ALD Applications
Room Hall 3D - Session AA1-MoA

Energy: Batteries and Energy Storage

Moderators: Christian Dussarat, Air Liquide Laboratories, **Jin-Seong Park**, Hanyang University

1:30pm **AA1-MoA-1 Enabling Fast Charging of Lithium-ion Batteries at Sub-Zero Temperatures with ALD coatings***, T. Cho, Y. Chen, D. Liao,* University of Michigan*; E. Kazyak,* University of Wisconsin*; D. Penley, **Neil P. Dasgupta**,* University of Michigan

Increasing the achievable charging rate of lithium-ion batteries (LIBs) is critical to the widespread commercialization of electric vehicles (EVs). However, it becomes increasingly challenge to charge batteries at low temperatures (< 5 °C), which is a major challenge facing adoption of EVs in cold climate

The primary factor limiting the ability of state-of-the-art LIBs to charge under both high-rate and low-temperature conditions is the propensity for Li metal to plate out on the graphite surface during charging.[1] The poor reversibility of Li metal in LIB electrolytes leads to rapid capacity fade, consumption of the electrolyte, and safety concerns. This problem is exacerbated in high-energy density cells with thicker electrodes, leading to energy-power tradeoffs.

To mitigate these effects, we have previously demonstrated that Li plating can be significantly suppressed during fast charging by implementing an atomic layer deposition (ALD) surface coating of a lithium borate-carbonate (LBCO) solid electrolyte directly onto calendered graphite anodes[2]. This ALD single-ion conductor has previously been shown to exhibit ionic conductivities above $2*10^{-6}$ S/cm and excellent electrochemical stability, including with Li metal.[3] In comparison to uncoated control electrodes, the LBCO a-SEI coating: 1) eliminates natural SEI formation during formation cycles, 2) decreases interphase resistance by >75% compared to that of the natural SEI, and 3) extends cycle life significantly under fast-charging conditions.

Building upon this demonstration of improved fast-charge ability with ALD coatings, in the current study, we demonstrate the ability of an artificial SEI layer deposited by ALD to also enable fast charging at sub-zero temperatures (down to -10 °C) while maintaining extreme fast charging rates (up to 6C) without Li plating[4]. This remarkable result is enabled by a synergistic combination of interfacial modification by ALD and fabrication of 3-D architected electrodes. These results demonstrate the power of decoupling interfacial and bulk mass transport effects under extreme charging temperatures, providing new fundamental insights into the factors that limit performance and result in cell degradation. In the future, the ability to fast-charge LIBs in cold environments will accelerate electrification of technologies in a broader range of geographic locations.

References

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3. E. Kazyak et al., *J. Mater. Chem. A* **6**, 19425 (2018)
4. T. H. Cho, Y. Chen, D. W. Liao, E. Kazyak, D. Penley, N. P. Dasgupta, *Submitted* (2024)

1:45pm **AA1-MoA-2 Atomic Layer Deposition of Lithium Borate and Borophosphate Thin Films for Lithium-ion Battery Applications***, **Tippi Verhelle**, A. Dhara, L. Henderick,* Ghent University, Belgium*; J. Meersschaut,* IMEC Belgium*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

Lithium-ion batteries (LiBs) play a vital role in modern society, but challenges arise from unwanted side-reactions at the electrolyte/electrode interface. A promising solution to this issue involves the application of an ultrathin, protective coating on the electrode using atomic layer deposition (ALD). Previous studies highlight ALD's effectiveness in addressing such challenges, emphasizing thickness control and conformality [1]. Our research focuses on advancing this strategy by developing lithium borophosphate as a coating material for enhanced LiB performance.

In the work of Kazyak et al. [2], who used ALD to obtain a lithium borate-lithium carbonate intermixed material, the potential use of lithium borates (albeit with carbon inclusion) was evidenced. In this work, we aimed to achieve ALD of pure lithium borate films, which served as a starting point for new and optimized lithium borate mixtures towards even more controlled electrochemical properties. Our aim is to intermix this pure lithium borate with lithium phosphate, leveraging the latter's stability. Despite lithium phosphate's inherently lower ionic conductivity, namely 1.4 x 10^{-10} S cm^{-1} as deposited by ALD [3], studies using other deposition techniques have demonstrated that combining it with lithium borate effectively enhances the conductivity [4].

Our research introduced a new process for depositing lithium borate, utilizing lithium bis(trimethylsilyl)amide (LiHMDS), H_2O and trimethylborate (TMB). At 250°C, the process exhibited linear growth, with a growth per cycle of 0.04 nm, and saturation for every precursor step (Fig. 1). This process displayed a variation in composition as indicated by ERD (Fig. 2) and electrochemical properties at different deposition temperatures. With impedance spectroscopy (EIS), we calculated the conductivity of an 80 nm lithium borate thin film deposited at 250°C to be 1.60 ± 0.03x 10^{-7} S cm^{-1}at 30°C, with an activation energy of 0.58 ± 0.01 eV (Fig. 3).

Integrating this lithium borate with the well-known lithium phosphate process [5] was achieved through a supercycle approach. Varying the number of lithium phosphate subcycles relative to a constant number of lithium borate subcycles resulted in coatings with distinct electrochemical behavior. Our findings offer practical insights for tailoring LiB coatings with controlled electrochemical properties, contributing to advancements in battery technology.

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2:00pm **AA1-MoA-3 Fluorine-free ALD Process Produces Fluorine-rich Cathode Electrolyte Interphase for Lithium Batteries***, **Giulio D'Acunto**, S. Shuchi,* Department of Chemical Engineering, Stanford University*; Y. Cui,* Department of Materials Science and Engineering, Stanford University; Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory; Department of Energy Science and Engineering, Stanford University*; S. Bent,* Department of Chemical Engineering, Stanford University; Department of Energy Science and Engineering, Stanford University

The continuous evolution of lithium-ion and lithium-metal batteries is pivotal for meeting the growing demands of high-performance energy storage systems. Central to this advancement is the enhancement of the cathode-electrolyte interphase (CEI), a critical component in determining battery efficiency and safety. A fluorine-rich CEI is widely recognized for its role in enhancing Li^+ ionic conductivity and chemical stability. A fluorine-rich CEI is typically achieved by using fluorinated solvents, fluorinated additives, or an artificial SEI comprised of fluorinated materials. This research introduces an innovative approach to CEI improvement through the application of atomic layer deposition (ALD). Our design approach aims to utilize i) the high reactivity of the ALD precursors toward the existing cathode binder (polyvinylidene fluoride, PVDF), and ii) the surface acidity of the deposited thin film to induce more anion decomposition, further enhancing the fluorination of the CEI.

Leveraging the nanoscale precision and uniformity of ALD, we chose to develop a LiAlxOy coating on lithium-nickel-manganese-cobalt-oxide (NMC) cathodes. Li(HMDS) and TMA are used as metal precursors and water as a co-reactant. An M1-O-M2-O super-cycle, where M1 and M2 refer to the metal precursors, and O represents water, is used for the $LiAl_xO_y$. After exploring process parameters to enhance Li content and achieve saturation, the coated NMC cathode was characterized by angle-resolved X-ray photoelectron spectroscopy (ARXPS). We found evidence of Li-F species comprising nearly 50% of the total fluorine species, in contrast to less than 10% for the uncoated NMC cathode. The effectiveness of the fluorine-rich coating was then evaluated with electrochemical measurements, comparing the ALD-coated NMC to the bare NMC. The capacity retention of the coated cathode outperforms by almost a factor six that of the bare cathode, using a baseline carbonate-based electrolyte. Moreover, the characterization of the CEI after 50 cycles in the battery shows that i) the F-rich ALD coating is preserved during cycling, working as an artificial CEI, and ii) the native CEI overlayer atop the ALD layer is more fluorinated due to the surface acidity impact. This novel approach using ALD to achieve a fluorine-rich artificial CEI via a fluorine-free cathode coating process offers a more environmentally friendly approach compared to traditional methods.

2:15pm **AA1-MoA-4 Atomic Layer Deposition of Interface-Engineered $Li_4Ti_5O_{12}$: Toward High-Capacity 3D Thin-Film Batteries***, **Jan Speulmanns**, S. Bönhardt, M. Czernohorsky, W. Weinreich,* Fraunhofer Institute for Photonic Microsystems IPMS, Germany

Atomic layer deposition (ALD) of Li-compound thin films has aroused significant interest in recent years. Promising applications are Li-ion thin-film batteries (TFBs), protective particle coatings, and neuromorphic computing. Here, we evaluate $Li_4Ti_5O_{12}$ (LTO) fabricated by ALD for 3D solid-state TFBs to power upcoming autonomous sensor systems.

The simultaneous increase of power and energy density of 3D TFBs can be achieved by coating the battery layer stack over microstructured substrates. The required conformal, pinhole-free deposition and stoichiometric control of nanometer-thin films on highly structured surfaces are only accessible via ALD. However, direct ALD of Li-compound anodes remains challenging.

In previous studies, we developed a thermal three-step ALD process for Li-containing oxides on 200 mm Si wafers. Lithium-tert-butoxide (LTB) and lithium hexamethyldisilazide (LiHMDS) were proven as suitable precursors, forming spinel LTO with low impurities. The excellent electrochemical behavior of LTO with LiHMDS was linked to the film texture.

In this work, we optimize the LTO ALD process with LTB toward 3D TFBs and evaluate the electrochemical performance for the first time. A process with a saturated growth per cycle of 1.06 Å $cycle^{-1}$ for 7 s LTB pulses was developed. An ALD temperature window between 240 and 320 °C was identified. The effect of the substrate on the initial growth and crystallization behavior was investigated. The crystallization-inhibiting effect of the titanium nitride current collector is suppressed by introducing an AlO_x interlayer.

Planar LTO films with various thicknesses of up to 75 nm were manufactured by ALD, increasing the footprint capacity from 1.5 to 4.3 µAh cm^{-2}. However, the C-rate performance of thicker films is inferior due to the low conductivities of LTO. 50 nm films demonstrate the optimum energy and power density. A footprint capacity of 1.95 µAh cm^{-2}, corresponding to 65 % of the theoretical capacity, was achieved at 50 C.

Next, we evaluate ALD LTO films as 3D TFB anodes. The conformality of the ALD process was improved by extending the LTB pulse and purge times to 11 and 20 s. The purge time is the key factor enabling a step coverage of 70 % for holes with an aspect ratio of 10:1. 3D samples with an area-enhancement factor of 9 obtained a footprint capacity of 19.8 µAh cm^{-2} at 1 C. The large capacity increase by a factor of 6.75 compared to planar samples is according to the conformality. The power performance of 3D LTO samples at high C-rates will be discussed. The superior performance of ALD LTO is a key enabler for high-volume production of on-chip high-capacity 3D TFBs.

2:30pm **AA1-MoA-5 ALD for Advanced Lithionic Devices: Hybrid Ultrathin Solid-State Electrolytes***, **Ilyass GHANDARI**, N. GAUTHIER, S. POULET,* CEA-LETI, France*; M. BECHELANY,* CNRS, France*; M. BEDJAOUI,* CEA-LETI, France

Innovative micro-supercapacitors (MSCs) such as LiPON based MSCs are emerging to address the technological challenges faced at higher frequencies (>kHz),especially energy harvesting and storage, which requires efficient materials coupled with improved microfabrication techniques to unlock the full potential of such devices. In this way, conformal and self-limiting surface reactions enabled by Atomic Layer Deposition (ALD) give great advantages to form and optimize Lithium based thin films compatible with complex geometries. Here in, a multidisciplinary approach was conducted to develop the thermal ALD process, characterize the physico-chemical properties and evaluate the electrical performances of nano-hybrid Solid State Electrolytes (SSE).

The thermal ALD process for ultrathin LiPON films (<25nm) is realized using Li-Bistrimethylsilylamide (LiHMDS) and Diethylphosphoramidate (DEPA) precursors in a deposition temperature range 300-350°C. To further optimize LiPON's electrochemical performances, Trimethyl Aluminium (TMA) and H_2O were pulsed to incorporate Al_2O_3 in SSE films. Ellipsometry was used to calibrate the growth rate of LiPON-based films. The microstructure was analyzed by X-Ray Diffraction (XRD) to highlight the amorphous nature of the thin films, indicating that the Al_2O_3 incorporation preserves favorable amorphous structure, which is a key characteristic for achieving excellent electrochemical performances [1]. The XPS spectra show typical core peaks (Li_{1s}, P_{2p}, O_{1s}, N_{1s}, Al_{2p}) corresponding to different LiPON based samples. The analysis reveals that Al_2O_3 insertion seems to impact the nitrogen environment. From N1s spectra (Fig.1), the peaks present two main components located at 397 eV and 399 eV, attributed respectively to a divalent nitrogen state (N_d) and a trivalent nitrogen state (N_t) [1], whose proportion evolves as a function of Al_2O_3 incorporation. Thus, the concentration of divalent nitrogen becomes predominant over trivalent nitrogen, inducing an increase in the N_d/N_t fraction when more Al_2O_3 is introduced. This variation has frequently been reported as a major factor in improving Li-ion mobility [1]. The Electrochemical Impedance Spectroscopy (Fig.2) addresses the changes in Li-ion conductivity of the LiPON films upon addition of Al_2O_3 concentration.

This work provides a solid ALD approach with promising potential to optimize the electrical performances (ie Li^+mobility, areal capacitance etc) in ultrathin SSE, shedding light on the application of such hybrid microstructures in several Lithionic devices such as micro-supercapacitors, micro-batteries and transistors.

1:ACS Appl.Mater.Interfaces2016,8,11,7060–7069

2:45pm **AA1-MoA-6 Low Temperature ALD of Vanadium Sulfide (Ultra)thin Films for Nanotubular Supercapacitors***, **Raul Zazpe**, M. Sepulveda, J. Rodriguez-Pereira, L. Hromadko, M. Kurka, H. Sopha, J. Macak,* University of Pardubice, Czechia

Metal sulfides (MSs) are materials exhibiting a great variety of interesting inherent properties including semiconducting nature, high electrical conductivity and capacitance, (photo)catalytic capability, excellent redox reversibility and their abundance and low-cost.[1] Thus, MSs nanomaterials are a prospective alternative in multidisciplinary applications demonstrating a promising performance in energy conversion and energy storage devices[1] sensors,[2] photodetectors,[3] and biomedical applications[4] among others. Among the wide range of MSs, vanadium-based materials exhibit outstanding electrical conductivity and capacitance together with an excellent redox reversibility and electrochemical properties.[5] Vanadium is an abundant element that exhibits multiple oxidation states, which provides a rich and versatile chemical reactivity. Consequently, vanadium sulfides have been explored as promising materials as electrode material for supercapacitors (SCs).[6]

Herein, we present for the first time the synthesis of vanadium sulfide (VxSy) by Atomic Layer Deposition (ALD) based on the use of tetrakis(dimethylamino) vanadium (IV) and hydrogen sulfide.[7] The (ultra)thin films V_xS_y are synthesized in a wide range of temperatures (100 - 225 °C) and extensively characterized by different methods. The chemical composition of the V_xS_y (ultra)thin films reveals different vanadium oxidation states and sulfur-based species. Extensive X-ray photoelectron spectroscopy analysis studies the effect of different ALD parameters on the V_xS_y chemical composition. We further explore the electrochemical properties of ALD V_xS_y (ultra)thin films as electrode material for supercapacitors by coating TiO_2 nanotube layers (TNTs) with different numbers of V_xS_y ALD cycles at 100 °C. Long-term cycling tests reveal a gradual decline of electrochemical performance due to the progressive V_xS_y thin films dissolution under the experimental conditions. Nevertheless, V_xS_y coated TNTs exhibit significantly superior capacitance properties, as compared to the blank counterparts. The enhanced capacitance properties exhibited are derived from the presence of chemically stable and electrochemically active S-based species on the TNTs surface.

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3:00pm **AA1-MoA-7 Boosted Zn^{2+} Storage Performance of Hydrated V_2O_5 by Defect and Heterostructure***, V. Nguyen, J. Kim, **Seung-Mo Lee**,* Korea Institute of Machinery & Materials (KIMM), Republic of Korea

The inherent sluggish Zn^{2+}diffusion and poor electronic conductivity limit the ion intercalation/deintercalation process in aqueous Zn-ion batteries (ZIBs) using an oxide-based cathode. Here, we demonstrated that a heterostructure in the form of defective hydrated V_2O_5 embedded in the porous carbon textile (d-VOH@CT) could tackle these issues. To obtain the d-VOH@CT heterostructure, a V_2O_5 layer was deposited on waste cotton textiles using atomic layer deposition (ALD), followed by pyrolysis. The carbothermic reduction of V_2O_5 ($C + V_2O_5 \rightarrow C' + V_2O_3 + VC + CO/CO_2(g)$) coated on cotton textile transformed the cotton into the porous carbon textile covered with a hybrid VC/V_2O_3 layer. In the air, this VC/V_2O_3 layer was naturally oxidized to defective hydrated vanadium oxide (d-VOH) flakes embedded in the porous carbon textile (CT). The additional edges created by crystal defects significantly promoted facile Zn-ion adsorption and intercalation. Expanded interlayer spacing and reduced crystalline domain size kinetically facilitated fast Zn-ion diffusion in d-VOH flakes with shortened diffusion paths. Moreover, the heterostructure of d-VOH on the conductive carbon textile triggered rapid charge transfer, leading to high rate capability and structural stability. The ZIBs fabricated using the d-VOH@CT cathode delivered a preferable reversible capacity of 416 mA h g^{-1} at 0.1 A g^{-1}, an impressive energy density of 293 W h kg^{-1}, and a long cycle life. In addition, the d-VOH@CT heterostructure was able to be used as a freestanding cathode for a flexible ZIB with outstanding mechanical robustness and electrochemical stability.

3:15pm **AA1-MoA-8 High Throughput Atomic Layer Deposition of Niobium Oxide Thin Film for Lithium-ion Battery Application***, S. Kamimura, C. Dussarrat,* Air Liquide Laboratories, Japan*; **Nicolas Blasco**,* Air Liquide Advanced Materials, France

Surface modification of cathode active materials (CAMs) by atomic layer deposition (ALD) is known to improve the structural stability, ionic interfacial conductivity, and consequent charge-discharge characteristics of lithium-ion batteries (LiBs). The powder ALD technique has been shown to be highly effective in producing inorganic films, even on the particles of CAMs, with high conformality, uniformity and self-limiting growth, providing exceptional control over film thickness down to sub-nanometer level. Although the current powder ALD technique can successfully handle large amounts of nanoparticles for conformal coating with ALD, it requires a large amount of precursor for high surface area when working with fine particles, causing unique challenges for the ALD precursor. The dosage of the precursor/co-reactant is directly related to the surface area of the particles; the larger the area, the longer the exposure time required, resulting in a longer process time. Therefore, an ALD precursor that enables a high growth rate of inorganic thin films is in high demand.

We have conducted the synthesis screening of several types of organometallic niobium precursors for ALD and have successfully deposited an ALD Nb_2O_5 film using an organometallic precursor called Nautilus. This precursor showed a higher volatility & higher growth rate than tris(diethylamide)(tert-butylimido)niobium (TBTDEN). The Nb_2O_5 thin film growth on Si wafer was evaluated by QCM, XPS and ellipsometry measurements, and an outstanding GPC of 2 Å/cycle was determined at 225 ^{o}C, increasing with reactor temperature while maintaining excellent step coverage.

Powder ALD with Nautilus precursor was performed at 250 ^{o}Cusing a fluidized bed reactor to achieve uniform Nb_2O_5thin film coating on CAMs. The TEM/EDS analysis shows that the entire surface of CAMs particles was uniformly covered with Nb_2O_5thin film with a thickness of ~1 nm even after 3 ALD cycles. The electrochemical performance measurements were conducted in R2032 coin-type cells (half cell). We clearly found that the Nb_2O_5thin film coating can suppress undesirable side reactions such as electrolyte decomposition on CAMs, and lead to the long-term cycle stability of discharge capacity. In the presentation, we will introduce the ALD characteristics of Nautilus and its LiB performance evaluation.

ALD Applications
Room Hall 3D - Session AA2-MoA

Applications in ULSI FEOL: Gate Electrodes & Contact Metals, High-K, and 3D Transistor Fabrication

Moderators: Scott Clendenning, Intel Corporation, **Christian Wenger**, IHP - Leibniz Institut fuer innovative Mikroelektronik

4:00pm **AA2-MoA-11 Thermal Atomic Layer Deposition of Boron Containing Oxide Films as Solid Sources for Doping of Advanced Memory Devices***, Y. Shen,* Beijing Superstring Academy of Memory Technology, China*; S. Yang,* Institute of Microelectronics, China*; **Jinjuan Xiang**,* Beijing Superstring Academy of Memory Technology, China*; J. Liu, J. Gao,* Institute of Microelectronics, China*; G. Wang, C. Zhao,* Beijing Superstring Academy of Memory Technology, China

In recent decades,with the continuous scaling downof devicedimensionsand the emergence of complex three-dimensional structures,conventional ion implantation cannot meet the requirements of non-damage and uniform doping of the nonplanar transistor architecture. Atomic layer deposition (ALD) is one of the mostpromising methods for forming controlled and conformal dopant-containing layer. Compared to plasma enhanced ALD, thermal ALD has better ability for achieving the required conformity conditions and high scalability for 3D structures with higher AR ratio. By combing of ALD with the heat-driven annealing,non-damage and conformal doping in Si can be achieved. However, ALD doping still faces many challenges, one of the big issues is that B_2O_3 films cannot grow sustainably, which hinders its further application [1, 2].

In this paper, Al_2O_3 and SiO_2 layer were used as enhance layer to promote the deposition of B_2O_3 by thermal ALD. By using Al_2O_3 interlayer, low lewis acidity of Al−OH- was formed. Boron is evenly distributed in $B_xAl_{1-x}O_y$ film with a content of about 15 at. %, which is higher than that in $B_xSi_{1-x}O_y$ film. After rapid thermal annealing, the maximum doping concentration of B can reach 2E20 atom /cm^3, and the doping concentration of Al in Si is low. When SiO_2 as the enhance layer, the maximum B doping concentration is 3E19 atoms /cm^3. In addition, the content of B in $B_xSi_{1-x}O_y$ film and doping concentration in Si are higher at low B:Si ratio of 4:3 than at B:Si of 5:1, which is mainly due to the fact that enough SiO_2 layer can promote the growth of B_2O_3 more effectively. Uniform and dose-controlled doping achieved by this thermal ALD doping is believed to have great application prospects in 3D structures device, especially for vertical stacked dynamic random-access memory (DRAM).

4:15pm **AA2-MoA-12 Plasma-Enhanced ALD of Thin Conductive Cu Films***, **Maria Gabriela Sales**, N. Nepal, P. Litwin, D. Boris, S. Walton, V. Wheeler,* U.S. Naval Research Laboratory

Interconnect vias are conduits that transport signals between circuit components, and are typically made of Cu due to its low resistivity, high thermal conductivity, low coefficient of thermal expansion, high melting temperature, and good mechanical properties. Traditionally, Cu interconnect vias are fabricated through electrochemical deposition which is followed by chemical mechanical polishing and various cleaning steps to get the Cu mostly conformal with the via structure. However, these processes tend to leave behind voids in the via and/or leftover Cu in areas with unwanted Cu growth. Atomic layer deposition (ALD) is a promising alternative technique to avoid such reliability issues because it is a saturating and self-limiting deposition process. Furthermore, the layer-by-layer nature of ALD allows for precise thickness control, which is an important consideration in the scaling of circuit components.

