycles lead to an increase in initial nucleation sites, thus making smaller Pd NPs with a larger coverage when comparing samples with the same Pd loading. When gradually increasing the applied number of TMA pulses from 1 to 10, the NP dimensions (coverage) can be tuned from high (low) to low (high). Based on this knowledge, an ALD based strategy is developed for the synthesis of well-designed Pd NPs, e.g. by adjusting the number of TMA pulses and applied ALD cycles.

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Tutorials
Room Live - Session TU2-WeA
Tutorial Session: Wednesday Live

Moderators: Paul Poodt, Holst Centre / TNO, Erwin Kessels, Eindhoven University of Technology, the Netherlands, Jean-François de Marneffe, IMEC

1:00pm **TU2-WeA-1 Wednesday Tutorial Welcome & Sponsor Thank You***,* ***Paul Poodt,*** TNO/Holst Center, The Netherlands, Netherlands

Thank you for joining our Tutorial! We wish to thank our Sponsors for their support!

1:15pm **TU2-WeA-2 Growth Mechanisms and Selectivity During Atomic Layer Deposition***,* ***Annelies Delabie,*** KU Leuven – University of Leuven/IMEC, Belgium **INVITED**

Area-selective deposition (ASD) holds the potential to build nanostructures from the bottom up, only where needed, with atomic precision in both vertical and lateral direction. The technique is of great interest for nano-electronic device manufacturing, as it can be applied for bottom-up deposition in small trenches or holes, or to create nanoscale structures with great accuracy by self-alignment. In addition, ASD can simplify complex integration flows and is a cost-effective approach that consumes less chemical products and energy as compared to traditional top-down patterning. Today, many materials can be deposited by atomic layer deposition (ALD), but only few ALD processes show selectivity. ASD is governed by a complex interplay of several processes, including adsorption, desorption, surface reactions and diffusion. Fundamental understanding of the mechanisms during ALD can contribute to the design of new ASD processes for a wider range of materials. This tutorial will therefore first address the growth mechanisms during ALD on an initially homogeneous substrate surface. Several quantitative growth models have been proposed to describe the initial ALD growth regime. Next, we discuss the mechanism of ASD in nanoscale patterns, and how the growth behavior during ASD can differ from regular growth on homogeneous substrates. Finally, we address strategies to minimize deposition in the non-growth surface area, while simultaneously maintaining or enhancing growth on the growth surface area.

2:15pm **TU2-WeA-6 Self-limiting Surface Reactions for Atomic-level Control of Materials Processing***,* ***Simon D. Elliott,*** Schrödinger, Inc. **INVITED**

ALE and ALD have in common that their defining characteristic is a self-limiting transformation of the surface in each cycle. This leads to the well-known advantages of the techniques - uniformity, conformality and digital control of thickness etched/deposited. In this tutorial we will examine how the chemical interaction between a gas and a surface can be either self-limiting or continuous. Looking at how this depends on process conditions (temperature or pressure) gives a straightforward way to understand the process window and account for the etch/growth rate. The simple procedure for estimating etch/growth rates from surface coverage will be presented. We will discuss the various potential sources of self-limiting chemistry, such as the concentration of substrate sites, availability of co-reagent fragments, exposure of gaseous reagent and diffusion along the surface. Examples will be given from both acid-base and redox-based chemical mechanisms of ALE and ALD.

3:15pm **TU2-WeA-10 Fundamentals of ALE – Optimizing Passivation and Etch****,* ***Mark Kushner,*** University of Michigan **INVITED**

The ideal process of plasma based atomic layer etching (ALE) consists, in principle, of two independent self-limiting steps. The first is passivation of an atomically smooth surface with plasma produced radicals with the goal of lowering the binding energy of the surface resident atoms. The second is removal of the passivated layer of atoms with the activation energy provided by plasma generated ions of carefully controlled energies. Ideal ALE, the removal of a single monolayer per cycle, is rarely achieved. There are narrow process windows in terms of how much activation energy can be delivered during the passivation step and how many passivants can be present during the etch step. In addition to the intrinsic chemistry of the ALE process, the quality of the process is ultimately determined by how well the fluxes delivered by the plasma to the surface can be controlled – all of which contribute to the ideality of the process. ALE of dielectrics (ALE-D), typically using fluorocarbon gas mixtures, proceeds through deposition of a thin polymer layer which provides the precursors for the etch step. As such, ALE-D begins as being non-ideal as the passivation step is not self-limiting. ALE-D is perhaps better described as controlled EPC (etch-per-cycle). Depending on polymer thickness and ion energies, the EPC can be a fraction of monolayer or many monolayers. In this tutorial, ideal and non-ideal ALE processes will be reviewed with an emphasis on the plasma properties required to achieve ideal behavior. Examples will be used from computer modeling of reactor scale plasma generation of passivants and etchants, and feature scale profile simulation. Halogen plasma based ALE of conductors will be used to illustrate the process window requirements for ideal EPC. Simulation of ALE-D of SiO2 and Si3N4 will be used to illustrate how control of plasma properties can produce controlled EPC, selectivity and surface smoothness. * Work supported by Lam Research Inc., TEL Technology Center America LLC and Samsung Electronics.

4:00pm **TU2-WeA-13 Questions & Answers**, *M Kushner,* University of Michigan*; A Delabie,* KU Leuven – University of Leuven/IMEC, Belgium*; S Elliott,* Schrödinger, Inc.*; **Jean-François de Marneffe**,* IMEC, Belgium

Feel free to ask questions to our Tutorial presenters

4:30pm **TU2-WeA-15 Session Over - View On Demand Presentations**, ***Erwin Kessels**,* Eindhoven University of Technology, Netherlands

You are now welcome to view all ALD/ALE On Demand Presentations

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