For proper implementation of ALD in the deposition of via structures, we need to study the key ALD processing conditions that produce Cu thin films with the desired chemical and physical properties and optimal electrical performance. In this work, we study a plasma-enhanced Cu ALD process in a Veeco Fiji G2 reactor equipped with a turbo pump and substrate biasing, using copper(I)-N,N'-di-sec-butylacetamidinate, or $[Cu(^{s}Bu\text{-}amd)]_2$, as our Cu precursor and H_2 plasma as our reducing reactant. We present a parametric study where we investigate the different growth conditions, i.e., growth temperature, precursor pulse, composition of gases in the plasma, and plasma power, among others, and observe how they affect Cu film growth. In-situ ellipsometry is used to monitor growth rate, post-deposition X-ray photoelectron spectroscopy (XPS) is used to analyze the film and interface chemistry, and atomic force microscopy (AFM) is used to examine the resulting film morphology. Initial results show metallic Cu films were successfully deposited using a 300 W Ar/H_2 plasma with a 20% Ar flow fraction and a 10-second plasma pulse duration. This demonstrates the feasibility of this PEALD Cu process; however, to-date films are limited in thickness, and possible approaches to overcome these issues will be discussed.

4:30pm **AA2-MoA-13 Selective Atomic Layer Deposition of Ultra-Thin Ru on W for Metal Contact***, **Rong Chen**, Z. Qi, E. Gu,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China*; B. Shan,* State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, China*; K. Cao,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

Atomic selective area layer deposition (ASD) of ruthenium has attracted considerable interest for various applications in nanoelectronics and due to its potential role in front-end-of-line (FEOL) contact in future technology nodes. In this talk, it provides insight into the effects of discrete feeding atomic layer deposition (DF-ALD) process and post-processing treatments on the nucleation of Ru film and selective growth on W/SiO2. DF-ALD process can improve the purging of excess physically adsorbed precursors, provide more reaction sites, and increase the nucleation density. With DF-ALD, ultra-thin and low-resistivity Ru thin film on W contact was obtained. According to KMC theoretical calculations, when there are excess physical adsorption precursors and chemically adsorbed reaction by-products around the reaction site, there is a lack of steric hindrance required for chemical reactions and the reaction is difficult to occur. Due to the size-dependent mobility of nanoparticles and differences in substrate adsorption energy, post-processing more easily promotes nucleation defects in non-growth areas migration to the growth area. It is an effective way to eliminate non-growth area defects and amplify selectivity. The inherently selective ALD process is successfully transferred onto W/TiN/SiO_2 nanopatterns with ~100 nm pitch and obtained high selectivity with 5–6nm films on W and no defects in the SiO_2 and TiN regions. The results indicate that inherently selective ALD is a robust and general tool that has excellent application prospects in FEOL processes, which provides an innovative avenue for self-aligned nanostructures.

4:45pm **AA2-MoA-14 Effect of High Precursor Dose on the IZO Film Property Uniformity Within Wafer Deposited by Thermal ALD***, **Yuting Chen**, P. Yuan, X. Ma, Z. Jiao, Y. Shen, L. Chai, J. Xiang, M. Zeng, H. Sun, G. Wang, C. Zhao,* Beijing Superstring Academy of Memory Technology, China

Recently, IGZO-based vertical channel-all-around (CAA) thin-film transistors (TFT) for 2T0C dynamic random access memory (DRAM) with better density advantages has attracted wide attention. Zinc-doped In_2O_3 (IZO)is a potential gate electrode material for CAA TFT device, because of its relatively low resistivity, and low process thermal budget, which is perfectly suitable for IGZO-based devices. IZO material property deposited by ALD on 12-inch wafer has been rarely studied. Usually, to achieve better step coverage on high aspect ratio (AR) vertical structure, higher precursor dose is necessary, compared with the saturation dose obtained on planar structure. Hence, in this work, thermal ALD IGZO/Al_2O_3/IZO film stack, which simulated the gate stack in CAA TFT device, were employed as the vehicle to investigate the IZO film property at high precursor dose. Moreover, the samples of precursor inlet and outlet regions were analyzed to reveal the film uniformity within 12-inch wafer. Unexpectedly, the IZO film of inlet region has the worse electrical properties. Materials characterization were conducted to elucidate the mechanism of heterogeneity. Although XPS results shows no difference in the In/Zn composition ratio between the inlet region and the outlet region, XRD results shows higher In_2O_3 crystallinity in inlet region than outlet region, which is also confirmed by AFM scans. Based on these results, it can be inferred that high-dose precursor at the inlet position may lead to insufficient ALD reaction process, resulting in many defects in the IZO film and degraded electrical properties. The non-uniformity of IZO film poses some challenges for subsequent process integration, such as the CMP process.

This work highlights the significant impact of different regions within 12-inch wafer on the properties of films at high dose. In spite step coverage can be improved by increasing the precursor dose, too much precursor will lead to degenerated film at inlet region.

5:00pm **AA2-MoA-15 Development of ALD Gate Dielectrics for TMD Nanosheet FETs***, T. Lee, B. Chao, Y. Chung, Y. Su,* TSMC, Taiwan*; B. Liu, C. Su, C. Kei,* Taiwan Instrument Research Institute, Taiwan*; C. Cheng, **Pinyen Lin**, I. Radu,* TSMC, Taiwan

Superior electrostatics control of monolayer (1L) TMDs holds great potential in advancing the scaling of nanosheet (NS) transistors in advanced technology nodes [1]. One critical aspect is to achieve a conformal dielectric layer on TMD NS channel using atomic layer deposition (ALD) [2]. The main challenge in achieving high-quality gate dielectrics is forming a good nucleation layer on the dangling bond-free TMD interface. This study successfully used the ALD technique to form a uniform AlOx thin film on 1L-MoS2 without damaging the material. Furthermore, good performance of MoS2 NS nFET is also successfully demonstrated.

5:15pm **AA2-MoA-16 ALD in Semiconductor Logic Manufacturing: Challenges Met and Opportunities Ahead***, **David Towner**,* Intel Corp. **INVITED**

Atomic Layer Deposition has played a unique, enabling role in the evolution of semiconductor logic device manufacturing.ALD's ability to bring atomic level control to thin film deposition is particularly critical to applications at the heart of transistor performance, such as High-K gate dielectrics and workfunction materials.With the progression to 3-D transistor structures like FinFETs and RibbonFETs, ALD's ability to conformally deposit on complex topography is unparalleled.This talk will present one industry expert's take on ALD's success stories as well as the many challenges ahead, including less glamorous but important factors such as cost and manufacturability.Special effort will be taken to highlight opportunities for further innovation as we continue to advance Moore's Law.

ALD Applications
Room Hall 3D - Session AA1-TuM

Applications in ULSI BEOL: Interconnects, Diffusion Barriers, & DRAM

Moderators: Mike McSwiney, Applied Materials, **David Towner**, Intel Corp.

8:00am **AA1-TuM-1 Leakage Control of DRAM High-k Capacitor Stack by Ald Sc_2O_3, Y_2O_3 Inter-Layer**, ***Randall Higuchi****, A. Babadi, C. Chen, B. Zope,* Merck KGaA, Darmstadt, Germany

The scaling of DRAM devices and subsequent increase in memory density requires shrinking memory cell size, which necessitates engineering of the capacitor and transistor of the memory cell. Scaling of capacitor presents challenges in size shrink capacitor size and area shrinking, and reduction in number of stored charges. These factors contribute to increase in capacitor leakage, wherein it is critical to maintain leakage current $<10^{-7}$ A/cm^2 at the operating voltage [1].

ALD oxide films of Hf & Zr, when crystallized to non-monoclinic phase have high dielectric constant, and, therefore, utilized in the DRAM capacitor stack to achieve high capacitance. However, grain boundaries of these crystalline films form dominant carrier conduction paths leading to increased leakage current. Amorphous, thin ALD Al_2O_3 layer in the middle of the high-k stack is known to engineer grain boundary structure in the film creating tortuous carrier conduction path leading to lower leakage current [1]. In this work, we investigated alternate oxide materials for inter-layer that improve leakage performance of the capacitor stack compared to Al_2O_3 inter-layer. Our work demonstrated that ALD Sc_2O_3 or Y_2O_3 can be utilized as inter-layer in the DRAM high-k stack. ALD Sc_2O_3 resulted in 33% improvement and ALD Y_2O_3 resulted in 50% leakage current improvement compared ALD Al_2O_3 (deposited using trimethyl aluminum) inter-layer. Additionally, both Sc_2O_3 and Y_2O_3 inter-layer resulted in lower EOT increase compared to Al_2O_3.

References:

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8:15am **AA1-TuM-2 ALD Deposited IGO with High Thermal Stability (~ 800 ^{o}C) by Controlling Crystallinity for Multi-bit Operation 2T0C DRAM**, ***Jae-Hyeok Kwag****, S. Choi, J. Sim, T. Cho, C. Park, Y. Song, J. Park,* Hanyang University, Republic of Korea

The 2T0C DRAM has advantages compared to conventional Si channel 1T1C in terms of high cell density (~ 6F^2), long retention time (> 400 s), and multi-bit operation using the current sensing mode [1-2]. Oxide semiconductors (OS) have advantages such as extremely low off current ($< 10^{-18}$ μA/μm) [3]. Recently, capacitor-less 2T0C DRAM using a low off-current IGZO (In-Ga-Zn-O) channel was proposed. Since the FEOL fabrication includes a high-temperature process, high thermal stability is required to apply OS channel FET to DRAM. However, the electrical properties of the OS channel FET degraded above the 400 ^{o}C post-annealing process [4]. In general, Ga doping improves the thermal stability of OS. Among the various deposition methods for OS, atomic layer deposition (ALD) is a promising candidate because of its characteristics that allow easy doping concentration adjustment and easy sub-nanometer scale thickness control.

In this study, thermal stability (~ 800 ^{o}C) of Ga-doped InO channel FET was verified by controlling the thickness using the ALD method, and the 3-line based multi-bit operation of the 2T0C DRAM was confirmed. First, the InO channel FET was evaluated. The 250 ^{o}C deposited 3-nm thick InO using DBADMIn precursor was adopted to the channel layer. The c-axis aligned C(222) crystalline InO FET exhibits superior electrical properties by lowering the grain boundary effect [5] but degraded after 800 ^{o}C post-annealing for 3 hours, as shown in **Fig 1.**.To achieve high thermal stability, InO was doped with Ga using the ALD super-cycle method. The thickness of Ga-doped InO (IGO) was also evaluated because it is responsible for crystallinity. As shown in **Fig 2.**, Above the 10 nm thickness of the IGO channel, FET exhibits superior thermal stability even after the post-annealing process at 800 ^{o}C for 3 hours. The 800 ^{o}C post-annealed 10 nm thick IGO FET was adopted because the on-current and field-effect mobility were similar to 400 ^{o}C post-annealed InO channel FET (InO: 55.5 cm^2/Vs, IGO: 58.9 cm^2/Vs). As shown in **Fig 3.**, the current sensing multi-bit operation is exhibited regardless of channel material, and the RBL current has similar values according to the WBL voltage because the mobility is similar with InO and IGO channel FET.

References

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8:30am **AA1-TuM-3 Improving Electrical Properties of ZrO_2 Dielectric Films Without Sacrificing Tetragonal Crystallinity via Gd Doping**, ***Seungwoo Lee****, Y. Choi, J. Jeong, J. Nam,* Kyung Hee University, Republic of Korea*; H. Oh, H. Kim, Y. Park,* SK trichem, Republic of Korea*; W. Jeon,* Kyung Hee University, Republic of Korea

ZrO_2 has been used as an insulator film for dynamic random-access memory capacitors for a long time due to its compatibility with TiN electrodes and the high maturity of the atomic layer deposition (ALD) process. Tetragonal ZrO_2 thin films with a high dielectric constant (~40) on TiN electrodes could be obtained relatively easily by ALD. However, there are limitations to using only ZrO_2 due to the leakage current problem. The inevitably present grain boundaries acted as the dominant carrier conduction path. Al-doped ZrO_2 effectively suppressed leakage current by reducing the grain size and inducing a winding conduction path, but it also caused the crystallinity of ZrO_2 to deteriorate. Therefore, further scaling requires new dopants that can replace the role of Al without sacrificing the tetragonal crystallinity of ZrO_2.

In this regard, this presentation discusses the results of employing Gd as a dopant to replace Al. The Gd_2O_3 ALD process for doping in ZrO_2 was designed utilizing a novel Gd precursor. We investigated the effectiveness of Gd as a dopant for ZrO_2 by fabricating metal–insulator–metal capacitors with Gd-doped ZrO_2 as an insulator film and analyzing its electrical properties. As the ratio of Gd_2O_3 in the dielectric increased, the capacitance density decreased, but the leakage current characteristics were noticeably improved. Furthermore, as a result of analyzing the crystallinity of the Gd-doped ZrO_2 thin film by X-ray diffraction analysis, it was found that Gd doping did not significantly deteriorate the tetragonal crystallinity of ZrO_2.

Acknowledgments This work was supported by the BK21 Plus program. The authors would like to thank SK Trichem for their support and permission to publish this collaborative work.

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8:45am **AA1-TuM-4 Area Selective Co ALD for Highly Reliable ULSI Interconnect System and the Establishment of ALD Process Design Framework**, ***Yukihiro Shimogaki***, The University of Tokyo, Japan **INVITED**

As ULSI becomes more highly integrated, the current density flowing through Cu multilevel interconnects increases, and it has become difficult to ensure device reliability owing to the emergence of wire breakage defects caused by electromigration. In addition, device performance degradation owing to RC delays is a major problem. To solve these issues, it is essential to form a liner layer with a material that exhibits good adhesion to Cu, suppresses electromigration, and crowns the Cu line with a metal cap during the damascene process. It is also important to increase the proportion of Cu in ultrafine Cu interconnects and reduce the effective resistance by employing a thin barrier metal with high Cu diffusion barrier properties.

To address these issues, we have reported that CoW alloy thin films synthesized by ALD have better Cu diffusion barrier properties than existing TaN and higher adhesion to Cu than Ta. We have also shown that Co can be selectively formed on the Cu surface by combining ALD and ALE, and can be used as a metal cap layer.

In this presentation, we report the results of the evaluation of the Cu diffusion barrier properties of CoW films and the development of an AS-ALD process for Co films. To develop an efficient AS-ALD process, we introduce a method to search for novel precursor compounds with appropriate vapor pressures, and a method to estimate and measure the adsorption equilibrium constants of the precursor candidates. We also introduce a method for in situ observation of the incubation cycle by reflectance spectroscopy of the growth surface, and report the results of our investigation of growth conditions and surface treatment methods that exhibit selectivity. These methods are summarized to establish a framework for the ALD process design.

Figure 1 shows the Co film growth on SiO_2 by ALD and ALD/ALE combination. CCTBA (Dicobalt hexacarbonyl tert-butyl-acetylene) was employed as the Co precursor, and a sequential supply of SO_2Cl_2 and HFAC was used for Co-ALE. Co-ALE was effectively remve the small nuclei formed on the SiO_2 during Co-ALD, which can be used to enhance the selectivity of Co AS-ALD. Figure 2 shows the leakage current of the L/S pattern electrodes with Co-ALD, Co-ALD with HMDS pretreatment, Co-ALD with HMDS pretreatment and ALE combination. Co-ALE and HMDS pretreatments effectively suppressed unwanted nucleation on SiO_2, while Co thin films were selectively grown on the Cu surface.

9:15am **AA1-TuM-6 Atomic Layer Deposition (ALD) of Transition Metal Dichalcogenides (TMDS) Layers as Metal Diffusion Barriers for Back-End-of-Line (BEOL) Applications***, A. Mane,* Argonne National Laboratory*; S. Katta, J. Morris, C. Phatak,* ***Jeffrey Elam,*** Argonne National Laboratory, USA

The aggressive pursuit of miniaturization in microelectronics has led to a significant reduction in the size of individual device features, consequently boosting device density on chip. This heightened density necessitates more metal interconnect wirings, which, in turn, requires a reduction in wiring dimensions and an increase in the aspect ratio of vias and trenches [https://irds.ieee.org/]. As a result, existing metal lines, typically composed of copper and a liner acting as a diffusion barrier, must undergo proportional shrinking. Scaling down the barrier layer creates a relatively larger volume for copper, effectively keeping resistivity low. However, conventional Ta/TaN thin barriers may exhibit poor performance below 3nm and eventually fail. Therefore, there is substantial interest in exploring new metal diffusion barrier materials, such as two-dimensional Transition Metal Dichalcogenides (2D-TMDs) which hold promise for serving as effective diffusion barriers at smaller thicknesses and layered structured [Deijkers *et al*., Adv. Mater. Interfaces 2023, 10, 2202426].

Here, we present our recent work on thermal low-temperature (200-400℃) ALD of MX_2 layers including MoS_2, HfS_2, and TaS_2. The ALD of these layers was investigated using in-situ quartz crystal microbalance (QCM) and spectroscopic ellipsometry measurements. Following optimization of the ALD processes, we applied ultrathin layers (4-10nm) of MoS_2, HfS_2, and TaS_2 on Si, SiO_2, and SiN wafers. Subsequently, MOS-type devices were fabricated by depositing 50nm thick copper dots using the sputtering deposition. These MX_2-intigrated MOS devices underwent testing via time-dependent dielectric breakdown (TDDB) measurements. The time-to-breakdown of structures under high electric field stress conditions and failure time were examined as functions of thickness and MX_2 layer chemistries. In addition to TDDB studies, the barrier properties of the MX_2 layers were evaluated using the standard buffer oxide etch (BOE) test. Various types of MX_2-based MOS structures were dipped in a BOE solution, and the etch rate of SiO_2 and SiN was determined and correlated to MX_2 chemistry. This wet etch test study is crucial for evaluating material stability, particularly concerning Cu metal adhesion and chemical stability, which are pertinent during the chemical mechanical planarization (CMP) process. Based on the obtained results, we underscore the potential of ALD for implementing 2D-TMD barriers in BEOL metallization applications.

9:30am **AA1-TuM-7 High-Quality Co Thin Film by Thermal ALD Using CCTBA Precursor by Controlling H_2 Dose***,* ***Jun Yamaguchi,*** *N. Sato, A. Tsukune, T. Momose, Y. Shimogaki,* The University of Tokyo, Japan

With the scaling of semiconductor integrated circuits, RC delay and power consumption have increased owing to higher line resistance, and reliability degradation due to electromigration (EM) has become a problem. The use of cobalt (Co) in interconnect layers has attracted attention as a solution to these issues. Co liner, Co cap, and Co interconnects replacing Cu, are expected to address these challenges. For these applications, it is necessary to form high-quality, low-resistance Co ultrathin films uniformly on both the macroscale (entire wafer) and microscale (via, trench). Therefore, the use of atomic layer deposition (ALD) is desirable. From the perspective of substrate damage and step coverage, thermal ALD is preferable to plasma-enhanced ALD. However, the chemical options available for thermal ALD are limited. For instance, while there have been reports of Co-ALD utilizing the $Co(DAD)_2$ precursor,[1] the issue arises from $Co(DAD)_2$ being a solid with a low vapor pressure. In contrast, CCTBA is a highly volatile liquid and an appropriate Co precursor. Therefore, in this study, we focus on the thermal ALD of Co using CCTBA.

Hot-wall ALD equipment was used for Co deposition. CCTBA and H_2 were used as the precursor and reactant, respectively, and N_2 was used as the carrier and purge gases, respectively. CCTBA was vaporized at 45℃ and bubbled with the carrier gas. The chamber temperature was maintained at 100℃. A sputtered Cu film was used as an underlayer. The composition of the Co film was measured using XPS, and the film thickness was determined using SEM.

Figure 1 shows the growth per cycle (GPC) of the Co film according to the CCTBA supply time. The GPC became saturated after 5 s, and the saturated GPC (0.05 nm/cycle) was smaller than the Co monolayer thickness (0.2 nm). This suggests that the deposition was self-limited via the surface saturation of the adsorbing precursors, which is typical of ALD. Figure 2 shows a cross-sectional SEM image of the Co film deposited on a Si trench structure with an aspect ratio of 8.4. Conformal deposition, a feature of ALD, has been achieved. Figure 3 shows the composition of the Co film versus the H_2 dose. As the H_2 dose increased, the amount of carbon impurities decreased, and the film purity improved. Figure 4 shows the XPS results for the Co film deposited under high H_2 supply conditions. No peaks of C and O, which were present in the CCTBA precursor, were observed, indicating the successful deposition of a high-quality Co film. The Co film resistivity was measured to be 27 μΩ·cm with a thickness of 36 nm.

9:45am **AA1-TuM-8 Improved Properties of Atomic Layer Deposited Ru Films by Providing Additional Reactant for Cu Alternative Interconnects***,* ***Jeongha Kim,*** *K. Sang Bok,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; T. Cheon,* Daegu Gyeongbuk Institute of Science & Technology (DGIST), Republic of Korea*; S. Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Ru emerges as a next-generation interconnect materials capable of overcoming the scaling limits encountered with Cu interconnect [1]. Generally, as the deposition temperature increases, the properties of metal thin films deposited by ALD improve due to the grain size increase and impurities reduction by the enhanced chemical reaction. But at deposition temperatures where the precursor thermal stability isn't ensured, its thermal decomposition occurs, leading to degraded in thin film properties such as increased resistivity owing to the significant impurities and retarded grain growth. In this study, a novel ALD-Ru process has been developed, which provides additional reactant followed to obtain high-performance ALD-Ru process capable of maintaining excellent properties, even at temperatures where precursor thermal decomposition happen. Here, a Ru metalorganic precursor, tricarbonyl(trimethylenemethane)ruthenium $[Ru(TMM)(CO)_3]$ was used for ALD-Ru. It was reported that by using this precursor, a high-quality film with a very low resistivity (~12.9 μΩ·cm) was obtained in ALD temperature window (260℃)[2]. But, the precursor thermal stability has been kept to ~260℃ and at 275℃, the thermal decomposition of the precursor started and the resistivity of the film deposited at 300 ℃ was again increased due to the incorporation of carbon impurity. In this study, to improve the properties of Ru thin film, ALD-Ru process was done at higher deposition temperature at 310℃. Moreover, to remove contamination of the film resulting from the precursor thermal decomposition, NH_3 has been provided as an additional reactant followed by providing the main counter reactant, O_2, which is called 6-step ALD process (figure 1). Thus, when only O_2 was used (4-step ALD), the GPC was as high as ~2.4 Å/cycle and with the additional injection of NH_3, the GPC decreased to ~1.3 Å/cycle. The resistivity of the film was as high as 20.1 μΩ·cm using a conventional 4-step process but with 6-step process, is was decreased to ~13.6 μΩ·cm. In addition, an increase in peak intensity was confirmed through XRD analysis (figure 2), indicating the improvement of the film crystallinity by 6-step ALD process. An ALD-Ru film with a thickness of 26 nm was obtained with an excellent physical and compositional conformality and nearly 100% step coverage at the hole feature with a high aspect ratio of ~25. In summary, 6-step ALD-Ru process to supply additional reactant followed by the main counter reactant can provide the valuable process option to obtain the high-quality metal film at higher deposition temperature where the precursor thermal decomposition.

ALD Applications
Room Hall 3D - Session AA2-TuM

Energy: Solar Energy Materials I

Moderators: Wei-Min Li, Jiangsu Leadmicro Nano-Equipment Technology Ltd., **Nathanaelle Schneider**, CNRS-IPVF

10:45am **AA2-TuM-12 ALD Layers and Interfaces in Next Generation Photovoltaics***,* ***Mariadriana Creatore,*** TU Eindhoven, Netherlands **INVITED**

Innovation in thin film and interface engineering has played an essential role in pushing the conversion efficiency of the most widespread photovoltaic (PV) technology, i.e. crystalline silicon-based (c-Si), towards its thermodynamic limit. In this respect, ultra-thin, conformal, high-purity Al_2O_3 thin films synthesized by ALD are key in c-Si PV manufacturing industry as they passivate the c-Si surface, thereby suppressing a major channel of electron-hole pair recombination.

Recently, we have explored the ALD synthesis of thin films for metal halide perovskite- based photovoltaics. The latter has rapidly reached a conversion efficiency of 26% and, when coupled with c-Si PV in a so-called tandem device, leads to efficiencies already beyond 33%.

In this contribution I will discuss the merits which ALD offers to perovskite-based PV by reviewing our work on NiO-based hole transport layers and discussing in depth the case study of ALD SnO_2. The latter is implemented in perovskite PV R&D and industry as buffer layer, i.e., imparting thermal and environmental stability to the device, while protecting the perovskite absorber and fullerene electron transport layer from the sputtering of the transparent top contact. More recently, ALD SnO_2 is explored as solvent barrier layer in the tunnel recombination junction of perovskite/perovskite tandem PV, to prevent the damage of the wide-gap perovskite absorber when processing the narrow band-gap perovskite cell. Although we can conclude that several ALD merits are already extensively acknowledged by the PV community, studies addressing ALD film growth on challenging substrates such as fullerenes and metal halide perovskites are rarely reported in literature. We are convinced that these studies provide a rationale to implement more efficiently these layers at device level and promote process upscaling. Therefore, this contribution will also highlight the adoption of *in situ* diagnostics, namely spectroscopic ellipsometry and IR spectroscopy, to characterize the ALD SnO_2 growth on two commonly adopted fullerenes, C60 and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). Our studies show that a substrate-inhibited growth occurs in the case of PCBM and, to a minor extent, in the case of C60, with respect to the traditional c-Si substrate. Moreover, IR spectroscopy highlights the loss of vibrational features of the ester group in PCBM upon SnO_2 growth, whereas C60 is chemically unaffected. We conclude that the delayed film growth and chemical modifications detected on PCBM are responsible for the consistently lower device performance when ALD SnO_2 is grown on PCBM instead of C60.

11:15am **AA2-TuM-14 Utilizing Low-Temperature Ald Technique to Investigate Perovskite Nickelates for Photovoltaic Applications***, **Anjali Choubey**, H. Hovde Sønsteby,* University of Oslo, Norway*; H. von Wenckstern,* University of Oslo, Germany*; O. Nilsen,* University of Oslo, Norway

Photovoltaic (PV) materials currently in use like silicon are well-established but approaching their theoretical limit, and halide-perovskites, even though developing rapidly, are toxic and unstable under environmental conditions. Developing new materials for PV applications is slowly becoming a crucial necessity. In this study, perovskite nickelates are investigated as an alternative to traditional PV materials. Nickelates are not only stable under environmental conditions, but they can also withstand photobleaching and thermal exposures. Additionally, they are well known for their metal-insulator phase transition, magnetic phase transition, and structural transition [1, 2]. This has made them very lucrative for various electronic, magnetic, dielectric, superconducting, and catalytic applications. However, there is not much data on the use of nickelates for PV applications, and we are trying to bridge that gap.

Some perovskite nickelates have shown bandgap tuning abilities by A-site substitution control [2-4]. In this work, Terbium nickelate ($TbNiO_3$) and Gadolinium nickelate ($GdNiO_3$) thin films fabricated using low-temperature atomic layer deposition (ALD) techniques were studied and characterized. X-ray diffraction gave information about the structure and crystallinity, x-ray fluorescence and x-ray photoelectron spectroscopy about the composition, and spectroscopic ellipsometry about the thickness and refractive indices of the deposited films. These investigations helped gain valuable insight into the extent of the semiconductive nature of these materials and how to exploit them for PV applications.

Reference:

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11:30am **AA2-TuM-15 Atomic Layer Deposition of Defect-Engineered TiO_x and TaO_x Protective Coatings for Photoelectrochemistry***, **Tim Rieth**, O. Bienek, J. Kühne, I. Sharp,* Walter Schottky Institut, Technische Universität München, Germany

Photoelectrochemical (PEC) energy conversion provides a viable route to chemical fuel production from solar light. In this approach, charge carriers generated within a semiconductor light absorber immersed in an electrolyte are used to drive electrochemical reactions. Several different PEC design approaches exist, ranging from single photoelectrodes to tandem configurations of photoanodes and -cathodes to buried photovoltaic junctions. However, common to each of these designs is a central materials challenge of achieving simultaneous stability, efficiency, and scalability. Furthermore, the coupling of the semiconducting photo absorber and catalytic components demands sophisticated solid state interface engineering. In this talk, we focus on the stabilization of this semiconductor/electrolyte interface with functional conformal coatings grown by plasma-enhanced atomic layer deposition (PE-ALD). We investigate defect-engineered electron-selective titanium oxide (TiO_x) protection layers for efficient InP photocathodes and identify ALD pathways to optimize interfacial and bulk charge transport, as well as to tune the driving force for photovoltage generation [1, 2]. Furthermore, we use PE-ALD to deposit ultra-thin tantalum oxide (TaO_x) protective coatings showing improved chemical stability compared to TiO_x in alkaline and acidic environments. We extend the utilization of TiO_x and TaO_x protective coatings to buried photovoltaic junctions and evaluate the respective suitability in terms of optical transparency, conductivity and stability, achieving unassisted solar-water-splitting efficiencies of 15%. Spectroscopic methods, including X-ray photoelectron spectroscopy (XPS), photothermal deflection spectroscopy (PDS), and spectroscopic ellipsometry (SE), are employed to characterize and understand the intentionally introduced defects and correlate electronic properties to the PEC performance. Overall, the presented TiO_x and TaO_x protective coatings represent an important step toward efficient and stable PEC devices, while the demonstrated ALD-based defect engineering generally enables electronic property control of ultra-thin layers.

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11:45am **AA2-TuM-16 Influence of Atomic Layer Deposition Tin Oxide Properties on the Performance of Perovskite Solar Cells***, **Bhavya Rakheja**, A. Hultqvist,* Uppsala University, Angstrom Laboratory, Sweden*; T. Törndahl,* Uppsala University, Sweden

Presently, the photovoltaic industry is dominated by single-junction silicon solar cells. As this technology is reaching its theoretical power conversion efficiency limit, the need to develop multi-junction solar cell structures, capable of producing more power per unit area, is rising. Multi-junction solar cells employ a combination of single-junction solar cells, each capable of absorbing complementary parts of the solar cell spectrum. Perovskite solar cells (PSCs) have witnessed tremendous success and their efficiency has improved from merely 3.8% in 2009 to more than 26% in a single-junction solar cell [1]. Moreover, PSCs have also demonstrated great efficiencies when used in tandem configurations with silicon and Copper indium gallium (di)selenide (CIGS) solar cells [1]. All top efficiency PSCs in a tandem structure employ tin oxide (SnO_x), grown using the Atomic layer deposition (ALD) technique, as an electron selective buffer layer. *The material properties of SnO_x are crucial for facilitating good electron transport while mitigating losses.*

The perovskite layer in a PSC is sandwiched between electron and hole-selective layers. These layers facilitate the transport of the generated charge carriers to their respective contacts. Good energetic alignment between perovskite and charge transport layers is pivotal in maximizing the solar cell's power output. As it has been established in several studies, the bandgap of ALD SnO_x is sensitive to the deposition temperature [2]; making it critical to optimize the band alignment between ALD SnO_x and adjacent layers. Moreover, other process parameters such as the choice of co-reactant can also affect the number of defects and; consequently, impact the power losses in a PSC [3]. In this study, we conduct in-situ quartz crystal microbalance studies and also investigate how the material, optical, and electronic properties of ALD SnO_x evolve as a function of deposition parameters, and their influence on solar cell's device parameters. In particular, we examine the effect of two co-reactants (H_2O and H_2O_2) and their respective doses. By fine-tuning ALD SnO_x deposition parameters and studying their influence on the device performance, one can establish an improved understanding toward the incorporation of ALD SnO_x in PSCs.

References:

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ALD Applications
Room Hall 3D - Session AA1-TuA

Energy: Solar Energy Materials II

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

1:30pm **AA1-TuA-1 Toward All-ALD Halide Perovskite Solar Cells***, G. Popov, A. Weiss, M. Ritala, M. Leskelä,* ***Marianna Kemell,*** University of Helsinki, Finland **INVITED**

Halide perovskite solar cells show solar conversion efficiencies > 26 %, making them the most promising emerging photovoltaics technology. Halide perovskites have the general formula ABX_3 where most often A = $CH_3NH_3^+$, $CH(NH_2)_2^+$ or Cs^+, B = Pb^{2+} or Sn^{2+} and X = I^-, Br^- or Cl^-. Methylammonium lead iodide $CH_3NH_3PbI_3$ is a well-known example.

Commercialization of the halide perovskite solar cells is still impeded by challenges in upscaling. High quality perovskite layers can be made on small areas but the currently used methods are not suitable for large production volumes.

We have addressed the scalability issue by developing atomic layer deposition (ALD) processes for halide perovskites and other materials in perovskite solar cells. Our approach is based on ALD of binary halides, followed by their chemical conversion to the desired perovskites. As the first step, we developed ALD processes for the binary metal halides PbI_2 [1], CsI [2], SnI_2 [3], $PbCl_2$ [4] and $PbBr_2$ [4]. Prior to our work there were no ALD processes for iodides, bromides or chlorides. Using the binary halides as the starting points, we can deposit the halide perovskites $CH_3NH_3PbI_3$ [1], $CsPbI_3$ [2] and $CsSnI_3$ [3]. ALD-PbI_2 film is converted to $CH_3NH_3PbI_3$ by exposing it to CH_3NH_3I vapor, whereas ALD-CsI film can be converted into $CsPbI_3$ by exposing it to the ALD process of PbI_2, and to $CsSnI_3$ by exposing it to the ALD process of SnI_2. Combining these with the ALD processes of $PbCl_2$ and $PbBr_2$ enables compositional engineering as a route to fine-tuned properties.

In a halide perovskite solar cell, the perovskite layer is sandwiched between n- and p-type semiconductor films. ALD processes for various n-type materials are readily available, whereas p-type materials are more challenging. We have developed low-temperature ALD processes that enable deposition of p-type PbS [5] on $CH_3NH_3PbI_3$ at temperatures below 100 °C, without damaging it. Furthermore, the PbS film also protects the $CH_3NH_3PbI_3$ film from degradation under ambient conditions, acting thus in a dual role as a functional layer and as an encapsulant. We have also developed a two-step process for p-type CuI [6] that is compatible with $CsPbI_3$. Our processes form the first steps towards making complete halide perovskite solar cells by ALD-based methods.

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2:00pm **AA1-TuA-3 Plasma-enhanced Atomic Layer Deposition of Tunable Cobalt Nitride Thin Films Enabled by Sequential N_2 Plasma Exposure***,* ***Matthias Kuhl,*** Technical University Munich, Germany*; L. Kohlmaier,* Technical University Munich, Austria*; I. Sharp,* Technical University Munich*; J. Eichhorn,* Technical University Munich, Germany

Transition metal nitrides form an interesting class of materials due to their mechanical hardness, tunable electronic and magnetic properties, and catalytic activity. In this context, cobalt nitride is a promising material both in the semiconductor industry and for electrochemical (EC) energy conversion. Despite these potential applications, there are limited reports on depositing cobalt nitride via atomic layer deposition (ALD), especially at lower temperatures (<200 °C). Such low temperature processes would provide enhanced processing compatibility, including for photolithography, and aid in preserving high quality light absorber/catalyst interfaces for photoelectrochemical (PEC) energy conversion applications.

Here, we report on the low-temperature (100 - 200 °C) plasma-enhanced (PE) ALD of cobalt nitride using cobaltocene $CoCp_2$ as precursor and either NH_3 plasma or H_2/N_2 plasma as co-reactant. The deposition at low temperatures is enabled by introducing a subsequent N_2 plasma pulse at the end of each PE-ALD cycle to regenerate surface sites for the subsequent precursor adsorption. We analyze the film growth characteristics and material properties by in-situ spectroscopic ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy. Varying deposition temperature and plasma gas composition can be leveraged to tune the Co/N ratio and thus the material properties from semiconducting to metallic. Lastly, we applied the thin films as heterogeneous catalysts for the EC oxygen evolution reaction. Overall, this work highlights the use of PE-ALD as a promising approach for depositing metal nitrides with tunable film properties at low temperatures.

2:15pm **AA1-TuA-4 Hybrid Solar Cells Comprising Inorganic and Organic Materials Through Vapor Phase Infiltration***, K. Ashurbekova,* 1. CIC nanoGUNE, Spain*;* ***Mato Knez,*** CIC nanoGUNE, Spain

Inorganic, organic and perovskite solar cells (SCs) have witnessed unprecedented progress in the past decade. Perovskite SCs, while highly efficient, encounter stability and toxicity concerns. Inorganic SCs excel in efficiency and durability but lack flexibility, prompting exploration of alternative technologies. In contrast, organic SCs offer flexibility, facing lower efficiency challenges. Despite the inherent limitations of each SC type, they have their own merits, promising a grand step forward if synergy is achieved. Combining the adaptability of organic SCs with the efficiency of inorganic ones may yield a hybrid versatile alternative. We are introducing new hybrid solar cell materials by applying vapor phase infiltration (VPI) to polymers.

We present a new hybrid materials set obtained after growing Sb_2S_3 and $Sb_2Se_3$by VPI inside the bulk and atop of diverse polymers including poly(triaryl amine) (PTAA), Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine] (PolyTPD), Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and Poly(3-hexylthiophene-2,5-diyl) (P3HT). PTAA, PolyTPD and PEDOT:PSS are excellent hole-transporting semiconducting materials, while P3HT is an efficient light absorber in the visible range. Metal chalcogenide light absorbent materials, such as Sb_2S_3 and Sb_2Se_3,have huge potential in photovoltaics owing to the suitable bandgap of 1.7 and 1.3 eV, and high light absorption coefficient above 10^4 and 10^5 cm^{-1}, respectively.For the VPI growth of Sb_2S_3 and Sb_2Se_3, $SbCl_3/H_2S$ and $SbCl_3/(Me_3Si)_2Se$ precursors were used, respectively. The hybridization process was monitored *in-situ* with a Quartz Crystal Microbalance (QCM). The monitoring allowed studying the saturation behavior of the VPI process and quantitatively controlling the loading of the inorganic precursors into the polymer. Scanning electron microscopy (SEM) showed infiltration in form of Sb_2S_3 and Sb_2Se_3 crystal growth throughout the whole polymer depth. TEM was used to examine the structure of the crystalline phase of the Sb_2S_3 and Sb_2Se_3 grown in the bulk and on top of the polymer. A complete photovoltaic characterization of a new set of hybrid materials, including thecurrent density–voltage (J–V) characteristic of SCs under illumination, power conversion efficiencies (PCEs) and the external quantum efficiency (EQE) of a device, was performed in 16 ITO pins SCs. Planar p-i-n SCs devices of the following structures were fabricated: ITO glass/polymer-Sb_2S_3//Sb_2Se_3 /ETL/Ag and ITO glass/polymer-Sb_2S_3//Sb_2Se_3/perovskite/ETL/Ag. C60/BCP was used as an electron transport layer (ETL). The results offer new solutions for sustainable solar energy.

2:30pm **AA1-TuA-5 Mitigating the Cross-Ion Migration Towards Perovskite Using a Conformal Layer of Alumina via Atomic Layer Deposition***,* ***Mayank Kedia,*** *C. Das, M. Saliba,* Forschungszentrum Jülich GmbH, Germany

Atomic layer deposition (ALD) of aluminum oxide (Al_2O_3) layers is an established technique for encapsulation and stabilization of active materials against environmental stressors. This is particularly important for sensitive perovskite materials, that react with moisture, light, O_2, etc. during the device operation conditions. [1] At the same time, the role of the ALD-Al_2O_3 barrier layer between the perovskite and charge transport material still requires further analysis.

In this study, we demonstrate the surface coverage uniformity of a <1nm ALD-Al_2O_3 layer on bare perovskite at room temperature. [2] Such a sub-nanometer ALD-Al_2O_3 coverage on the different perovskite facets reduces surface defects enhancing the device performance from 19.2% to 20.1%. This ultra-thin layer of ALD-Al_2O_3 acts as a barrier layer for the diffusion of degraded byproducts of the aged spiro-OMeTAD preventing perovskite's transition to amorphous phases. Consequently, the ALD-Al_2O_3-based device retains 75% of its initial power conversion efficiency as compared to 10% for pristine devices after 180 days of shelf-aging, followed by 1000 min of maximum power point tracking under ambient conditions. Finally, this study deepens the mechanistic understanding of the ALD-Al_2O_3 as an impermeable layer, highlighting the multifaceted role of buffer layers in interface engineering.

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2. **Kedia, M.**, Das, C., **Saliba, M.**, (2024) Stabilizing perovskite solar cells using a conformal impermeable layer of alumina via atomic layer deposition. *(submitted)*

2:45pm **AA1-TuA-6 Thermoelectric Properties of Sb_2Te_3-based Ferecrystals based on Atomic Layer Deposition***, J. Yang, D. Shin, S. Lehmann, A. Bahrami,* ***Korneli Nielsch,*** Leibniz Inst. of Solid State and Materials Research / IFW-Dresden, Germany

Atomic layer deposition is a very versatile technology for the deposition of thin films with precise thickness control on large areas, non-planar surfaces and 3D objects. The chemical reaction is surface limited, well defined and works in most cases at low temperatures (RT to 250 °C). For a number of classical van der Waals 2D materials, there have been reports on ALD of transition metal dichalcogenide (TMDC) of MoS_2, SnS_2, WS_2 and WSe_2, which also included the electronic characterization as a field effect transistor (FET).

In this work, we have fabricated by atomic layer deposition (ALD) multilayers of layered materials based on topological insulators and van der Waals materials, called *ferecrystals.* These ferecrystals can be tailored to exhibit unusual properties such as high electrical conductivity or low thermal conductivity or magnetic properties. A detailed ferecrystal study was performed on ferecrytals of Sb_2Te_3 and SbO_x, which has been grown at the same temperature as single layers of Sb_2Te_3. Without post-annealing, the electrical and thermoelectric characterisation of the highly ordered samples have been performed with the ZT-chip setup. In general, the carrier mobility is very high >150 Vs^2/cm^2 and is even improved when the thickness of the Sb_2Te_3 layers is reduced and the number of SbO_x layers (typically 2 nm thickness) is increased. Detailed XRD investigations have been performed and an enhanced crystalline order is observed in the ferecrystal system compared to individual layers of Sb_2Te_3. We have grown ferecrystals based on Sb_2Te_3 and Sb_2Se_3 with tetrahedral and orthorhombic crystal structure, respectively. The p-type hole carrier concentration of Sb_2Te_3 films can be enhanced through the sublayer doping of Sb_2Se_3. The highest carrier concentration achieved was 2.5×10^{19} cm^{-2} when the thickness ratio of Sb_2Te_3 to Sb_2Se_3 was (4 nm/2 nm). Further reduction of the Sb_2Te_3 thickness resulted in a high Seebeck coefficient of 172 µV/K at room temperature.h

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2. J. Yang, J. Li, A. Bahrami, N. Nasiri, S. Lehmann, M. Cichocka, S. Mukherjee, **K. Nielsch**, „Wafer-scale Growth of Sb_2Te_3 Films via Low-temperature Atomic Layer Deposition for Self-Powered Photodetectors", ACS Appl. Mater. Interfaces 2022, 8, 2101334

3:00pm **AA1-TuA-7 Atomic Layer Deposition for Photoelectrochemical Solar Fuel Production***,* ***Lionel Santinacci,*** CNRS/Aix-Marseille Univ., France **INVITED**

Since H_2 is now considered as a key energy vector, its production through water electrolysis coupled to a renewable power supply is envisioned as a large-scale production scheme. In parallel to the various electrolysis approaches, H_2 and O_2 production from H_2O photoelectrolysis appears to be a more straightforward process. It has opened an attractive, though challenging, field of investigations that ultimately tackles direct water dissociation using an unbiased photoelectrochemical cell (PEC) under sunlight: solar fuel production. The recent remarkable conversion yield of 19%,[1] reported on unbiased PEC built with expensive and unstable III-V semiconductors (SCs) associated to platinoid catalysts, is very promising but the H_2 production remains more expensive than from fossil sources . The field needs therefore to significantly improve yield, stability and cost.

In the recent years, it has been shown that ALD can play a valuable role to address such challenges. Photoelectrodes can be significantly improved by (i) surface structuring inducing a better light harvesting and a higher active surface area, (ii) by co-catalysts improving the reaction kinetics and enhancing the photocurrent and (iii) by protective films extending the electrode lifetime. ALD exhibits key advantages to achieve such improvements and recent literature has shown numerous successful examples of photoelectrode modifications. ALD is, indeed, known to be well-suited to conformally coat nanostructured surfaces with either continuous pinhole-free layers or uniform particle collections. After a short reminder on the basics of water photosplitting (principle, materials of interest and current challenges), this review will therefore show how ALD can be implemented in the field. Although it is a minor application, specific materials can be synthetized by ALD but the mains uses of this technique consist of fabricating nanostructured electrodes, deposit co-catalysts, passivate or modify the semiconductor/electrolyte junctions and prevent corrosion. In most cases, materials combination is the appropriate way to reach better performance and durability and ALD is, of course, a good tool for such approach.

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ALD Applications
Room Hall 3D - Session AA2-TuA

Energy: Catalysis and Fuel Cells

Moderators: Riikka Puurunen, Aalto University, Finland, **Ruud van Ommen**, Delft University of Technology

4:00pm **AA2-TuA-11 ALD Young Investigator Award Finalist Talk: How Instability Can Be Beneficial for Electrocatalysis: The Case of Nickel Sulfide Oxygen Evolution Reaction Precatalyst***,* ***Miika Mattinen,*** University of Helsinki, Finland*; J. Schröder, G. D'Acunto, T. Jaramillo,* Stanford University*; M. Burke Stevens,* SLAC National Accelerator Laboratory*; M. Ritala,* University of Helsinki, Finland*; S. Bent,* Stanford University

Water electrolysis is a key technology in building a sustainable world based on renewable energy. Hydrogen gas (H_2) produced by water electrolysis can be used, for example, as a fuel and reactant in diverse industries including chemical and steel manufacturing. Of the two half-reactions occurring inside water electrolyzers, the oxygen evolution reaction (OER) limits the efficiency. Thus, development of highly active, stable, and affordable OER catalysts is critical. Nickel-iron metal alloys, oxides, and hydroxides are among the most active OER catalysts in alkaline electrolytes. Their activity is attributed to oxyhydroxide species formed under OER conditions.[1] Recent studies looking at other promising Ni compounds such as NiS_x have found them, too, to transform to oxyhydroxides. Thus, all the Ni(Fe)-based catalysts listed above may be described as precatalysts to the active oxyhydroxide.[2] However, the effect of the precatalyst material on the activity and structure of the active catalyst as well as the role of electrolyte impurities (e.g. Fe) remain poorly understood.

To answer these questions, we deposited crystalline NiS_x (β-NiS with traces of Ni_9S_8) thin films by ALD using $NiCl_2$(TMPDA) (TMPDA = *N,N,N',N'*-tetramethyl-1,3-propanediamine) and H_2S at 165 °C. The ALD NiS_x films were compared to NiO, $Ni(OH)_2$, and Ni precatalysts deposited on SnO_2:F electrodes by ALD and other methods. Electrochemical measurements in 0.1 M KOH (purified from iron) and X-ray photoelectron spectroscopy revealed that all the precatalysts convert to an oxidized phase ("NiOOH") under OER conditions, yet at substantially different rates ($NiS_x \approx Ni(OH)_2 >>$ Ni > NiO). Fast conversion is beneficial for achieving high current densities. We are investigating the structure of the formed oxidized phase using *operando* X-ray absorption spectroscopy.

Iron impurities in the KOH electrolyte incorporate into the (pre)catalysts reaching up to 30 metal-%. This added iron greatly increases the OER activity and stability of the catalysts. Compared to synthesis of multimetal catalysts, incorporating iron from the electrolyte simplifies synthesis and can accelerate the conversion to the active catalyst. The highest iron concentration and best OER performance is found for the fastest converting precatalysts, i.e. NiS_x and $Ni(OH)_2$. Understanding of the structural evolution of OER precatalysts together with the conformality of ALD enables engineering of high-performance electrodes for alkaline electrolyzers.

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2 Kawashima et al., *Chem. Rev.*, 2023, **123**, 12795

4:15pm **AA2-TuA-12 Diffusion–Reaction Modeling for Atomic Layer Deposition on Spheres: Comparison with Experimental Data***, **Niko Heikkinen,*** VTT Technical Research Centre of Finland*; J. Yim, J. Järvilehto,* Aalto University, Finland*; S. Saedy,* Delft University of Technology, Netherlands*; P. Brüner, T. Grehl,* IONTOF GmbH, Netherlands*; E. Haimi, J. Velasco, C. Gonsalves,* Aalto University, Finland*; R. van Ommen,* Delft University of Technology, Netherlands*; J. Lehtonen,* VTT Technical Research Centre of Finland*; R. Puurunen,* Aalto University, Finland

Diffusion–reaction (DR) modeling is a powerful tool to estimate reactant travel and film formation in atomic layer deposition (ALD) in high-aspect-ratio (HAR) features [1]. The modeling work of conformality evolution on (modelling-wise) one-dimensional features (circular pores and channels) has been extended to porous materials described by an average pore size, tortuosity and porosity, still keeping the geometry one-dimensional through considering the slab geometry [2]. While a slab can describe well the case of planar surfaces (e.g. membranes), typically particles used as catalyst supports resemble more spheres or cylinders.

We have recently extended ALD diffusion–reaction modeling to describe spheres and cylinders in addition to slabs [3]. Our study showed for example that the reactant exposure requirement for full saturation increases in the order spheres < cylinders < slabs.

Here, we extend the earlier theoretical work [3] and compare modeling to experimental studies on high-surface-area alumina spheres. Two case examples are presented: zinc on alumina using the recently reported $Zn(acac)_2$ reactant [4] (one reaction step in a fixed-bed reactor, with $Zn(acac)_2$ dose varied), and platinum on alumina using the well-known $MeCpPtMe_3$ reactant (5 cycles with oxygen as counter-reactant, in a fluidized bed reactor, with exposure time varied). Alumina spheres with diameters of 1, 1.8 and 2.5 mm were employed, with a specific surface area on the order of 200 m^2/g. Modelling results are found to agree reasonably well with the experimental data.

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4:30pm **AA2-TuA-13 Highly Durable Pt Based Fuel Cell Catalysts via Atomic Layer Deposition***, **Xiao Liu,** H. Liu, Y. Gao,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China*; B. Shan,* State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, China*; R. Chen,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

The activity and durability of carbon supported Pt based electrocatalysts (Pt/C) are unchanging goals for the widespread application of hydrogen fuel cells. Under the harsh operation conditions of fuel cell, pure Pt nanoparticles (NPs) suffer from great electrochemical dissolution, leading to serious stability decay. To address this challenge, overcoating Pt NPs with organic capping agent, polymer layers, inorganic carbon-based nanoshell or metal oxide (MO_x), nitride has been recognized as a prospective strategy to prevent the direct exposure of Pt surface. Atomic layer deposition (ALD) is known for its atom-level control accuracy over the film growth on substrates or NPs based on self-limiting chemical half-reactions. Herein, an effective strategy is developed to improve the activity and durability of Pt catalyst for hydrogen fuel cell based on atomically surface and interface modification on Pt nanoparticle, which is a promising scale-up approach via selective atomic layer deposition. Selective ALD of metal oxides such as TiO_2, ZnO, SnO_2 have been performed on Pt/C electrocatalysts by a custom-made fluidized-bed reactor. The behavior of selective deposition is controlled by the reactor temperature, oxygen source and number of ALD cycle. Following post treatments such as nitriding and high temperature reduction are performed to precisely control the surface structure of supported Pt nanoparticles. The activity and durability of Pt based electrocatalysts have been enhanced via selective ALD and following post treatment. N doped TiO_2 (N-TiO_2) is demonstrated to selectively deposit on the low coordination sites of Pt NPs and expose (111) facet without changing their size distribution and wasting the electrochemical active surface area. The selective decoration of N-TiO_2 could effectively inhibit the intrinsic degradation of Pt NPs and prevent the electrochemical sintering during accelerated durability tests. Besides, the intrinsic activity of Pt NPs is also enhanced based on ultra-thin ZnO coating. The prepared uniform PtZn intermetallic nanocrystals with the size of 2.50 ± 0.65 nm achieve outstanding single-cell performance with the mass activity of 0.48 A mgPt^{-1} at 0.9 V and 10.42% loss of mass activity after 30000 voltage cycles, which is superior to commercial Pt/C. The enhanced activity and durability is attributed to the decreased binding energy of Pt-oxygen intermediates for weakly polarized surface Pt atoms and suppressed electrochemical Ostwald ripening.

4:45pm **AA2-TuA-14 Catalyst on Top? Importance of the Final Layer of an ALD Deposited Catalyst. Ni-Fe Catalysts Deposited by ALD***, **Ruben Blomme,*** Ghent University, Belgium*; R. Ramesh,* Ghent University, Belgium, India*; L. Henderick, M. Minjauw, P. Vereecke, M. Adriaens, C. Detavernier, J. Dendoven,* Ghent University, Belgium

H2 is considered a crucial energy carrier in the transition to a more sustainable future. It serves as an essential feedstock for many industries and can also be used as an alternative, low-emission fuel for keyindustrial processes, such as steel production. However, the renewable method to produce H2, viawater electrolysis, is currently uncompetitive compared to the fossil fuel-based alternative.

One aspect in which the efficiency of water electrolysis can be improved is through the development of effective catalyst materials. Currently, noble metal-based catalysts are utilized for H2 production, but this approach is not sustainable in producing the required amount of H2 due to the high cost and scarcity of these metals.

To address this, alternative catalysts are under development, with some of the more promising materials being transition metal oxides and phosphates. The use of Atomic Layer Deposition (ALD) allows for the precise control during the catalyst production process, including conformal layer-by-layer control and compositional tailoring. Previous works on ALD development of metal phosphate materials, such as iron[1], nickel[2], and cobalt[1,3], have demonstrated their viability and effectiveness as Oxygen Evolution Reaction (OER) catalysts.

In this study, a series of Ni-Fe mixed phosphate materials were deposited via a supercycle approach and quantified for their electrochemical performance. Notably, during the deposition process, there was a preferential incorporation of Ni over Fe across all measured samples (Fig. 1). According to X-ray fluorescence (XRF) measurements, the effectiveness of one NiPO ALD cycle in a NiPO – 4 FePO process is twice that of the same ALDcycle in a pure NiPO deposition.

The order of the ALD processes in the supercycle recipe and the overall film thickness had significant impact on the performance as a catalyst material. The most noteworthy effect of customizing the ALD sequence was observed when the cycle sequence in the supercycle was reversed to ensure FePO was deposited as the final layer (Fig. 2). This resulted in an overall potential gain of 20 mV (at 10 mA/cm^2) for materials with identical composition.

By increasing the thickness of the deposited layer, additional gains could be achieved. These findings align with previous reportsthat observed the restructuring of cobalt phosphate materials to oxides/hydroxides with a significantly increased electrochemical active surface area[4].

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[2] Dalton Trans., **51**, 2059, (2022)

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5:00pm **AA2-TuA-15 Enhanced Oxygen Evolution Reaction Catalysts by PE-ALD: Atomically Dispersed Co_1 and Fe_1 Supported on Ultra-thin Films of Doped NiO_x***, **Ina Oestroem,*** University of New South Wales, Australia*; M. Favaro,* Helmholtz Zentrum Berlin, Germany*; P. Burr, B. Hoex,* University of New South Wales, Australia

Hydrogen production through water splitting is hindered by the anodic oxygen evolution reaction (OER), which has a complex, sluggish mechanism leading to a high overpotential.Nickel oxide-based catalysts (NiO_x) are a highly active, cheaper alternative to the precious metal catalysts of IrO$_2$ and RuO$_2$. Plasma-enhanced atomic layer deposition (PE-ALD) is a powerful tool for optimising thin films to increase OER activity. This work employs PE-ALD, using O$_2$ and H$_2$ plasma, to atomically disperse Co$_1$, Fe$_1$, and Fe$_1$Co$_1$ at the surface of thin films of SnNiO$_x$. The films were conditioned by 600 cycles of cyclic voltammetry (CV) at 20 mV/s, testing their stability and formation of the catalyst OER-active structure. Electrochemical Impedance Spectroscopy (EIS) was employed (0.1 – 10^4 Hz and 1.5 – 1.7 *vs* RHE), after 20 cycles, and at the end of the 600 cycles, to investigate the changes in double layer capacitance (C$_{dl}$) and charge transfer resistance (R$_{ct}$). The apparent activity was studied with linear sweep voltammetry (LSV) at 1 mV/s, and the durability by chronopotentiometry (CP) at 10 mA/cm^2 for 12 hrs. The 12 hr CP tests were followed by rest and another CP for 1 hr, showing further improvements in activity after a recovery period. The turn-over frequency (TOF) at different potentials was obtained through redox peak integration and C$_{dl}$. Our results show that atomically dispersed Co$_1$ and Fe$_1$ produced via H$_2$ plasma, in contrast to an O$_2$ plasma, further improved the OER activity of thin films of SnNiO$_x$. The best OER catalyst is Fe$_1$Co$_1$/SnNiO$_x$ with 284 mV of overpotential at 10 mA/cm^2 on FTO, compared to 320 mV for Ru on glassy carbon (GC) in 1M NaOH, with remarkable stability and durability after prolonged CP test. Tafel analysis and EIS suggest the improved performance is due to a lower R$_{ct}$. All-electron hybrid Density functional theory (PEB0/pob-TZVP) provided insights into the thermodynamics of the OER mechanism and electronic properties of the catalysts. X-ray diffraction, X-ray photoelectron spectroscopy, and soft X-ray absorption characterised the atomic structure, active sites oxidation state and coordination environment. The morphology and conformality were analysed with atomic force microscopy (AFM), scanning tunnelling electron microscopy (STEM), and spectroscopic ellipsometry (SE). This work shows that the OER activity of SnNiO$_x$ can be improved by atomically dispersed Fe$_1$Co$_1$ by PE-ALD and that the catalysts are stable after prolonged CP tests. Our study highlights PE-ALD as a promising technology for optimising low-cost catalysts with high atom economy and atomic-level precision.

5:15pm **AA2-TuA-16 Optimization of Photocurrent Response of Atomic Layer Deposited Ti$_x$Fe$_{2-x}$O$_3$ Photoanodes***, **Anjan Deb**, A. Vihervaara, G. Popov, M. Chundak, M. Heikkilä, M. Kemell, M. Ritala, M. Putkonen,* University of Helsinki, Finland

Hematite (α-Fe$_2$O$_3$) has attractive properties, such as a low band gap energy (1.9-2.2 eV), abundant availability and high chemical stability, for photoelectrocatalytic applications such as water splitting and organic micropollutant decomposition (Liu, et al., 2023). However, it has also several limitations, including low optical absorption coefficient and a short minority carrier diffusion length ranging from 2-4 nm. To address this intrinsic problem of hematite, researchers are exploring the use of nanoscale fabrication techniques and doping with aliovalent cations, such as Ti^{4+}, as a potential solution. Atomic layer deposition (ALD) is a promising technique that enables the deposition of pinhole free thin films with precise atomic-level composition and thickness control over an extensive surface area and high aspect ratio surfaces (Leskelä & Ritala, 2002).

In this study, we employed response surface methodology (RSM) based face-centred central composite design (FC-CCD) for modelling and optimization of photocurrent response of Ti$_x$Fe$_{2-x}$O$_3$ thin film photoanodes grown by ALD. Two ALD process, FeCp$_2$ + O3 and Ti(OMe)$_4$+H$_2$O, were combined to grow the Ti$_x$Fe$_{2-x}$O$_3$ thin film photoanodes. Deposition parameters such as total number of ALD cycles (film thickness), cycle ratio of TiO$_x$ to FeO$_x$ (the dopant concentration) and deposition temperature were chosen as the independent factors while the photocurrent densities (PCD) at 1.23V and 1.70V vs RHE were considered as response. Thin film depositions were carried out according to the FC-CCD design matrix (Figure 1-a) based on the level of experimental factors presented in Table 1. After deposition, all the films were subjected to annealing at 500°C for 1 hour in air and evaluated for photocurrent response using a photoelectrochemical cell under standard illumination of AM 1.5G, 100 mW/cm^2. Linear sweep voltammetry (LSV) method was used to record the photocurrent responses at 1.23 and 1.70V vs RHE (Figure 1-b) at water oxidation conditions (pH ≈ 13.2).

After fitting the experimental data to the second-order polynomial equation, a mathematical model was developed that correlates the experimental variables with the response. The analysis of model parameters indicates that film thickness and dopant concentration are the most important elements that govern the PCD of Ti$_x$Fe$_{2-x}$O$_3$ photoanode. The predicted PCD values using the model equations agreed well with the experimental data (R^2=0.95 for PCD@1.23V and R^2=0.98 for PCD@1.7V vs RHE) as shown in Figure 2. This study demonstrated the effectiveness of RSM based modelling to predict the photocurrent response of photoelectrode materials.

ALD Applications
Room Hall 3 - Session AA-TuP
ALD Applications Poster Session

AA-TuP-1 Scalable Fabrication of Catalysts for Proton Exchange Membrane Water Electrolysis*, **Peter M. Piechulla**, M. Chen,* Delft University of Technology, Netherlands*; M. Kräenbring, F. Özcan, D. Segets,* University of Duisburg-Essen, Germany*; J. van Ommen,* Delft University of Technology, Netherlands

The phenomenal growth in renewable power generation has even further increased research interest in the fields of energy storage and material conversion through electrolysis. A key element in any electrolysis process is a catalyst tailored to the targeted reaction, e.g. platinum group metals (PGMs) for water splitting. Due to the immense scale of the problem, and the cost and scarcity of PGMs, economical use of these materials is imperative. Hence, catalysts are typically dispersed on a support material, e.g., Pt-loaded carbon black (Pt/C) as cathode catalyst in proton exchange membrane water electrolysis (PEMWE). Compared to bulk Pt, a larger fraction of atoms is exposed at the surface, thus leading to a higher catalytic activity per unit weight of Pt. Traditional fabrication methods for Pt/C, such as incipient wet impregnation, allow control over the amount of deposited Pt; however, the morphology and dispersion are very difficult to control with this method.

In this work, we propose an alternative and economically feasible fabrication route for Pt/C catalyst layers based on ALD. We have previously shown that Pt/C can be fabricated via atmospheric pressure ALD on particles in a fluidized bed (FBR-ALD), a method that is readily scalable [1]. In contrast to traditional fabrication methods, we can control the morphology and achieve a finer dispersion of deposited Pt [1, 2], which enables higher catalytic activity at reduced Pt loading. First, we use FBR-ALD to fabricate tailored Pt/C for PEMWE. Second, to establish the relationship between morphology and performance, we characterize the material using (HR)TEM and rotating disk electrode (RDE) measurements. From the latter, we infer the electrochemically active surface area (ECSA) as a relative indicator for performance. However, a full assessment of Pt/C requires testing in real-world applications, which is why we go one step beyond bare catalyst characterization and demonstrate the use of ALD-made Pt/C in lab-scale PEMWE cathodes. In conclusion, we demonstrate, for the first time, the fabrication of Pt/C via atmospheric pressure FBR-ALD, and its performance in PEMWE cathodes.

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AA-TuP-3 Synergetic Effects of Nanoscale ALD-HfO_2 Coatings and Bionic Microstructures for Anti-Adhesive Surgical Electrodes: Improved Cutting Performance, Antibacterial Property, and Biocompatibility*, **Jahra Mariam,*** Picosun Oy, Finland

Electrosurgery uses electrical energy for the exact expulsion of diseased tissues with concurrent cutting and coagulation capabilities. These days, electrosurgery is the favored strategy for more than 90% of all surgeries because of its advantages, like better control, quicker hemostasis, and reduced patient pain. To meet the strict requirements of modern electrosurgery, it was crucial to develop a feasible approach to improve the overall performance of surgical electrodes including anti-adhesion and heat dissipation. In this work, we studied a coupled electrode with micro/nano hierarchical structures that are the coated surface that was found to have excellent blood antiadhesive properties when heated above a certain temperature. Additional experiments revealed that the use of a coupled electrode had notable benefits in minimizing cutting forces, thermal damage, and the amount of tissue adhesion. As a result, we chose a coupled electrode with micro/nano hierarchical structures that are made by applying nanoscale hafnium dioxide (HfO2) coatings onto bionic microstructures (BMs). The HfO2-coated electrode is superior to other electrodes in reducing the characteristics of cutting force, thermal damage, and tissue adhesion. Moreover, the electrode exhibited excellent antibacterial properties against E. coli and S. aureus, in addition, the non cytotoxic behaviour of HfO2 is verified, which indirectly proves the biocompatibility of the coupled electrode. This multifunctional coupled electrode is a highly promising candidate for advancing the field of electrosurgery. Its versatility and capabilities make it an indispensable tool for various surgical procedures. With its impressive performance and potential, this electrode is poised to revolutionize the way we approach surgical intervention.

AA-TuP-4 Plasma Enhanced Atomic Layer Deposition of Hafnium Oxide (HfO_2) Thin Films for MIS and MIM Devices*, **Pallabi Paul**, E. Brusaterra, I. Ostermay, E. Bahat Treidel, F. Brunner, O. Krüger,* Ferdinand-Braun-Institut, Leibniz-Institut für Höchstfrequenztechnik (FBH), Germany

Vertical GaN-based devices are gaining significant attention as an alternative to Si and SiC-based counterparts [1]. There is a rising trend in integrating amorphous oxides developed by atomic layer deposition (ALD) method as gate insulator material in such devices, driven by their favorable properties, such as, relatively high permittivity, large band gap and high breakdown electric field [2,3].

Our work focuses on investigating the structural, chemical and electrical properties of HfO_2 layers fabricated by plasma enhance atomic layer deposition (PEALD) on n-type GaN substrates. The HfO_2 films were developed at 250°C by PEALD technology employing the SI 500 PEALD cluster system from SENTECH Instruments GmbH. Tetrakis(dimethylamido)hafnium (TDMAH) and O_2 plasma served as precursors, respectively, resulting in a growth per cycle of about 0.2 nm/cycle along with a very good uniformity over 100 mm diameter. The film properties and phase transition behavior were characterized by scanning electron microscopy, atomic force microscopy, X-ray reflectometry and X-ray photoelectron spectroscopy techniques. Optimized process parameters enabled films with high refractive index, high density, good stoichiometry, and low impurities; which are crucial for their suitability in device applications. Further, the stability and durability of annealed (at 350°C and 500°C) PEALD HfO_2 layers were examined. Presently, we are investigating the capacitance-voltage characteristics of these layers within MIS (metal-insulator-semiconductor) capacitor structures in order to comprehensively understand the interface trap charges and hysteresis behavior. The obtained data will be compared to our previous work using alternative stacks of thermal and PEALD Al_2O_3 layers [4]. Further, the breakdown field strength of HfO_2 films in comparison to Al_2O_3 based layers will be presented using MIM (metal-insulator-metal) devices.

Ongoing experiments on PEALD HfO_2 layers are executed to evaluate the potential enhancement in device performance as compared to Al_2O_3 multilayer stacks. HfO_2 is anticipated to exhibit a lower sub-threshold slope and a larger gate span, resulting in lower gate charge for the same modulation, thus enhancing energetic efficiency; along with broadening the material portfolio available for such applications.

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AA-TuP-5 Improving the Thermoelectric Properties of α-Mgagsb Through Powder Atomic Layer Deposition*, **Irene Garcia**, A. Bahrami, P. Ying, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

In recent years, Mg-based materials have started rivalling the performance and reliability of commercial Bi_2Te_3 thanks to doping and phase engineering. Through the application of Powder Atomic Layer Deposition (pALD) on thermoelectric powders, it is possible to create heterogeneous interfaces at grain boundaries. This modification alters carrier and phonon scatterings, ultimately enhancing the material's thermoelectric performance. In our study, we investigate the impact of coating α-MgAgSb with Sb_2Te_3 layers using pALD. The results indicate a consistent and linear decrease in total thermal conductivity as the number of coating cycles increases. To the best of our knowledge, this study marks the first report on the use of non-oxide pALD coatings for thermoelectric optimization. Our findings underscore the efficacy of pALD in reducing thermal conductivity, thereby opening up new avenues for future research on the deposition of oxygen-free semiconductors and pure metals at grain boundaries. This innovation holds promise for further advancing the field of thermoelectric materials.

AA-TuP-6 Industrially Scalable Atomic Layer Deposition of Superconducting Thin Films of Tin on Large Area Wafer Substrates with Applied® Picosun® Morpher™, ***Shashank Shukla**, A. Ghosh, J. Mariam, S. Datta, S. Muhammad, S. Younis, A. Sood,* Applied Materials Inc., Finland

Thin-film TiN is known to have one of the highest kinetic inductances in superconducting materials, which has implications in a wide range of applications – such as high frequency single photon detectors, ultra-sensitive current detectors, hybrid quantum systems and protected qubit devices (1) . We report on the demonstration of Atomic Layer Deposition (ALD) process of thin film TiN, on large area Si wafer format (300 mm) with Applied® Picosun® Morpher™ class of ALD reactors, with the future possibility of industrial scalability of such films. Atomically thin layers of 100nm TiN films were deposited on 300 mm and 200 mm Si wafers at elevated temperatures with a GPC (growth per cycle) of 0.2 Å/cycle, resulting in uniform TiN films with an effective resistivity of ~150 µΩ-cm. 15 nm of TiN test deposition resulted in a film with refractive index of 1.35, and with a 1σ non-uniformity of 1.35%. This demonstrates the quality of films that can be deposited with ALD for large wafer formats and the near-future possibility of batch ALD of films that are critical for advanced technologies like superconductors and quantum computing devices. X-ray diffraction studies are being undertaken to assess the crystallinities and crystal orientations of the films. Further to our studies, these TiN films will be sent for critical temperature resistivity measurements and XPS analysis for surface defects and surface elemental compositions. All these results will be summarized in our poster presentation. (1)Abigail Shearrow, Dave Awschalom, David I Schuster et al., 2018, Appl. Phys. Lett. 113, 21260

AA-TuP-7 High-performance Dichroic Filters by Atomic Layer Deposition for Large-Scale Neutrino Detectors, *Y. Hu,* Raytum Photonics, Inc; ***Feng Niu**, S. Lekarz, W. Lu,* Raytum Photonics, inc.

High-performance dichroic filters (DFs) are key photon wavelength sorting devices for Cherenkov and scintillation light in water- and scintillator-based neutrino detectors. Future detectors, DUNE and THIEA, require high-performance large-area DFs at a low cost. DFs are traditionally manufactured by various physical vapor deposition (PVD) techniques with many intrinsic drawbacks such as high cost, and poor large size uniformity. Atomic Layer Deposition (ALD) has been well established for precise thickness control, excellent large-area uniformity, super conformity for coatings on complex surfaces, and low growth temperatures, thus provides an excellent solution to manufacturing various bandpass DFs requiring tight specs for multiple dielectric layer coatings and for precise wavelength positioning and steepness on large area flat and curved glass and polymer substrates.

Raytum Photonics is specialized in developing advanced ALD technology for optical applications. In this presentation we will demonstrate that a long pass (LP) edge filter in 360-500nm with a high transmission band ≥ 90% at 400-500nm, and a low transmission in the blocking band < 400nm has been achieved by ALD consisting of 64 dielectric layers on a variety of glass substrates up to 4-inch diameter in size. The cut-on edge around 400nm is sharp with about 10nm broadening. We will further demonstrate that a short pass (SP) DF in 320-500nm with a high transmission band around 85% < 400nm was successfully fabricated all by ALD consisting of 48 dielectric layers on 100mmx77mm B270 glass substrates with excellent uniformity (<1%) and a sharp cut-off edge with around a 10nm broadening. Optical loss mechanisms, light angular performance, and medium dependence for further improvement were investigated and will be presented.

This work presents a cost-effective DF fabrication method by ALD coating technique for large-scale neutrino detectors with a potential path for commercialization. Prototypes of both LP and SP DFs have been demonstrated and an ALD batch process is being developed and DFs are being produced and are scheduled for the detector performance test in liquid argon at Brookhaven National Lab.

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AA-TuP-8 Remarkable Productivity and Performance of Flexible Indium Zinc Oxide Thin Film Transistors through Composition Engineering via Atmospheric Pressure Spatial Atomic Layer Deposition, ***Chi-Hoon Lee**, K. Yoo, D. Kim, C. Park, J. Park,* Hanyang University, Korea

Indium-zinc oxide (IZO) thin-film transistors (TFTs), a form of amorphous oxide semiconductors (AOSs), are gaining recognition as ideal channel materials in TFTs. Their attributes include a wide band gap, high on-off ratio, excellent electron mobility, and robust thermal and mechanical reliability. The creation of IZO thin films with varying metal cation ratios has been pursued using methods such as thermal evaporation, chemical vapor deposition (CVD), wet solution process, pulsed laser deposition, sputtering, and atomic layer deposition (ALD). ALD has proven effective in managing nanoscale thickness and adjusting the metal cation ratio, but its low deposition rate hinders industrial productivity. To address this, spatial atomic layer deposition (S-ALD) was proposed. S-ALD, capable of operating at atmospheric pressure, spatially separates the precursor and reactant using an inert gas, thus enhancing the deposition rate.

Our research utilized AP S-ALD to investigate the growth of IZO thin films with varying metal cation compositions. We examined how these compositions influenced the physical and chemical properties of the IZO films. Various characterizations were conducted to thoroughly evaluate the films. Physical properties were analyzed through Hall measurements, X-ray diffraction (XRD), and atomic force microscopy (AFM), exploring the electrical properties, crystallinity, and surface roughness. Chemical properties were evaluated using X-ray photoelectron spectroscopy (XPS), confirming the presence of carbon impurities and changes in the oxygen defect ratio.

Our analysis indicated that the characteristics of IZO films significantly influence the performance of IZO TFTs. We found that indium 43 at% IZO films, demonstrating superior TFT mobility (45.7 $cm^2/V\cdot s$) and reliability (ΔV_{TH} = 0.63 V), were most suitable for use as active layers in TFTs. Moreover, a bending test performed on these films confirmed their mechanical stability. The findings suggest that IZO TFTs developed via AP S-ALD hold promise for future applications in the flexible electronics industry.

AA-TuP-9 Investigation into ALD-CuS_x as a Precatalyst for Electrochemical CO_2 Reduction, *M. Suominen,* Aalto University, Finland; ***Miia Mäntymäki**, M. Mattinen,* University of Helsinki, Finland; *J. Sainio,* Aalto University, Finland; *M. Putkonen,* University of Helsinki, Finland; *T. Kallio,* Aalto University, Finland

Power-to-X concepts make use of excess renewable energy by converting it into valuable chemicals, fuels or heat. One attractive power-to-X concept is the electrochemical reduction of CO_2 to form more valuable chemicals. In this work, we studied the electrochemical reduction of CO_2 in a flow cell with the aim of transforming CO_2 into formate.[1] Gas diffusion electrodes comprising of O_3-modified single-walled carbon nanotubes were coated with CuS_x precatalyst films using ALD. Two different CuS_x processes were studied in this work, using either $Cu(thd)_2$ or $Cu(acac)_2$ as the copper precursor and H_2S as the source of sulfur. $Cu(thd)_2$ depositions were done at 130 °C and $Cu(acac)_2$ depositions at 160 °C. Different electrode configurations and electrolysis conditions were studied and optimized. The best results were obtained using the $Cu(acac)_2$ precursor, which appears to form a copper(I) sulfide based on XPS quantification of Cu and S, and X-ray diffraction experiments.

Optimized electrolysis conditions (0.5 M $KHCO_3$ (aq) at 40 °C, Figure 1) resulted in Faradaic efficiencies for formate formation in the range of 40 to 50%. Other electrolysis products included H_2 and CO in all experiments. Most of the S was lost during the electrolysis experiments. Sulfur leaching has also been reported in previous studies with CuS_x precatalysts formed using other techniques.[2] Our experiments with ALD copper modified electrodes showed that sulfur plays an integral part in the electrolysis process despite apparently leaching out of the precatalyst in the early stages of the reaction. In a comparison experiment, metallic copper films deposited onto the same electrode and used in the same electrolysis conditions resulted in H_2 as the main reduction product, highlighting the importance of sulfur in obtaining significant amounts of formate in the flow cell system.

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AA-TuP-11 *In-Situ* Crystallization of Atomic Layer Deposited TiO_2/MoO_x Stack for Metal-Insulator-Metal Capacitor Application, ***Chaeyeong Hwang**, W. Jeon,* Kyung Hee University, Republic of Korea

Metal-insulator-metal (MIM) structures, such as capacitors in DRAM devices and blocking oxides in NAND flash memory devices, play a crucial role in determining the operational characteristics of various memory semiconductors. To enhance the performance of these devices, securing high capacitance with low leakage current in MIM capacitors is essential [1].

Among the various high dielectric constant (*k*) materials, TiO_2 is considered the most promising due to its very high dielectric constant of 170 when in a rutile crystalline structure. Additionally, various atomic layer deposition (ALD) processes for TiO_2 thin films have been developed, making TiO_2 a highly promising candidate. However, achieving a rutile crystalline phase in TiO_2 requires the use of electrodes with crystalline similarity, such as Ru or MoO_2, presenting a limitation [2].

Furthermore, the proposed electrodes, Ru and MoO_2, have critical limitations in adapting to actual applications due to severe morphology degradation during subsequent processes. Ru tends to oxidize to RuO_2 or RuO_4 and reduce to Ru easily due to its relatively low reduction-oxidation resistance, resulting in surface morphology degradation [3]. During the formation of MoO_2, a reduction process inevitably leads to agglomeration phenomena that adversely affect MIM capacitor leakage current [4].

Therefore, in this study, we developed an in-situ crystallization of TiO_2/MoO_x to form a rutile-TiO_2/MoO_2 stack for achieving enhanced MIM capacitor characteristics with high capacitance density and low leakage current simultaneously. Various stack structures with varied TiO_2 and MoO_x film thicknesses were examined. By conducting various analyses, it was revealed that the enhancement in the MIM capacitor properties was attributed to the capping layer formed by a portion of the TiO_2 film preventing agglomeration during the reduction process of MoO_x.

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AA-TuP-13 ALD SiO_2 Provides Efficient Ge Surface Passivation with a Tailorable Charge Polarity, ***Oskari Leiviskä,*** Aalto University, Finland*; H. Liu,* Aalto University, Finland, China*; J. Fung,* Aalto University, Finland, Hong Kong*; J. Isometsä, V. Vähänissi, H. Savin,* Aalto University, Finland

Atomic layer deposited (ALD) thin films have proven to be a highly effective method to reduce electronic recombination losses caused by defects present at the Si surfaces. Likewise, germanium (Ge) surfaces suffer from the same recombination problem and indeed, various ALD-based surface passivation schemes have been tried recently on them as well. The current methods utilize mainly so-called field effect passivation based on the negative fixed charge present in the film, such as aluminum oxide (Al_2O_3). The fixed charge induces an electric field to the vicinity of the substrate surface and thus prevents surface recombination by repelling electrons away from the surface. The negative charge can, however, be detrimental for certain applications. Therefore, there is a motivation to find a material which provides either a positive fixed charge or even better the ability to tailor the charge polarity.

In this work we propose plasma-enhanced atomic layer deposited (PE-ALD) silicon oxide (SiO_2) layers as a positive charge containing material for passivation of Ge surfaces and apply them as further charge tailoring interlayers for Ge/Al_2O_3 interfaces, as was demonstrated previously for Si/Al_2O_3 interfaces. First, we study 10 nm thick PE-ALD SiO_2 films on n-type single-crystalline Ge wafers from which the charge polarity is determined. Next, the impact of PE-ALD SiO_2 layers at Ge/Al_2O_3 interface is studied by varying the SiO_2 interlayer thickness in the range of 1-20 nm. The passivation quality is monitored by measuring the minority carrier lifetime (τ_{eff}) and the thin film charge (Q_{tot}) is determined from contactless capacitance-voltage (C-V) measurement.

The results demonstrate that a bare PE-ALD SiO_2 film provides lifetimes in a similar range (> 1 ms) as previous state-of-the-art Ge surface passivation schemes. Surface recombination is seen to increase when depositing negative corona charge at the surface (i.e. effective neutralization of fixed charge) indicating the formation of positive charge on the Ge/SiO_2 interface. Figure 1 presents both the τ_{eff} and the Q_{tot} obtained with an SiO_2 interlayer with varying nominal thickness at Ge/Al_2O_3 interface. C-V measurements show that ALD SiO_2 interlayers at the Ge/Al_2O_3 interface allow us to tailor the effective charge polarity from negative to positive by gradually increasing the SiO_2 layer thickness from ultrathin to thicker layers. Changes in the interlayer thickness at the Ge/Al_2O_3 interface caused a shift from negative effective charge to positive as the thickness of SiO_2 increased. This also influences the τ_{eff} measured from these samples, implying an altering presence of field-effect passivation.

AA-TuP-14 Optimization of Thin Film Encapsulation Layers by ALD and SALD for Perovskite-Silicon Tandem Solar Cells, ***Aubin Parmentier,*** *D. Coutancier,* Institut Photovoltaïque d'Île de France (IPVF), France*; T. Bejat, S. Cros,* Commissariat aux Energies Atomique et Alternatives (CEA) Liten, France*; D. Muñoz-Rojas,* Université Grenoble Alpes, CNRS, Grenoble INP, LMGP, France*; N. Schneider,* Institut Photovoltaïque d'Île de France (IPVF), France

In the context of decarbonization of energy production, new types of photovoltaic solar cells are elaborated to achieve higher power conversion efficiencies at lower manufacturing costs. One particular solution is considered: tandem silicon-perovskite cells, which combine a silicon bottom cell with a perovskite-based top cell that have reached 33.9 % efficiencies [1]. However, those new architectures come with new challenges. Perovskite are sensitive to humidity, which severely limits their long-term stability. One possible solution to protect them from extrinsic degradation and increase their durability is the use of efficient barrier layers, often referred as encapsulation layers. [2].

Thin Film Encapsulation (TFE) is a powerful method to encapsulate solar cells. Among the various thin film deposition method available, Atomic Layer Deposition (ALD) is an attractive technique. Indeed, it enables the deposition of thin films of controlled thickness, uniform, dense [3], with very low pinhole defect densities and at low temperature (< 100 °C to avoid damaging the perovskite top cell [4]).

Indeed, inorganic or hybrid organic-inorganic nanolaminate structures synthesized by ALD are very promising have Water Vapor Transmission Rate (WVTR, the physical quantity used to quantify barrier properties to water vapor diffusion [5]) values up to the order of magnitude of 10^(-6) g.m^(-2).d^(-1) [6]. They have already been successfully applied to OLED, which have even more demanding requirements than perovskite cells [7]. In addition, encapsulation films must have sufficient mechanical properties to prevent cracks forming in them when subjected to shocks, and especially bending stresses. There are many candidate materials, most of which are metal oxides (to name but a few: 〖TiO〗_2 [8], 〖ZrO〗_2 [9], MgO [10]). They are often combined in nanolaminate structures with their metalcone hybrid counterparts [6], opening up a wide range of possibilities for the synthesis of encapsulating films.

As water permeation measurements are time-consuming, we are developing strategies to more efficiently screen encapsulation solution and take full benefit from ALD advantages (film versatility, atom-level control of thickness). This study proposes the optimization of nanolaminate layers using numerical simulations and helium permeation measurements. The comparative results obtained with helium diffusion are extrapolable to the results that could be obtained with water [11].

Finally, this study compares the benefits and challenges of ALD and SALD (Spatial ALD).[12].

AA-TuP-15 Atomic Layer Deposition of Thermoelectric Al -Doped Zno (Azo) Films on Flexible Ion Track Etched Pet Templates, ***Esa Alakoski,*** Jamk University of Applied Sciences, Institute of New Industry, Jyväskylä Finland*; S. Kinnunen,* University of Jyväskylä, Department of Physics, Jyväskylä, Finland*; T. Laine,* Jamk University of Applied Sciences, Institute of New Industry, Jyväskylä, Finland*; T. Girish,* Aalto University, Department of Chemistry and Materials Science, Finland*; J. Julin,* University of Jyväskylä, Department of Physics, Jyväskylä, Finland*; M. Karppinen,* Aalto University, Department of Chemistry and Materials Science, Finland

Atomic scale thickness control and superior conformality make ALD the optimal deposition method for preparing nanostructured coatings and in the case of TE materials coatings with tailored thermal and electronic properties [1]. Even more freedom for "the atomic architect" is given by the development of MLD (Molecular Layer Deposition, "The ALD of organic materials") and the ability prepare organic/inorganic hybrid coatings and superlattice structures.[2] With superlattice structures thermal conductivity of a TE thin films can be significantly reduced e.g with ZnO:HQ(Hydroquinone) by a factor of 1/50 [3]. The most promising field of application of thin film TE devices is in wearable electronics, miniaturized biomedical devices and sensors.

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AA-TuP-16 Improvement of Interfacial Properties of $ZrO_2/Al_2O_3/TiN$ Capacitors Grown by Atomic Layer Deposition through Ar Plasma Treatment

***HyeongJun Kim**, H. Yang, W. Lee,* Soongsil University, Republic of Korea

The development of next-generation Dynamic Random Access Memory (DRAM) capacitors emphasizes the scaling of devices by employing high-k dielectric materials to achieve high capacitance and low leakage current at a smaller cell size. DRAM capacitor currently utilizes dielectric material of ZrO_2 and Al_2O_3-based multilayers in mass production. This multilayer structure has been used thanks to its high dielectric constant, appropriate bandgap, and excellent leakage current characteristics. However, challenges arise due to the decrease in dielectric thickness, and it is difficult to maintain the physical properties of the thin film itself or to deteriorate properties due to interfacial layers forming between the electrode and the dielectric film.

While significant study on atomic layer deposition (ALD) is underway for excellent high-k oxides such as ZrO_2, chemical-reaction-based deposition processes have been reported to result in the formation of undesired low-permittivity interfacial layers between the electrode and dielectric layer. This persistent issue leads to degradation in the electrical properties of capacitors. To decrease the so-called extrinsic dead layer effect, the bottom electrode should be prevented from the oxidation or the already formed interfacial layer should be reduced again.

In this study, Ar plasma treatment was applied to planar capacitors of ZrO_2/Al_2O_3 dielectric layer and TiN bottom electrode to suppress the interfacial low-k layer (TiOx, TiOxNy) formed between the bottom electrode and the dielectric film. ZrO_2 and Al_2O_3 thin films were deposited through an ALD process at 300°C with cyclopentadienyl tris(dimethylamino) zirconium and trimethyl aluminum as Zr and Al precursors, respectively. High density (~200 g/m^3) O_3 was used as an oxygen source for both ALD process. Au top electrode was deposited through a thermal evaporation process. Consequently, (top) 60 nm $Au/ZrO_2/$ 4 nm Al_2O_3/100 nm TiN (bottom) structure was fabricated with various thickness of ZrO_2. To investigate the plasma treatment effect on the interface and capacitor property, Ar plasma treatment was conducted before and after the deposition of the ZrO_2 dielectric film at 300°C. Regardless of the plasma sequence, extrinsic dead layer between Al_2O_3 and TiN was removed and interfacial component of equivalent oxide thickness was decreased from 4.0 nm to 2.9 nm. Furthermore, by controlling the time and power of Ar plasma treatment, the feasibility of plasma treatment in three-dimensional structures was investigated. For Ar plasma treatment time of 4 – 10 min and power of 100-200 W, the capacitance was increased by about 38% with negligible variations.

AA-TuP-17 Enhancing Resistive Switching Properties of TiO_2 Thin Films Grown by Atomic Layer Deposition through Pyramid-Structured PDMS Substrate

***Jaejun Lee**, K. Lyu, W. Lee,* Soongsil University, Republic of Korea

The Resistive Random Access Memory (RRAM) is a type of non-volatile memory that has garnered significant attention for its potential advancements in the field of electronic storage. Recently, a well-fabricated RRAM device has been adopted as a key memristive artificial synaptic device for neuromorphic computing applications. RRAM operates based on the reversible Resistive Switching (RS) phenomenon, where the resistance state can be switched between Low Resistance State (LRS) and High Resistance State (HRS) through set operations (transitioning from HRS to LRS) and reset operations (transitioning from LRS to HRS). RRAM has advantages such as non-volatility, allowing data preservation even when power is off, low power consumption, and high speed. However, in commonly used flat RRAM, controlling precise RS is challenging due to the random occurrence of Conductive Filaments (CF). This leads to issues with non-uniform RS characteristics, impacting parameters like set/reset voltage and on/off ratio. To address these issues, researchers are exploring methods such as creating a pyramid-structured substrate[1] or inserting electrode materials between insulators[2] to induce the formation of CFs.

In this study, a polydimethylsiloxane (PDMS) polymer substrate with a pyramid structure, rather than a flat substrate such as Si single crystal, was utilized to induce the formation of CFs in specific regions, aiming to enhance the electrical characteristics. The RRAM device was fabricated by sequentially depositing a bottom electrode, insulator, and top electrode onto the PDMS substrate. The device fabrication involved using a thermal evaporator to deposit Au for both the bottom and top electrodes. The insulator was grown by atomic layer deposition (ALD) to ensure the complete coverage of 3D structured bottom electrode to prevent short-circuiting between top and bottom delectrodes. The insulator layer was deposited using Titanium tetraisoporoxide (TTIP) and H_2O to form TiO_2. Through these steps, an RRAM device with an $Au/TiO_2/Au/PDMS$ structure was created.

The fabricated device was characterized by I-V measurements to evaluate stability, set/reset voltage, and resistance, deriving the on/off ratio with respect to the number of RS cycles. The results demonstrated stable set/reset voltages of 3.15±0.36V and -1.44±0.35V, respectively, even after 1000 RS cycles, ensuring a sufficiently high and stable on/off ratio. This presentation discusses the impact of the pyramid structure on resistance change characteristics and proposes a method to enhance RRAM technology.

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AA-TuP-19 Nucleation of Ald Grown Gate Dielectrics on WS_2 Using Low Temperature Oxygen Plasma Pretreatment

***Robert Grubbs**, D. Cott, J. Swerts, B. Groven, T. van Pelt, S. Nemeth, P. Morin, C. de la Rosa, G. Kar,* IMEC, Belgium

Due the ever decreasing device size driven by the electronics industry, the future of channel materials for small transistors is heading toward the use of two dimensional transitional metal dichalcogenide (2d TMD) materials. 2d TMDs are beneficial in the short channel regime because of their potential high on-to-off current ratios and because of their potentially high channel mobilities, or conductance, between the source and the drain. Beyond TMD electrical and structural quality, two large challenges exist for the implementation of TMDs into transistors. First is the electrical contact of source and drain metals to the TMD and second is the deposition of a nanometer thin, high quality, high k, defect free dielectric material on top of the TMD to form the critical transistor gate dielectric. To tackle the second challenge, the surface of WS_2 TMD was functionalized with a low temperature remote oxygen plasma which enabled nucleation sites to form on the surface of WS_2 without catastrophic destruction of the long-range order of the WS_2. From these nucleation sites, ALD HfO_2 and Al_2O_3 using TMEAH (tetrakis(methylethylamido)hafnium)/H_2O and TMA (trimethylaluminum)/H_2O at 200C was deposited as the gate dielectric and a 5 nm thin layer with 100% coverage could be achieved at increased oxygen plasma exposures. This WS_2 functionalization / nucleation process was explored by measuring the effects of oxygen exposure and temperature and their resulting effect on the ALD deposited gate dielectric film. The ALD gate dielectric coverage and its effects on the underlying 2D materialwas quantified with AFM, XPS, photoluminescence and Raman spectroscopy. This research has led to a process where multi-layer WS_2 can be functionalized and a high-quality gate dielectric can be successfully deposited on the TMD channel materials.

AA-TuP-21 New Method for Ohmic Metal to Si Contact Formation Utilizing Highly Charged ALD Dielectric

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Ohmic contacts are typically achieved by increasing the charge carrier concentration under the metal by heavily doping the surface layer of the semiconductor substrate. However, such a heavy doping can cause damage to the semiconductor crystal structure and increase electrical losses via charge carrier recombination. Moreover, the doping processes require the use of high temperatures, which adds process complexity and restricts the use of certain material combinations. Thus, it would be highly beneficial for the entire semiconductor industry if the ohmic contact could be formed without external doping.

Here we propose a novel concept for ohmic metal to semiconductor contact formation. We utilize a specific atomic layer deposited (ALD) dielectric that is known to have a high charge density when deposited on top of semiconductor. A schematic of the concept is depicted in Figure 1. The charge present in the dielectric induces an electric field to the underlying substrate. Depending on the polarity of the charge, electric field pushes one type of carrier to the bulk and attracts the other towards the surface, leading to the formation of either electron or hole rich surface layer similarly to conventional external doping via phosphorus or boron, respectively. We propose that by etching suitable openings into the dielectric and by depositing a metal layer on top, an ohmic metal to silicon contact could be achieved. The dielectric-attracted carriers should drift underneath the openings and enable current flow in the metal-Si interface.

For experimental testing of the proposed concept, we selected Al_2O_3 as the ALD dielectric, Si as the substrate and Al as the metal. To characterize the quality of the formed Al to Si contact, we fabricated transfer length method test structures and carried out I-V measurements on them. An example of the obtained I-V curves is presented in Figure 2. The results reveal that an ohmic contact can be achieved with the proposed structure, and that the contact resistivities can get as low as 1.10 mΩcm^2, which is comparable to that of conventional heavily doped contacts (1 mΩcm^2). As the contact resistivity can be supposedly lowered by increasing the Al_2O_3 charge with e.g. different ALD precursors, higher post-deposition anneal temperatures and nanostructuring the substrate surface, the proposed concept might have potential to dethrone heavy doping as the industry standard for achieving low-resistivity ohmic contact.

AA-TuP-23 Atomic Layer Deposition of Titanium-Sulfide Films- a Study of Growth, Crystallinity, and Electric Properties*, **Zsófia Baji,*** Centre for Energy Research, Hungary

Since the success of graphene, 2D materials have gained tremendous research interest. Layered 2D semiconductors have recently become widely studied materials as they can be applied in nanosized transistors, photodetector LEDs, solar cells, and sensing devices. Due to their atomically smooth surfaces, the built-in trap concentration can be minimal, and therefore more stable and higher performance devices can be fabricated from them. 2D materials with sizable bandgaps, such as transition metal dichalcogenides have been in the focus of research, as they lack the drawback of the absence of an intrinsic band gap in graphene. The advantages of ALD, including the precise thickness and compositional control and the conformal coating of complex geometries, make it attractive for the surface engineering of these devices.

Titanium sulphide (TiS_2) is a transition metal dichalcogenide with a layered structure similar to that of MoS_2: the strong covalent bonding within the atoms of S-Ti-S forms a sheet like arrangement with the Van der Waals forces holding the layered structure together. Electronic properties of TiS_2 are unique, as the Ti atomic sheets surrounded by chalcogen atoms are highly conductive, and the material exhibits semiconducting or semi metallic properties, with arguments in the literature for both options. TiS_2, however, is not only interesting for theoretical considerations, but also very promising for a number of applications: As the interplanar gap opens the possibility of ion intercalation, it can be applied as cathode material in Li, Na, and Mg ion batteries and hydrogen storage. TiS_2 also shows interesting catalytic properties that can be used as counter-electrode in dye sensitized solar cells. The atomic layer deposition of Ti-sulphides has been possible, but the present work explores the use of Ti-isopropoxide combined with H_2S for this purpose and compares its feasibility with the more widespread precursors.

The deposition took place in a Picosun SUNALE^{TM} R-200 type ALD reactor. Hall measurement in the Van der Pauw configuration was used to determine the specific resistivity, the carrier concentration and the mobility of the deposited layers. Scanning electron microscopic images were taken by a LEO 1540 XB system, transmission electron microscopic imaging was performed using a Titan Themis 200 image corrected TEM/STEM microscope. The atomic force microscope in use for the present work was an AIST-NT, SmartSPM 1010 instrument.

AA-TuP-25 Improved Mechanical Integrity of Li-ion Battery Anode Materials Coated with Al_2O_3 by ALD*, **Liliana Stan**, X. Zhou, D. Hou,* Argonne National Laboratory*; H. Xiong,* Boise State University*; L. Zhu,* Purdue University*; Y. Liu,* Argonne National Laboratory

Group IV elements and their oxides (Si, Ge, Sn, SiO, SnO_2, etc) are considerable candidates as anode materials for high energy Li-ion batteries. They have much higher theoretical capacity than commercial graphite anode. However, these materials often suffer from structure degradation due to large volume change during cycling. To address this issue, different approaches have been explored including nanostructuring, doping, and surface coating. Al_2O_3 coating by ALD is considered a viable approach to improve the mechanical stability of high-capacity anode materials.

In this study, we used operando focused ion beam–scanning electron microscopy (FIB-SEM) to visualize the surface morphology change of Sn µm-sized particle coated by ALD with Al_2O_3 of different thicknesses (3 nm, 10 nm and 30 nm). We lithiated the Sn particles in operando mode and directly observed the morphology evolution in both coated/uncoated particles during cycling. Although the fracture of Al_2O_3 is inevitable, the Al_2O_3 breaks into a few smaller pieces instead of completely pulverization. The patches of Al_2O_3 that cover the surface of Sn particles provide local protection and reduce crack formation at the early stage of volume expansion. Interestingly, the 3 nm Al_2O_3 coating layer provides better protection than the 10 and 30 nm coating layers. Overall, the Al_2O_3 coating improves the mechanical property of large volume change anode materials and stabilizes their electrochemical cycling performance.

AA-TuP-27 Superior Reproducibility of Forming-Free Memristive Operation in Carbon Doped HfO_x Film*, **Minjong Lee**, Y. Hong, J. Kim, D. Le, D. Kim,* University of Texas at Dallas*; R. Choi,* Inha University, Republic of Korea*; J. Rohan, G. Yeric,* Cerfe Labs*; J. Kim,* University of Texas at Dallas

Transition metal-oxide (TMO) memristors have received significant attention for advanced memory applications. The new paradigm of forming-free memristor, introducing additional defects, created a pathway for highly reliable and reproducible memristive operation [1]. In this context, C. A. Paz de Araujo et al. reported born-ON memristive characteristics in spin-on carbon-doped NiO films, which is expected to be correlated electron random-access-memory (CeRAM) with forming-free characteristics [2]. While this technique effectively triggers the prototype's operational mechanism, spin-on deposition exhibits notable limitations in fabricating integrated circuits, particularly for 3D architecture.

In this study, we present the development of a prototype born-ON HfOx memristor achieved through atomic layer deposition (ALD). Carbon was introduced into the HfOx film using a super-cycle approach of atomic and molecular layer deposition (ALD and MLD) processes (Fig. 1a). We confirmed that the combination of ALD and MLD processes enables controllable carbon concentration ranging from 0 to 22% and above. Among these, the HfOx memristor with 15% carbon exhibits born-ON memristive operation. Variability was checked for five batches, and each batch consistently exhibited born-ON memristive behavior with consistent low and high resistance states (LRS and HRS) (Fig. 1b). These born-ON characteristics also provide reasonable device-to-device variations with micrometer-scaled device area (Fig. 2a). Interestingly, the IOFF decreases with a smaller device area, whereas the ON current (ION) does not change significantly. This implies that scaling down the device area to the nanoscale for memristive layers could potentially result in a higher ON/OFF current ratio with reduced IOFF. Moreover, this provides clear evidence that IOFF is more likely to homogeneously transport in the HfOx layer. The homogeneous transport for IOFF in HfOx devices can address stochasticity issues associated with the inhomogeneous size and spatial distributions, ensuring reliable operation for device/batch variations [3]. We thus believe that this carbon doped HfOx memristor stands out as a promising candidate for reliable emerging memory applications.

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AA-TuP-28 Atomic Layer Deposition of Niobium Oxide using (Tert-butylimido)tris(diethylamino)niobium and Anhydrous Hydrogen Peroxide for Ferroelectric Hafnia Applications*, **Jin-Hyun Kim**, T. Ford, M. Lee, D. Le, T. Chu, D. Kim,* University of Texas at Dallas*; M. Benham, J. Spiegelman,* RASIRC*; S. Kim,* Kangwon University*; J. Kim,* University of Texas at Dallas

The ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) has attracted extensive attention due to its robust ferroelectric properties and compatibility with back-end of line (BEOL) processes. Our previous research successfully demonstrated the fabrication of BEOL-compatible HZO films as thin as 4 nm using anhydrous hydrogen peroxide (H_2O_2) to achieve low operating voltages and high endurance.[1] However, when processed at low temperatures, HZO films face reliability challenges, including fatigue, imprint, and retention. In addition, the reduction in film thickness leads to an increase in leakage current, which poses a serious challenge to further scaling. The drive for device size scaling also affects electrode thickness, which subsequently limits the tensile stress that is critical for promoting the ferroelectric orthorhombic phase formation in HZO films. Several methods have been proposed to further continue the scaling. One of the potential solutions is to dope or insert a thin layer of niobium oxide (Nb_2O_5) in the TiN/HZO/TiN stack. Recent studies have shown that doping HfO_2 with niobium oxide enhances its dielectric constant while suppressing leakage current.[2] In addition, inserting Nb_2O_5 film between the ferroelectric La-doped HZO and TiN electrode improved the ferroelectric response and reliability.[3] Thus, to reduce the leakage current and promote the formation of ferroelectric orthorhombic phase during scaling, strategies such as Nb doping and interface engineering will be explored.

In this study, we will demonstrate the Nb_2O_5 ALD using (tert-butylimido)tris(diethylamino) -niobium (TBTEA-Nb) and HZO ALD process using TDMA-Hf/TDMA-Zr supercycle, both using anhydrous H_2O_2. We aim to investigate Nb doping and interface modification on the TiN/HZO/TiN stack, with variations in HZO film thickness.The effects of Nb_2O_5 on dielectric constant, leakage current, and polarization changes in ferroelectric HZO capacitors will be quantified using Keithley 4200A-SCS parameter analyzer and Agilent 4284A CV meter. In addition, the crystallization and composition of the films will be verified by grazing incidence X-ray diffraction and X-ray photoemission spectroscopy. The detailed experimental procedure and results will be presented.

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AA-TuP-29 Atomic Layer Deposition of Cobalt Phosphide for Efficient Water Splitting

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Transition-metal phosphides (TMP) prepared by atomic layer deposition (ALD) are reported for the first time. Ultrathin Co-P films were deposited by using PH_3 plasma as the phosphorus source and an extra H_2 plasma step to remove excess P in the growing films. The optimized ALD process proceeded by self-limited layer-by-layer growth, and the deposited Co-P films were highly pure and smooth. The Co-P films deposited via ALD exhibited better electrochemical and photoelectrochemical hydrogen evolution reaction (HER) activities than similar Co-P films prepared by the traditional post-phosphorization method. Moreover, the deposition of ultrathin Co-P films on periodic trenches was demonstrated, which highlights the broad and promising potential application of this ALD process for a conformal coating of TMP films on complex three-dimensional (3D) architectures.

AA-TuP-30 SnS_2 Thin Film with in-Situ and Controllable Sb Doping via Atomic Layer Deposition for Optoelectronic Applications

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SnS_2 thin film with in-situ and controllable Sb doping via atomic layer deposition for optoelectronic application

Abstract:SnS_2 stands out as a highly promising two-dimensional material with significant potential for applications in the field of electronics. Numerous attempts have been undertaken to modulate the physical properties of SnS_2 by doping with various metal ions. Here, we deposited a series of Sb doped SnS_2 via atomic layer deposition (ALD) super-cycle process, and compared its crystallinity, composition, and optical properties to those of pristine SnS_2. We found that the increase in the concentration of Sb is accompanied by a gradual reduction in the Sn and S binding energies. The work function is increased upon Sb doping from 3.98 eV (SnS_2) to 4.79 eV (Sb doped SnS_2 with 9:1 ratio). When integrated into photodetectors, the doped SnS_2 layers showed improved performance, demonstrating increased peak photoresponsivity values from 19.5 A/W to 27.8 A/W at 405 nm, accompanied by an improvement in response speed. These results offer valuable insights into next generation optoelectronic applications based on SnS_2.

AA-TuP-31 Effects of Alkali-Metal Doping on Current Amplification of Titanium Oxide Thin Film Transistors Prepared by Atomic Layer Deposition

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Thin-film transistors (TFTs) have been used as pixel-control switching devices, chemical, gas, and ion sensors. Previously, we demonstrated nanometer-thick titanium oxide TFTs (TiO_2-TFTs) as gas and UV sensors where the drain current was drastically changed by contacts with oxygen, dry air, nitrogen, and UV light [1]. In this study, we fabricated extremely surface-sensitive TFTs using titanium-oxide channels with a thickness of 16 nm as alkali metal detect sensors. The fabricated TFTs showed high current amplification in the order of mA due to sodium adsorption. We used aluminum-silicate multiple films as the sodium adsorption layer. It was reported that aluminum-silicate multiple films exhibited adsorption abilities of sodium, potassium, and cesium [2]. Thus, the nano-channel TFTs with the aluminum-silicate was expected to have strong electric conduction modulation by the adsorption of these. In this paper, the TFT was fabricated and its operation mechanism was discussed by electrical measurements and device simulation.

TiO_2 was deposited on a Si/thermally oxide SiO_2 substrate using atomic layer deposition.The TiO_2 thickness was at 16 nm. The plasma excited humidified argon was used as the oxidizing agent in the ALD. Subsequently, a heat treatment at 500 °C for 30 min in an atmospheric atmosphere was carried out for crystallization. 100 nm thick Ti electrodes were formed by electron-beam evaporation using a metal mask. For the gate electrode, the oxide film was area-selectively removed and In was fabricated. Finally, 10 nm of aluminum-silicate was deposited as an alkali-metal adsorption layer using room temperature atomic layer deposition. In this study, a combination of monolayer of aluminum-silicate and 15 layers of SiO_2 were deposited repeatedly for 10 cycles. Fig. 1 shows the structural diagram of the TFT.

Fig. 2 shows the relation between drain current and alkali-metal chloride concentration. The adsorption was performed by immersion of the sample in NaCl, KCl and CsCl solutions for 30 minutes each, rinsing with deionized water and drying for 3 hours under atmospheric conditions. The drain current decreases at 100 mM and 1 M for NaCl and KCl. With regards to enhanced drain currents in TiO_2-TFTs, it is considered that the alkali-metal suppressed defect levels in the TiO_2 band gap and thus improves the conductivity of TiO_2. T. Singh et al. reported that in mesoporous TiO_2, alkali-metal doping suppressed oxygen vacancies in TiO_2 and enhanced electrical conduction [3]. We believe that the TiO_2-TFT fabricated in this study can be used as alkali-metal sensors and high-mobility switching devices.

AA-TuP-33 Development of Antibacterial Neurostimulation Electrodes via Hierarchical Surface Restructuring and Atomic Layer Deposition

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Surgical site and post-implantation infections are amongst the most devastating complications after surgical procedures and implantations. Additionally, with the increased use of antibiotics, the threat of antibiotic resistance is significant and is increasingly being recognized as a global problem. Therefore, the need for alternative strategies to eliminate post-implantation infections and reduce antibiotic use has led to the development of medical devices with antibacterial properties. In this work, we introduce a two-step process using femtosecond laser hierarchical surface restructuring and atomic layer deposition for deposition of ultra-thin and ultra-conformal metal oxide thin films for development of electrochemically active antibacterial platinum-iridium electrodes targeted for use in neurostimulation and sensing/recording applications. It will be demonstrated that due to the unprecedented increase in the surface area of the electrodes post-restructuring, the ALD-deposited antibacterial metal oxide thin films on hierarchically restructured electrodes are capable of releasing sufficient antibacterial metal ions to kill Escherichia coli and Staphylococcus aureus, two common types of bacteria responsible for implantation infections.

AA-TuP-35 Stabilization of Ni-YSZ Fuel Electrodes using an ALD-Grown Aluminum Titanate Interlayer

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The degradation of the fuel electrode in solid oxide electrolysis cells (SOECs) currently limits their large-scale commercial adoption. This degradation is primarily caused by the agglomeration of nickel in the fuel electrode, resulting in irreversible loss of electrochemical performance. To address this challenge, Atomic Layer Deposition (ALD) was utilized to grow an aluminum titanate (ALT, Al_2TiO_5) film as a chemical anchor. This anchor prevents the migration of nickel in the yttria-stabilized zirconia (YSZ) electrode network. During the standard temperature range for manufacturing SOECs, ALT breaks down into aluminum oxide (Al_2O_3) and titanium oxide (TiO_2), which then bond with the nickel particles and YSZ framework respectively to form the anchor. This process prevents nickel from agglomerating and maintains the number of active sites from the initial nickel loading, thus extending the lifespan of SOECs.

In experiments with YSZ button cells, it was demonstrated that an ultrathin ALT interlayer, measuring < 5 nm in thickness, infiltrated into the porous YSZ electrode, significantly improved the thermal stability of the nickel in these cells. This improvement was evident in the cell's electrochemical performance, shown through current-voltage (IV) polarization curves and Electrochemical Impedance Spectroscopy (EIS), and in reduced migration and agglomeration of nickel, as seen in SEM cross-section images. The study's findings demonstrate that a 2 nm-thick ALT interlayer deposited by ALD does not adversely affect the cell's ohmic resistance and effectively prevents nickel sintering and the loss of active area during high-temperature accelerated stress testing. However, thicker ALT layers, while improving nickel stability, impede oxygen ion transport in the electrode and significantly increase the cell's ohmic resistance of the cell, leading to a decline in performance.The ALD ALT chemical anchor for the fuel electrode in SOECs enhances the long-term stability of SOECs, providing an efficient method of storing excess energy from various low-cost and renewable electricity sources as hydrogen fuel, as well as the reverse in fuel cell mode to produce energy from chemical fuels.

AA-TuP-36 ALD-NiOx Thin Film Growth using Ni(dmb)$_2$ Precursor for FaPbI$_3$-based Perovskite Solar Cells*, **HYO SIK CHANG**,* Chungnam National University, Republic of Korea

Charge transporting materials in perovskite solar cells (PSCs) have played an important role in improving the efficiency. Solution-based spin coatings cause the perovskite to dissolve and degrade the device's stability. Recently, inorganic hole transporting materials (HTMs). such as CuOx, MoOx, and NiOx are used to overcome the disadvantages of organic materials in PSC, such as long-term operational instability, low charge mobility, and incompatible processes. Specifically, NiOx in PSCs exhibits many advantages such as valence band matching with most perovskite absorbers, excellent electron blocking, high transparency, and thermal stability.

In this study, NiO for HTM were grown by atomic layer deposition (ALD) using Ni(dmamb)$_2$ precursor and H_2O, O_3 oxidants. Physical, electrical, and chemical characteristics such as Ni/O atomic ratio, and NiO conductivity in NiO thin films are being studied by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), UV-Vis., etc. In addition, we deposited FAPbI$_3$films using a co-evaporation method, and optimized the film thickness and heat treatment. FAPbI$_3$ perovskite solar cell using vacuum deposition process shows 15~19 % conversion efficiency. The FaPbI$_3$ perovskite properties following ALD-NiOx thin film growth will be discussed.

AA-TuP-37 Atomic Layer Deposition of Ultra Low-K Amorphous Boron Nitride for Futuristic Inter Metal Dielectric*, **Inkyu Sohn**, J. Park, S. Lee, J. Seo, J. Yoo, S. Chung, H. Kim,* Yonsei University, Korea

Scaling down of electronic components encounters a notable obstacle due to the reducing processing speed resulting from increasing RC delays associated with higher resistance and capacitance. Diminishing the dimensions of interconnects, which are metal wires responsible for linking various electronic components on a chip, is essential for achieving device miniaturization and non-conducting (dielectric) layers isolate these interconnects from each other. Until now, the majority of research has concentrated on reducing the resistance of scaled interconnects. This is because integrating dielectrics through low-temperature deposition processes, which are compatible with complementary metal–oxide–semiconductors, presents significant technical challenges. Materials used for interconnect isolation must possess low relative dielectric constants (κ values), act as effective diffusion barriers to prevent the migration of metal into semiconductors, and exhibit thermal, chemical, and mechanical stability. In particular, the International Roadmap for Devices and Systems (IRDS) advocates the advancement of dielectrics with relative dielectric constants (κ values) below 2 by the year 2028. Current low-κ materials, including silicon oxide derivatives, organic compounds, and aerogels, exhibit κ values surpassing 2 and have inadequate thermo-mechanical properties. Recently, Shin et al., have demonstrated ultralow-κ properties of amorphous boron nitride (a-BN) which is deposited by plasma-enhanced chemical vapour deposition (PE-CVD). The synthesized a-BN shows ultralow κ value of 1.15 at operating frequency of 1 Mhz. However, with the paradigm shift of memory from conventional planar structures to 3D architectures such as 3D DRAM or monolithic 3D integrated device, there is a need for atomic layer deposition (ALD) processes that can conformally deposit materials onto the intricate 3D structures. Here we report 4 nm thick a-BN films deposited by plasma enhanced atomic layer deposition (PE-ALD) with ultralow κ values of 1.43 (close to that of air, κ = 1) at operation frequencies of 1 MHz. The growth per cycle (GPC) is confirmed to be ~0.12 Å/cycle at 350 ℃ and the thickness of synthesized film linearly increased with the number of ALD cycles. The RMS roughness is only 1.23 nm even at 30 nm thick of a-BN which indicates the formation of smooth surface of our ALD process. Also, XPS shows the stoichiometric a-BN and TEM, XRD, Raman confirms the amorphous nature of BN. Our results demonstrate that ALD a-BN process holds the potential for application in the realization of next-generation 3D integrated devices.

AA-TuP-38 Approach to Quantitatively Imaging the Equivalent Oxide Thickness of a High-K Oxide Film on Silicon: A Dc-Free Scanning Capacitance Microscopic Method*, **Mao-Nan CHANG**,* Department of Physics, NCHU, Taiwan*; C. WANG,* Institute of Nanoscience, NCHU, Taiwan

Scanning capacitance microscopy (SCM) is a well-known and reliable technique for surface electrical analysis, providing electrical images of a nanometric area. For many years, SCM has been an important method to observe and to analyze the carrier distributions and p-n junctions in semiconductor materials and devices. Recently, the signal intensity model for SCM measurements was well-established and used to develop novel applications, such as evaluating equivalent physical thickness and dielectric constant of a thin dielectric piece. The signal intensity model also provides a good opportunity to explore the subtle relation between the SCM signal and the electrical thickness for an oxide film on silicon. In this work, a novel and promising method using dc-free SCM to quantitatively evaluate and image the equivalent oxide thickness (EOT) of a high-k oxide/SiO_2 stacked film on silicon was developed. The sample structure used in this work was a high-k oxide/SiO_2 stacked film on a p-type silicon substrate with an Ohmic back-contact electrode formed by aluminum deposition and thermal annealing. After atomic layer deposition for growing the high-k oxide, thermal annealing at different temperatures was performed in an ambient N_2. A scanning probe microscope system (Bruker Dimension ICON) equipped with an SCM module was used to acquire the differential capacitance signals of the samples. A conductive tip was used to perform dynamic dc stress at sample biases of 3 V, 4 V, and 5 V. Upon the dc stress, a dc-free SCM method was employed to observe the time-dependent variation of equivalent oxide thickness induced by charge-retention loss. Using reliable references, *e.g.*, SiO_2 on Si, a control line showing the linear relation between SCM signal ratio and EOT ratio was obtained in order to convert the differential capacitance signals into EOT values. In other words, one can convert the SCM image into EOT image through image operation. The time-dependent EOT variation indicated that the spontaneous charge de-trapping after dc stress is very limited for high-k oxide/SiO_2 stacked films. In comparison with a thermally-grown SiO_2 film on Si, charge retention in the high-k oxide/SiO_2 stacked film was obvious and kept for a long time after dc stress. Similar phenomena were observed under different dc stress conditions. It is worth to notice that the dc-free SCM method also avoids the impact induced by dc voltages for evaluating the EOT of the high-k oxide/SiO_2 stacked film.

AA-TuP-39 Investigation of Thermal Atomic Layer Deposition for Vertical-Channel IGZO FET with Good Performance and Thermal Stability*, J. Xiang,* Beijing Superstring Academy of Memory Technology, China*; X. Duan,* Institute of Microelectronics of the Chinese Academy of Sciences, China*; X. Ma, P. Yuan, **Yuting Chen**, L. Chai, Z. Jiao, Y. Shen, G. Wang,* Beijing Superstring Academy of Memory Technology, China*; D. Geng,* Institute of Microelectronics of the Chinese Academy of Sciences, China*; C. Zhao,* Beijing Superstring Academy of Memory Technology, China

Emerging computing applications such as ChatGPT and AR/VR are demanding memory chip for larger capacity and lower power consumption. IGZO-based DRAM has attracted considerable attention recently due to the extremely low off-current and BEOL compatibility of IGZO FETs. And vertical channel transistors are a promising approach to realizing 3D DRAM. In this work, we utilized thermal ALD process to deposit IGZO channel for vertical channel FET. By utilizing a fully thermal ALD process during IGZO-channel/GI deposition and applying appropriate gate film stack, the fabricated vertical channel FET exhibits good device performance and thermal stability, which is an excellent result among ALD-IGZO FETs.

AA-TuP-40 Improved Stability of Pt Catalyst for Sustainable Hydrogen Generation*, **Mingliang Chen**, P. Piechulla,* TU Delft, Netherlands*; M. Kräenbring, F. Özcan, D. Segets,* University of Duisburg-Essen, Germany*; J. van Ommen,* TU Delft, Netherlands

Green hydrogen is gaining increasing attention as a means of transport and energy storage worldwide. The proton exchange membrane water electrolyzer (PEMWE) is one of the promising methods for producing green hydrogen. In PEMWE, platinum group noble metals are commonly utilized to achieve high-efficiency hydrogen production. For example, Pt-loaded carbon black (Pt/C) is typically used as a catalyst at the cathode side, as no other catalysts can currently outperform Pt in hydrogen evolution reaction (HER) [1]. However, as a noble metal, the cost and scarcity of Pt soon become a bottleneck when scaling up hydrogen production to relevant outputs to partially replace, e.g. fossil fuels.

One potential solution for the economical use of Pt is to minimize its loading in PEMWE while maintaining the performance of the cell. To maximize the utilization efficiency of Pt, better control of the morphology and dispersion of the catalyst should be ensured. Therefore, Pt/C has been synthesized with atomic layer deposition (ALD) to achieve lower loading and enhanced catalytic performance with smaller and more uniform particle sizes as compared to those produced by conventional incipient wet impregnation. However, low Pt loading entails new challenges regarding the long-term stability of the catalyst [2]. In this work, the loading and particle size of Pt are first controlled by ALD. Afterwards, a thin layer of protective material (for example, SiO2) is coated on the outer surface of Pt or the carbon substrate to enhance its stability. Finally, accelerating stability testing of those catalysts was performed in a laboratory PEMWE setup. We demonstrate that by carefully selecting the thickness of the layer and the materials used for the protective coating can be ensured that the intrinsic activity of Pt is not compromised, while strongly increasing the stability.

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AA-TuP-41 Atomic Layer Deposition of Palladium Nanoparticles for Catalytic Applications*, B. Bawab, R. Zazpe, J. Rodriguez-Pereira,* ***Jan M. Macak,*** University of Pardubice, Czechia

Platinum group metals such as Pt, Ru, Pd, Ir, etc., have superior performance for various catalytic applications [1]. Due to their scarcity, efforts were being made to reduce or replace these noble metals. Atomic Layer Deposition (ALD) is one among the best technique to facilitate lowering of loading mass on a support of interest [2,3]. Furthermore, ALD is the most suitable technology that can decorate high aspect ratio and high surface area substrate architectures [4]. Due to the governing surface energy variations between noble metals and support surfaces, the growth initiates as nanoparticles (NP) and with a further increase in ALD cycles the agglomeration among NP's dominates over the individual NP size increase, thus developing thin films of relatively higher thickness. The surface energy variations are also known to increase the nucleation delay of noble metals including Pd. In this regard our efforts were laid to improve the functionality with pretreatments on carbonaceous supports which were shown promising to reduce the nucleation delay of ALD deposited Pd.

For electrocatalytic applications, it is important to choose the right substrates. Among the available ones, carbon papers (CP) and titania nanotube (TNT) layers are best choices considering their physio-chemical properties, availability, vast literature, and low costs incurred using these as support substrates in electrocatalysis and photocatalysis. Several surface modifications for CP's and variations on morphological aspects of TNT layers had attracted a great attention form applied fields due to their improved surface area, conductivity, and stability [5-8]. Uniformly decorating these CP's and TNT layers by NPs of catalysts proved to be highly efficient with no boundaries on applications, as shown in our recent papers [9-10].

The presentation will introduce and describe the synthesis of Palladium NPs by ALD on CP substrates [9] and TNT layers with high aspect ratios [10]. It will also includethe corresponding physical and electrochemical characterization and encouraging results obtained in electrocatalysis.

AA-TuP-43 Optimizing Izo Tft Performance Through Al Doping Cycle Control via Atmospheric Pressure Spatial Atomic Layer Deposition*, K. Yoo, D. Kim, C. Lee, D. Kim,* ***Chang-Kyun Park,*** *J. Park,* Hanyang University, Korea

Oxide semiconductors exhibit excellent electrical properties and thickness uniformity in the amorphous state, and notably low leakage currents, making them desirable materials. Among the notable materials in this category is indium gallium zinc oxide (IGZO), introduced by Hosono Group. In IGZO, indium aids carrier generation, gallium suppresses carriers, and zinc helps in network connectivity between materials. Deposition methods for obtaining such oxide semiconductors include sputtering and atomic layer deposition (ALD). While sputtering offers high productivity, it lacks precise control over ion composition and often requires complex equipment setups with multiple targets. Additionally, it faces challenges in achieving uniformity in large-area deposition and coating thickness. On the other hand, ALD enables precise control over ion composition and ensures excellent thickness uniformity even in complex, high aspect ratio structures. However, ALD still suffers from low productivity due to its inherent purge time. Spatial ALD (S-ALD) has emerged as a promising approach that retains the advantages of conventional ALD while improving productivity and enabling applications in flexible displays [1,2].

In this study, we employed Atmospheric Pressure Spatial ALD (AP S-ALD) to investigate the effects of substituting gallium ions with cost-effective aluminum ions in IGZO, aiming to enhance productivity in the display industry and secure competitiveness in the flexible electronics market. as shown in **Fig 1**, By utilizing AP S-ALD, we established a window for ALD deposition of In_2O_3, ZnO, and Al_2O_3 films with higher productivity compared to conventional ALD methods. Focusing on IGZO TFTs, we divided the deposition process into different cycles of aluminum incorporation (0, 1, 2, 3 cycles) and examined the electrical characteristics of the films, as shown in **Fig 2**. We observed a decrease in carrier concentration with increasing aluminum cycles, leading to a positive shift in threshold voltage (V_{TH}) and a decrease in mobility, indicating a direct correlation with carrier variation, as shown in **Fig 3**. Optimal reliability was achieved in the region where oxygen vacancies were minimized with increasing aluminum cycles, demonstrated by successful bending tests under conditions mimicking a 1 mm radius for 50,000 cycles in **Fig 4**. Through this study, we validate a method to enhance productivity in flexible display manufacturing by optimizing deposition techniques and incorporating cost-effective ion substitutions.

AA-TuP-44 Effect of One ZrO_2/HfO_2 Thickness of ZrO_2/HfO_2 (Zr/Hf=1/1) Laminate on Characteristics for Non-volatile DRAM*,* ***Tomomi Sawada,*** *T. Nabatame,* National Institute for Materials Science, Japan*; T. Onaya,* The University of Tokyo, Japan*; H. Miura, M. Miyamoto, K. Tsukagoshi,* National Institute for Materials Science, Japan

Ferroelectric Zr-doped HfO_2 (HZO) film has been widely investigated as capacitor insulator for future non-volatile DRAM [1,2]. HZO film was generally fabricated from ZrO_2/HfO_2 laminate film, and the Zr/Hf ratio of the ZrO_2/HfO_2 film was controlled by changing the numbers of ZrO_2 and HfO_2 cycle during ALD. However, the influence of thickness of one ZrO_2/HfO_2 layer in the ZrO_2/HfO_2 laminate with the same Zr/Hf ratio on characteristics are not currently understood. In this study, we investigated characteristics of TiN/HZO (ZrO_2/HfO_2 =1/1)/TiN capacitors with various thicknesses of one ZrO_2/HfO_2 layer.

TiN/HZO/TiN capacitor was fabricated as follows: A 10-nm thick ZrO_2/HfO_2 laminate film was deposited on p^+Si/TiN substrates via ALD at 300°C using tris(dimethylamino) cyclopentadienyl zirconium and hafnium precursors and H_2O gases. The thickness of one ZrO_2/HfO_2 layer was varied to 0.098, 0.20, 0.29, and 0.39nm by changing ALD cycles of 1/1, 2/2, 3/3, and 4/4. TiN top electrode was deposited on the ZrO_2/HfO_2 film. Finally, post-metallization annealing (PMA) was carried out at 300, 400, and 500°C in N_2.

All as-grown ZrO_2/HfO_2 films had an amorphous structure. The ZrO_2/HfO_2 films started crystallizing at 400°C when the thickness of one ZrO_2/HfO_2 layer became ≥0.20nm. The crystal structure was mixture of cubic/tetragonal/orthorhombic (C/T/O) and monoclinic phases. On the other hand, we found that the ZrO_2/HfO_2 film with one ZrO_2/HfO_2 layer (0.098nm) remained an amorphous structure at 400°C and started crystallizing at 500°C.

C-V measurements of capacitor was performed at a sweep voltage of ±0.5V and a 10kHz. The dielectric constant (*k*) value was estimated from capacitance at 0V before polarization. The *k* values of all as-grown and PMA300°C capacitors exhibited about 20 regardless of the thickness of one ZrO_2/HfO_2 layer. The PMA400°C capacitors with one ZrO_2/HfO_2 layer (≥0.20nm) exhibited larger *k* values of about 27 compared to that (*k*=20) of the one ZrO_2/HfO_2 layer (0.098nm). Furthermore, the *k* values of the one ZrO_2/HfO_2 layer (≥0.20nm) increased up to 32-35 at PMA500°C. The ferroelectricity was observed at PMA above 400 and 500°C for one ZrO_2/HfO_2 layer (≥0.20nm) and (0.098nm), respectively, according to C/T/O structure as explained. All PMA500°C capacitors exhibited superior breakdown electric field of above $3.0MVcm^{-1}$ at $J=10^{-2}Acm^{-2}$.

We concluded that low temperature crystallization and large *k* value can be obtained when the thickness of one ZrO_2/HfO_2 layer become ^{3}0.20nm in the ZrO_2/HfO_2 laminate film.

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AA-TuP-45 Plasma-enhanced Atomic Layer Deposition of Niobium Carbide using a New Nb Precursor and H_2 Plasma and its Application to Diffusion Barrier for Cu and Ru Interconnects*, **Chaehyun Park**, M. Kweon, S. Kim, S. Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Nb-based compounds including NbC_x, and NbN_x show a unique combination of properties, such as high melting temperature, good chemical stability, excellent electrical properties, and low resistivity [1] [2]. Due to these outstanding characteristics, Nb-based compounds have been researched for various applications, including hard surface coatings, superconducting devices, gate electrodes and copper interconnect diffusion barrier in semiconductor devices [1]. Thin films of Nb-based materials have been deposited by a variety of techniques, such as physical vapor deposition (PVD), and chemical vapor deposition (CVD). But this method is not expected to be adequate for use in future microelectronic devices which has narrow features with high aspect ratio. Therefore, achieving precise thickness deposition in complex and narrow 3D structures has become increasingly challenging. In this respect, atomic layer deposition (ALD) emerges as the optimal method for fabricating Nb-containing thin films with potential applicability in future technologies. In this study, ALD processes using the new liquid cyclopentadienyl-based Nb precursor, and various reactants such as H_2, NH_3 molecules, and its plasma were reported. Preliminary results indicate that, Figure 1, among these reactants ALD-NbC_x and NbN_x can be controllably deposited using H_2 plasma and NH_3 plasma as a reactant. As a result, we were able to create carbides (ca. 6 % nitrogen) and nitrides (ca. 3 % carbon) through ALD processes. Further experiments were done mainly using H_2 plasma to deposit NbC_x due to its better properties than NbN_x. The NbC_x thin films were grown at the temperature of 350 °C by shower head type PE-ALD reactor (IOV dX1 PEALD, ISAC RESEARCH, Korea). The self-limiting growth behavior was shown with both precursor pulsing and reactant pulsing and the saturated growth rate was approximately 0.19 Å/cycle. Film composition varied with deposition conditions and was characterized by 4-point probe (resistivity), SEM (thickness), TEM (step coverage and thickness), XRR (density and thickness), XRD (crystallinity), XPS (composition) and RBS (impurity) etc. We applied the ALD-NbC_x films to a diffusion barrier for Cu and Ru interconnects as well as gate electrodes and the results will be presented at the conference.

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AA-TuP-46 Ultrahigh Plasma Resistance of Y_2O_3 Thin Films Prepared by Atomic Layer Deposition for Uniform 3D Coatings*, J. Jeon, H. Kim, S. Jang, H. Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea*; C. Park, Y. Lee,* KoMiCo Ltd., Republic of Korea*; G. Yeom, J. Choi,* Sungkyunkwan University (SKKU), Republic of Korea*; **Sun Gil Kim**, S. Kim, H. Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea

As memory and logic devices are dramatically scaled down, the importance of etch processes for semiconductor manufacturing has been highlightened. To achieve the etch uniformity and selectivity of sub-nanometers patterns with high aspect ratios, the plasma density in etch chambers increases and the composition of plasma gas is becoming more diverse. As a result of exposure to these plasma etching conditions, the inner parts which compose the etch chamber are attacked, resulting in fatal particle contamination on wafers. Therefore, it is necessary to research etch chamber coating materials which have remarkable plasma resistance to attain high production yield by minimizing particle sources. Among ceramic coating materials, yttrium oxide (Y_2O_3) has been highlightened as a material replacing conventional Al_2O_3 coatings since it exhibits outstanding plasma resistance. Also, it is important to fabricate highly dense films with standout step coverage to apply for the delicate 3D parts coatings. Atomic layer deposition (ALD) emerges as a promising technology for the chamber parts coatings due to its self-limiting deposition characteristics, enabling uniform and high density film deposition on complex 3D structures. This study introduces ALD method of Y_2O_3 films, employing a novel yttrium precursor (ARYA™ supplied by AirLiquide) and three reactants (H_2O, O_3, and O_2 plasma). It is confirmed that Y_2O_3 films were successfully deposited without impurities using the ALD process through X-ray photoelectron spectroscopy(XPS) analysis. Furthermore, the crystalline structure and characteristics of the Y_2O_3 films were investigated by X-ray diffraction(XRD) and high-resolution transmission electron microscope(TEM) analysis depending on the reactants. Also, plasma resistance of the ALD Y_2O_3 films was evaluated using diverse mixtures of CF_4, O_2, and Ar gases, exhibiting superior resistance compared to sputter-deposited Y_2O_3 films. Additionally, we introduced the atomic layer annealing (ALA) process to increase grain size, achieving higher plasma etch reseistance. This study demonstrates that Y_2O_3 thin film coatings with ALD provides high plasma resistance in diverse etch conditions, preventing severe particle contamination during semiconductor manufacturing process.

AA-TuP-47 Atomic Layer Deposition of Copper Metal: Promising Cathode in Thin-Film Lithium-Ion Batteries*, **Niloofar Soltani**, A. Bahrami, M. Hantusch, E. Dmitrieva, K. Nielsch, D. Mikhailova,* Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, Germany

Since conversion and intercalation reactions during battery charging and discharging may cause substantial volume changes and irreversible structural transformations that severely affect cathode performance, copper metal has been shown to be a reliable substitute for conventional Li-ion hosting cathodes. However, similar to the shuttle effect in Li-S batteries, the main obstacle coupling Li and Cu is the deposition of reduced Cu^{2+} on the surface of Li during charging. In this study, the diffusion of Cu ions towards the Li foil was suppressed by employing a carbon-coated separator. Moreover, the high-rate capacity of 596 mAh g_{Cu}^{-1} at a current density of 837 mA g_{Cu}^{-1} was achieved by employing 100 nm thick Cu-film fabricated by atomic layer deposition (ALD), owing to its high surface area, which facilitated rapid redox reactions. With metallic Sb anode, a Cu-Sb full cell exhibits a reversible discharge capacity of 117 mAh g_{Cu}^{-1} (12.3 µAh cm^{-2}) at a relativity high current density of 837 mA g_{Cu}^{-1}. Constructing Cu thin films via ALD might open up new opportunities for replacing traditional Li ion-hosting cathodes in Li-ion microbatteries.

AA-TuP-49 Phosphite Doping of ALD SiO_2 Membranes Significantly Enhances Proton Conductivity for PEM Water Electrolysis*, M. Weimer, **Sara Harris**,* Forge Nano*; J. Jin, Z. Lin, K. Yim, L. Cohen, D. Esposito,* Columbia University*; A. Dameron,* Forge Nano

Water electrolysis powered by renewable sources can generate carbon-free, energy-dense hydrogen (H_2), to enable industrial decarbonization. Large-scale deployment of conventional alkaline and proton exchange membrane (PEM) electrolyzers is hindered by a higher levelized cost of H_2 by water electrolysis versus H_2 production by carbon-intensive steam methane reforming. To decrease this cost, overall cell efficiencies can be improved by reducing the ohmic overpotential required to drive proton (H^+) transport across the membrane, which is especially sensitive to membrane thickness.[1] Significant work has been done to reduce the thickness of Nafion membranes down to 50-200 *u*m while keeping the safety-critical H_2 crossover below acceptable limits, but a fundamental limit to this path is apparent.[2] We have been exploring dense ALD SiO_2 as a proton conducting oxide membrane (POM) thinner than 1 *u*m as a replacement. In this thickness regime, lower H^+ conductivities than Nafion are acceptable so long as the membrane material has lower H_2 permeabilities limiting H_2 crossover rates below maximum acceptable levels.[3] Baseline ALD SiO_2 POM had poor H^+ conductivity and superior H_2 permeability relative to Nafion-211 (24.5 *u*m). To improve H^+ conductivity, novel P precursors were explored, as motivated by work on phosphorus-doped silica glass membranes.[4] Phosphate (PO_4^{-3}) species were successfully doped into the film across a range of temperatures, 100-250°C, using ABC-type ALD as measured by x-ray photoemission spectroscopy (XPS) and[4] substantial PO_4^{-3} incorporation required extended exposures below 250°C. Increasing PO_4^{-3} content was tracked by observing a red shift in the Si-O peak at 1100 cm^{-1} with Fourier transform infrared spectroscopy (FTIR), correlating XPS data. Figure 1 shows the inverse relationship of temperature with H^+ Conductivity for SiO_2 films with and without PO_4^{-3} doping. The best-performing membrane is PO_4^{-3} doped SiO_2 film deposited at 100°C with H^+ conductivity of **$2.2x10^{-3}$ S/cm**, as measured by electrochemical impedance spectroscopy. This H^+ conductivity is almost an order of magnitude higher than previously reported ceramic membrane measured under the same conditions[5] and approaches the range of thin Nafion, $1.2x10^{-1}$ to $8.0x10^{-2}$ S/cm.[6] Importantly, H_2 permeabilities of the SiO_2 membranes remained ≈ 10^{-10} cm^2/s after PO_4^{-3} incorporation, while electronic leakage current remained low. Together, these results point towards the viability of PO_4^{-3}-doped SiO_2 ALD films as a promising material to realize sub-micron thick high H^+ conducting ceramic membranes for efficient and safe water electrolysis to enable a competitive green H_2 market.

AA-TuP-50 Deposition of Pt Nanodot on Carbon Powder Using Noble Pt Precursor and Stabilization of Nanodots*, T. Teramoto, C. Dussarrat,* K.K. Air Liquide Laboratories, Japan*; **Nicolas Blasco**,* Air Liquide Advanced Materials, France

Proton exchange membrane fuel cell (PEMFC) is a promising technology contributing to decarbonize industrial and societal activities by transforming chemical energy, typically hydrogen, into useful electric power in an efficient and clean way. Carbon-supported Pt catalyst is widely used for PEMFC applications due to its high electrochemical activities compared to other elements. However, the high cost of Pt catalyst is a significant hurdle to spread the commercialization of the large-scale utilization of PEMFC. Extending the lifetime of PEMFC is a conventional approach to improve the long term cost/performance of this technology. In this regard, several methods are attempted to improve durability of Pt catalyst on carbon support, for example, minimization of Pt nanodot agglomeration by precise size control of Pt nanodot, utilization of mesoporous carbon support, and applying metal oxide nanostructure formed by atomic layer deposition (ALD) around Pt nanodot.

This study proposes the low temperature formation (~150 °C) of carbon supported Pt catalyst via the use of a novel precursor, so called Plato, with H_2 or O_2 as coreactant in a pulsed CVD process. The process temperature using the Plato precursor is much lower compared to the ALD process using $Pt(MeCp)Me_3$, typically around 250~300 °C. The deposition of Pt nanodots was performed using Fluidized bed reactor (FBR) to achieve uniform and high dispersion of Pt nanodots on carbon supports. Transmission electron microscope (TEM) analysis indicates high dispersion of Pt nanodots on carbon support. Also, membrane electrode assembly (MEA) was prepared using the Pt/C catalyst samples made by Plato precursor and conventional $Pt(MeCp)Me_3$ precursor, and electrochemical performance using a test cell was evaluated. Also, area-selective ALD of metal oxide on a commercial Pt/C catalyst were attempted to enhance the stability of the catalyst.

AA-TuP-52 Hydrophilic Treatment of Porous PTFE Filter Membranes for Aggressive Chemical Environments*, **Rubab Zahra**, P. Kauranen,* LUT University, Finland*; M. Putkonen,* University of Helsinki, Finland

Polytetrafluoroethylene (PTFE) is a unique polymer with excellent thermal and chemical stability. However, PTFE is hydrophobic due to its low surface energy which restricts its use in applications where hydrophilicity is required. Achieving permanent hydrophilic modification of PTFE is a challenging task. Through atomic layer deposition (ALD) of inorganic oxides on PTFE substrates, it has been shown that the resulting material can survive extremely corrosive chemical environments while maintaining its hydrophilicity. In this study, we analyzed two samples of PTFE filter membranes with aspect ratios of 24 and 1000. PTFE surface was activated using ozone pretreatment and then ZrO_2 was deposited at three different ALD temperatures of 100, 150, and 200°C by using 300 cycles of tetrakis(ethylmethylamino)zirconium(IV) (TEMAZr) + oxygen source in Beneq TFS-200. Either H_2O or O_3 was used as an oxygen source. The pulse times were increased for PTFE filter membranes with an aspect ratio of 1000, to analyze its influence on the coating penetration depth. The effect of the selected oxidizer, film thickness, and deposition temperature was evaluated on the hydrophilicity and stability of membranes in an aggressive chemical environment. Using contact angle measurements, SEM/EDS cross-section analysis, water filling ratio inside the pores of samples, and thermal and chemical stability of coated membranes it was observed that ALD of ZrO_2 imparted permanent hydrophilicity and good coating penetration for PTFE sample with an aspect ratio of 24 whereas limitations in penetration depth for samples with a high aspect ratio of up to 1000 is discussed in detail. The findings of this study suggest that ALD can effectively enhance the hydrophilicity of PTFE without affecting its inherent chemical and thermal stability.

AA-TuP-54 Atomic Layer Deposition of Copper-Zinc Catalysts on Gas Diffusion Layers for the Electrochemical Reduction of CO_2*, **Lovelle Manpatilan**, S. Bianco, E. Tresso, S. Porro, J. Zeng,* Politecnico di Torino, Italy

Copper has been identified as an exceptional catalyst for the electrochemical reduction of CO_2 into value-added fuels and chemicals. By adding secondary metals such as Zinc, the product selectivity and performance of copper catalysts can be enhanced. This study presents Atomic Layer Deposition (ALD) as a novel technique for depositing Copper-Zinc electrocatalysts on Gas Diffusion Layers. ALD is a suitable deposition technique on microporous substrates due to its ability to provide uniform deposit thickness, precise stoichiometry control, and high substrate conformance. Copper acetate, copper acetylacetonate, and diethyl zinc will be used as the metallic precursors, with water as the reactant. The ALD cycle ratio between the copper and zinc precursors will be tuned to control the Cu-Zn composition, and the optimum growth conditions will be identified. For comparison, separate Cu and Zn catalysts will be synthesized using ALD. The structural, morphological, compositional, and electrochemical properties of the Cu-Zn catalysts will be evaluated against the Cu and Zn catalysts to determine the effect of Zn addition to Cu. Finally, flow cells and membrane electrode assembly will be used to assess the selectivity, performance, and stability of the catalysts for CO_2 reduction.

This research is part of the European Union Horizon 2021 Marie Skłodowska-Curie Doctoral Networks (MSCA-DN) ECOMATES program for the "Electrochemical conversion of CO_2 into added value products via highly selective bimetallic MATerial and innovative process dESign". Furthermore, the research aims to contribute to the current understanding of ALD in electrochemical CO_2 reduction and facilitate the design of other copper-based bimetallic electrocatalysts in the future.

Note: Submission for the poster session, not the oral presentation

AA-TuP-56 New ALD Materials for DRAM/3D-DRAM Scaling*, **Tejinder Singh**,* Eugenus, Inc.

As the Semiconductor industry pushes the boundaries of power, performance, area and cost, Atomic Layer Deposition (ALD) solutions are required for the next generation of Logic, Memory & Packaging applications. In this presentation, we present new ALD materials for next-generation DRAM/3D-DRAM devices.

1. **Application: DRAM Bitline Barrier Metal** - We present our ternary Ti-Si-N ALD film that has proven to have superior barrier properties for high temperature thin film providing an alternative to Physical vapor deposition (PVD). PVD based TiN film is a widely used diffusion barrier layer (Figure 1). However, deposition of ultra-thin TiN exhibits pronounced islanding which leads to rough film with polycrystalline grain structure. Furthermore, inhomogeneities due to grain boundaries offer diffusion pathways and lead to device degradation. We present our findings on the diffusion barrier properties of amorphous ternary alloy films composed of Ti, Si and N (TiSiN), an excellent alternative to TiN films. These films were grown using Atomic Layer Deposition (ALD) technique on the Eugenus 300mm QXP commercial mini-batch reactor.
2. **Application: DRAM Top & Bottom Capacitor Electrode:** We start with ALD TiN/TiSiN film and demonstrate it's step coverage with >98%. We then explore new materials for DRAM/3D-DRAM capacitor electrode such as VN/MoN deposited using ALD process in Eugenus 300mm single chamber multi-station reactor. ALD Molybdenum nitride (MoN) films were deposited via ALD using Mo solid precursor and NH3 at process temperature up to 550oC. The MoN film thicknesses were 4 to 12nm and characterized by various methodologies. Similarly, VN film was deposited using ALD process on non-pattern and pattern wafer with high aspect ratio (>90:1). Both MoN/VN show promising film properties such as higher Work Function and Lower Resistivity as compared to TiN and can be used for next-generation DRAM capacitor electrode.
3. **Application: DRAM Capacitor High-k oxide:** One of the challenges for DRAM capacitor high-k oxide is to achieve >100% step coverage. However, current ALD processes can achieve 90% step coverage. We have developed a liquid precursor delivery ALD process module that can deposit several high-k ALD films with very high dielectric constant and step coverage > 100%. High-k films (ZrO/HfO) deposited have low leakage current, excellent step coverage, excellent uniformity, and accurate composition control.

In summary, this paper presents new materials (TiSiN, TiN, VN, MoN, ZrO, HfO, MoO) deposited in Eugenus ALD reactors to meet next-generation DRAM/3D-DRAM scaling challenges.

AA-TuP-57 Low Temperature Plasma-Enhanced Atomic Layer Deposited Boron Nitride Thin Films for Low-κ Dielectric Applications*, D. Le, S. De, T. Chu, J. Kim, D. Kim, M. Lee, M. Markevitch, **Jiyoung Kim**,* University of Texas at Dallas

To mitigate parasitic capacitance within the interconnect capping layer and/or inter-metal dielectric, the integration of low-*κ* dielectric materials is necessary for high-speed integrated circuit applications [1]. However, the inherent low density of such materials often compromises the material mechanical property during integration process [2]. Recently, boron nitride (BN) has been demonstrated as a potentialcandidate due to its high thermal conductivity and robust mechanical strength in comparison to existing low-κ dielectric materials, such as boron carbon nitride (BCN) [3], silicon oxycarbonnitride (SiOCN) [4], etc. However, the conventional vapor-phase deposition process temperature requirement for BN (>400 C) is generally exceeding the BEOL compatible range.

In this study, we report a BEOL compatible highly conformal BN deposition process through plasma-enhanced atomic layer deposition (PEALD), in which tris(ethylmethylamino) borane (TEMA-B) and ammonia (NH_3) are employed as the metal and nitrogen sources. The deposition process is carried out within the range of 200–350°C. To validate the deposition of BN as well as material composition, X-ray photoelectron spectroscopy (XPS) is employed. Additional materials character techniques, including X-ray reflectivity (XRR), Raman spectroscopy, atomic force microscopy (AFM), etc., will be utilized to comprehensively evaluate the properties of the thin films. Furthermore, to determine the dielectric constant of BN, metal-insulator-metal (MIM) capacitors will be fabricated, with C-V and I-V measurements conducted for thorough characterization. The detailed experimental procedure and results will be presented.

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AA-TuP-61 Carrier Conduction Mechanisms in MIS Capacitors with Ultra-Thin Al_2O_3 at Cryogenic Temperatures*, **Joel Molina-Reyes,*** National Institute of Astrophysics, Optics and Electronics, Mexico

The study of the physical mechanisms associated with charge transport through thin Al2O3 films and the charge trapping phenomena are of great importance in the development of advanced Al2O3-based electron devices. These mechanisms have been studied at ambient temperature, as well as in temperature ranges above 300K. However, it is becoming highly relevant to consider cryogenic temperatures for these physical phenomena in order to develop devices for aerospace and cryoelectronic applications (like superconducting devices applied to sensing and quantum computing). In this work, a study comprising the electrical characterization and analysis of the electrical response of metal-insulator-semiconductor (MIS) Al/Al2O3/Si capacitors in a temperature range from ambient temperature down to 3.6 K is presented.

Ultra-thin Al2O3= 6, 2 nm were used as insulating layers by thermal ALD, thus ensuring high reproducibility in their physical and electrical characteristics. Current-voltage and electrical stress measurements were performed on the capacitors in the specified temperature range, and the experimental data obtained were analyzed using current transport equations to model the conduction mechanisms that allow charge transport through the Al2O3. Energetic parameters associated with trap levels within the Al2O3 bandgap corresponding to (1) trap-assisted tunneling and (2) direct-tunneling as main conduction mechanisms for 6 and 2 nm of

Al2O3 respectively, were obtained and their temperature dependences were associated with the presence of physical material defects. Additional phenomena that limit charge transport were also observed, such as (a) charge trapping in the bulk of Al2O3 upon the application of electrical stress at ambient temperature and (b) silicon freeze-out at cryogenic temperatures. For MIS devices, freeze-out represents the universal limit for carrier transport when silicon reaches 25 K. Our findings constitute an effort at understanding the physical phenomena that govern the electrical behavior of thin-film Al2O3-based capacitors, especially at cryogenic temperatures, given that these materials and devices are of great importance for applications in CMOS-based cryoelectronics and quantum technologies, among others.

AA-TuP-63 Alumina Coating of Diamond Filler Using Atomic Layer Deposition to Produce Thermal Interface Material*, **Hiroya Ishida**, K. Shibuta,* Sekisui Chemical Co., Ltd., Japan*; M. Groner, J. Gauspohl,* FORGE NANO, Inc.

Composite materials consisting of fillers and resins can provide performance or functionalities that single materials cannot, and so are widely used in industry. Examples include the thermal interface materials (TIMs) employed in various electronic devices for thermal management, for which there is a greatly increased demand. With the advent of 5G communications, large amounts of data must be transferred between devices and cloud-based services at high speeds. Associated semiconductor devices such as wireless communications antennas, CPUs and GPUs must operate at high frequencies and so generate large amounts of heat, which can have a major impact on their performance and service life. TIMs are typically inserted between silicon dies and heatsinks or heat spreaders to release heat and so maximize performance. These materials are employed in smartphones, communications modules, automobiles, computer servers and industrial equipment. The thermal conductivity of TIMs directly affects the performance of semiconductors, and so the selection of an appropriate TIM is as important as the module and package design with regard to thermal management.

TIMs having high thermal conductivity allow flexibility in both the module design and assembly location. The use of appropriate materials is also a vital aspect of meeting market requirements and producing advanced TIMs with greater functionality and versatility. The thermal conductivity of a composite material is determined by both the filler and the resin, in addition to the filler proportion, as summarized by the Bruggeman model. Diamond has the highest thermal conductivity of all bulk materials, and so a high diamond filler content will increase the thermal conductivity of a composite. However, the limited compatibility of diamond with matrix resins limits the practical loading levels. Chemical modification of diamond surfaces to improve compatibility has been demonstrated but is still not well understood or sufficiently established. On this basis, the present study attempted to generate thin alumina coatings on diamond fillers using atomic layer deposition as a means of improving the compatibility of this filler with resins. The resulting alumina layers on diamond exhibited enhanced reactivity with silane compounds and increased the compatibility of diamond with a silicone resin without decreasing the thermal conductivity. Alumina-coated diamond specimens were also characterized in detail and the results are reported herein.

AA-TuP-65 Hf-Doped IGZO/IZO Heterojunction Thin-Film Transistors Fabricated by Atomic Layer Deposition for OLED Display*, T. Kim, **Kang Min Lee,*** Korea University, Republic of Korea

Metal oxide thin films, widely used as channel materials for thin-film transistors (TFTs), have advantages such as high transparency, low leakage current, high uniformity, and high on/off ratio, making them useful for driving display and flexible electronics. However, they still have a lower mobility than low-temperature polycrystalline silicon (LTPS) TFTs and require high temperatures annealing process (>300 °C). Notably, the process temperature needs to be reduced for operation at flexible substrates; however, this leads to a degradation in electrical properties.

To solve this problem, we developed a heterojunction oxide-based TFTs with planar and mesh-patterned channel layers, exhibiting enhanced flexibility and superior electrical characteristics. In addition, by utilizing Hf-doped IGZO/IZO heterojuction structures, we could improve the device bias stability with a low-temperature process. The incorporation of a mesh pattern expanded a quasi two-dimensional electron gas (q-2DEG) region, enhancing the TFT performance with flexibility. Moreover, when combined with OLEDs, the devices exhibited very operation in severe bending conditions, showcasing their usefulness for the future flexible display. More detailed results including transfer curve characteristics will be presented at the conference.

AA-TuP-66 Precise Tuning of Tamm Plasmon-Polaritons Resonances with sub-Nanometer Accuracy by Atomic Layer Deposition*, **Mantas Drazdys**, E. Bužavaitė-Vertelienė, D. Astrauskytė, Z. Balevičius,* Center for Physical Sciences and Technology, Lithuania

During the last decade, much attention has been given to photonic crystal (PC) structures covered with a thin metal layer on top of PC. A type of surface mode can be generated in PC-metal structures, the so-called Tamm plasmon-polaritons (TPP), appearing at the boundary between the PC and the metal layer. TPPs are optical states, which are similar to the electron states proposed by I. Tamm and can occur in the energy band gap at a crystal surface. These energy band gap regions are the stop band of the PCs due to the Bragg reflections in the periodic structure. The TPPs are non-propagating states which can be excited in both p- and s-polarizations. The optical dispersion properties of TPPs lead to simple optical configurations without additional couplers (prisms or gratings) which are necessary for excitations of well-known surface plasmon polaritons (SPPs). This opens new possibilities for various applications such as optical biosensors, bandgap filters, nanolasing, and others. For further technological progress in these applications, precise tuning of the optical properties of the TPP-based nanostructures as well as the plasmonic resonance position in the spectra is necessary, therefore, atomic layer deposition (ALD) is a very suitable technique with monolayer-by-monolayer growth of angstrom resolution. In this study, we demonstrate the potential capability to control TPP by applying ALD as a highly precise technique for plasmonic applications. Spectroscopic ellipsometry and polarized reflection spectroscopy identified the TPP resonances in the photonic band gap (PBG) formed by periodically alternating silicon oxide and tantalum oxide layers. The TPP resonance dependence on Al_2O_3 layer thickness was evaluated, where 3 nm of Al_2O_3 layer thickness difference corresponded to ≈3 nm shift of TPP minima, demonstrating precise control capabilities when the ALD method is used.

AA-TuP-67 Rotating Drum ALD – an Alternative Approach for ALD Coating of Powders*, **Mario Krug**, M. Radehaus, M. Höhn,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany*; P. Heizmann,* University of Freiburg, Germany

Particle agitation is a crucial point for applying coatings on powder materials. Here, an alternative approach of a rotating drum within a tubular hot-wall reactor is presented. The rotating drum is a gas-flow-through-type drum offering a powder capacity of up to 100 cm^3. The powder agitation is realized by a special geometry in combination with the rotational speed of the drum. Different to a classical rotary kiln the rotating drum provides an easy-to-change and easy-to-clean option for batch processing under research and development conditions. A high freedom for experimental studies on a broad variety of powders is given by adjusting the powder particle agitation independently from the gas flow setting.

Moreover, this setup addresses important process capabilities, like tailor-made coating process designs, processing powders with broader particle size distributions and possibility of a gas phase pre- or post-treatment without vacuum break at temperatures of up to 1050 °C. Because of the modular design adaptations of the drum geometry, gas input and gas output openings as well as particle retention filters are possible without excessive effort using cost effective graphite as drum material which is passivated by a CVD-TiN coating. In case of the technological need of very thick coatings the transition from ALD to thermal CVD (standard or pulsed) can be realized using the same setup.

The experimental setup of the laboratory scale coating facility is described. Furthermore, the results of an example process of Al_2O_3- as well as $AlTiO_x$-coating on $LiNi_{0.5}Mn_{1.5}O_4$ particles (LNMO) are presented.

AA-TuP-69 Improving Ferroelectricity of Hafnia-Based Ferroelectrics by Adopting Anti-Ferroelectric Interfacial Layer*, **Dae Haa Ryu**, J. Lee, T. Choi,* Sejong University, Republic of Korea

Hafnia-based ferroelectrics (FEs) are one of the most promising candidates for next-generation non-volatile memory owing to their scalability and complementary metal-oxide-semiconductor (CMOS) compatibility. However, they have limitation in endurance properties which need to apply high operating voltage for switching ferroelectric polarization. On the other hand, hafnia-based anti-ferroelectrics (AFEs) have advantages for fatigue effect because their movement of defects are much smaller than ferroelectrics in phase transition. Furthermore, AFEs show high speed operation due to their rapid switching of polarization, unlike the gradual polarization reversal in ferroelectrics. In this study, AFE and FE $Hf_{(1-x)}Zr_xO_2$ (HZO) were consisted multi-layer heterostructure for utilizing their advantages (i.e., lower fatigue and non-volatile switching). In this structure, fatigue effect could be decreased without reducing its remnant polarization in few nano-meter thickness. By controlling the interface between AFE and FE materials, it is possible to reduce the leakage current, a critical issue in electronic devices of a few nanometers, caused by naturally formed suboxide.

Acknowledgements

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AA-TuP-70 Atomic Layer Deposited p-type SnO Thin Film Transistors: Effect of Deposition Temperature on Device Performance and Stability*, **Kham M. Niang**, B. Bakhit,* University of Cambridge, UK*; J. Parish,* University of Bath, U.K.*; J. Driscoll,* University of Cambridge, UK*; A. Johnson,* University of Bath, UK*; A. Flewitt,* University of Cambridge, UK

Recently, p-type tin monoxide thin film transistors (SnO TFTs) produced by atomic layer deposition (ALD) has been gaining attention due to good reported device performance (field effect mobility, m_{FE} ~1 $cm^2V^{-1}s^{-1}$) and the relative ease in producing phase pure tin monoxide thin films when using a Sn (II) containing precursor.[1] This is a promising step towards realizing complementary metal oxide semiconductor (CMOS) circuits using TFTs when combined with, n-type amorphous oxide (such as indium gallium zinc oxide) TFTs.[2,3]

Various novel Sn (II) precursors have been reported recently. The most commonly used of these is bis(1-dimethylamino-2-methyl-2-propoxy)tin,[4] and the corresponding TFTs show superior performance with m_{FE} ~ 1 $cm^2V^{-1}s^{-1}$ and I_{ON}/I_{OFF} ~ 10^6 at maximum processing temperature of 250 °C.[1] We have also previously reported ALD SnO thin films using a new precursor called Sn (II) bis(*tert*-butoxide), with TFTs exhibiting m_{FE} ~ 0.6 - 2 $cm^2V^{-1}s^{-1}$ and I_{ON}/I_{OFF} ~ 10^3- 10^4 after performing post annealing at temperatures between 250 - 350 °C.[5]

Here, we will report on further optimization of the ALD process conditions with this precursor including the deposition temperature and post-annealing temperature. We will show how these conditions affect the thin film morphology, grain size and the consequent TFT performances. We will also show how ALD technology allows us to easily and consistently produce SnO TFTs with either predominantly p-type conductivity or more pronounced ambipolarity. Finally, we will report the stability of the SnO TFTs under gate bias stress tests.

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AA-TuP-72 Oxide Based Neuron Devices Employing ALD Grown Dielectrics and Channel Layer*, **Jung Wook Lim**,* YUSEONG-GU GAJEONGDONG 218 ETRI, Republic of Korea*; J. Lee, C. Yu,* UST, Republic of Korea

Artificial neural networks has demonstrated remarkable performance in learning tasks and extensively explored in recent years [1-2]. However, due to substantial power consumption and the processing of massive data, a more efficient spiking neural network approach, mimicking the human brain, has emerged as an alternative, and active research is current underway. To address these challenges, research has been conducted on CMOS-based neuron devices [1]. However, due to the intricate structure, there is still a demand for the adoption of neuron devices using 1T (a single transistor) architecture non-silicon-based semiconductor materials. Our research group implemented synaptic devices based on oxide semiconductors, demonstrating excellent linear learning characteristics [3]. In this study, we aimed to realize the firing characteristics of neuron devices in a 1T structure concerning electrical stimulation by leveraging charge trap techniques employed in this research. The neuron device with a 1T structure features a bottom gate configuration, as illustrated in Figure 1. The semiconducting channel and dielectric layers were sequentially deposited using ALD, effectively trapping charges at the interface. Under regular and repetitive electrical stimuli with a consistent voltage magnitude and pulse duration, as positive charges become trapped, the transistor's transfer curve exhibits a rapid negative shift. Furthermore, with the continued accumulation of pulse stimuli, once surpassing a critical threshold, a sudden current flow occurs, leading to firing. When applying periodic stimuli to the gate electrode of the neuron device with a voltage of 11 V and varying pulse durations of 100, 300 and 500 µs, while maintaining a pulse interval of 300 ms, the firing patterns of drain current manifested as depicted in Figures 2 (a) to (c). The on/off ratio of the firing current was approximately 10^3, and as the pulse duration increased, there was a tendency for a decrease in the frequency of firing. As firing drain current needs to be converted to the voltage signal when transmitted to the subsequent synaptic devices in the neural network circuit, requiring a conversion of current signal to voltage signal by connecting a resistor, Figure 2 (d) shows the transformation of the current signal in Figure 2 (c) into a voltage signal. Although we successfully emulated the firing characteristics of neurons with a 1T structure based on oxide semiconductors, the actual human brain exhibits more intricate firing patterns.

AA-TuP-73 MgF_2-Based Conformal Anti-Reflection Coatings on Highly Curved Lenses by Atomic Layer Deposition*, Yuma Sugai,* Shincron Co., Ltd., Japan*; H. Sugata, T. Sugawara,* Shincron Co. Ltd.,, Japan*; S. Muhammad, J. Hämäläinen, N. Lamminmäki, J. Kostamo,* Picosun Oy, an Applied Materials company, Finland

Anti-reflection (AR) coatings are crucial for a myriad of optical applications. The demand for conformal AR coatings over non-planar substrates, such as three-dimensional (3D) glass or curved lenses, is increasing. While physical vapor deposition (PVD) techniques—including electron beam evaporation and ion beam sputtering with planetary rotation—have been commonly employed for such AR coatings, these methods are struggling to maintain conformality over substrates with high aspect ratio, small dimensions or significant curvature. In response to these limitations, AR coating using Atomic Layer Deposition (ALD) emerges as a promising solution capable of achieving uniform coatings on such complex surfaces.

In this study, ALD was utilized to deposit multilayer AR films composed of MgF_2, SiO_2, Al_2O_3, and HfO_2. Notably, MgF_2 thin films are desirable for top layer due to their low refractive index (sub 1.4), wide spectral transparency from the ultraviolet to the infrared region, and considerable chemical stability. First, optimizing the thickness uniformity of the four distinct films using the Applied® Picosun® R-200 Advanced [1] was performed, then their individual optical properties were investigated. This information supported the design of a seven-layer AR film, and the AR layers onto substrates with highly curved lenses were subsequently deposited. Then, the optical performance of the coated lenses, focusing on reflectance was measured. Our measurements indicate that conformal AR coatings on lenses with pronounced curvature were successfully deposited. The research highlights the potential for achieving highly uniform AR coatings with precise optical control in areas such as medical optics, photonic integrated circuits, and meta-surface devices.

In conclusion, this study conclusively demonstrates the superiority of ALD-based AR coatings on complex geometric surfaces, offering an effective alternative to traditional PVD methods when confronted with their intrinsic constraints. With further optimization of the material stack and refinement of the deposition process, ALD presents a scalable and reliable avenue for fabricating novel AR coatings.

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AA-TuP-74 Enhanced Uniformity of Optical Films on Highly Curved Lenses using Atomic Layer Deposition for Small to Mid-Sized Batch Production*, Hironori Sugata,* *Y. Sugai, R. Sugawara, T. Sugawara,* Shincron Co., Ltd.,, Japan*; S. Muhammad, J. Hämäläinen, N. Lamminmäki, J. Kostamo,* Picosun Oy, an Applied Materials company, Finland

In the field of optics, the generation of anti-reflective (AR) coatings on high-curvature convex lenses, crucial for various applications, has been predominantly realized through Physical Vapor Deposition (PVD) methods like evaporation and sputtering. While conventional PVD techniques with planetary rotation can achieve a non-uniformity (NU) ≤ 5% on lenses over 30 mm in diameter, maintaining thickness uniformity remains a challenge. Notably, Atomic Layer Deposition (ALD) equipment manufacturers typically advertise coating NUs of 1% to 3% over flat substrates, with claims of conformal coating over 3D structures [1]. However, uniformity can vary with material and process conditions, and there is a lack of detailed literature on uniformity achievements in ALD mass production. Our study demonstrates marked improvements in film thickness uniformity through ALD for small to mid-sized batch processing.

In this study, a R-200^{TM} Advanced ALD system, manufactured by Picosun Oy (Espoo, Finland,) was utilized to conduct a small-scale batch test run. A custom fixture was designed, allowing simultaneous deposition of a single-layer 300nm thickness SiO2 on 36 convex lenses. Thickness uniformity was evaluated using the USPM-RU-W NIR Microspectrophotometer from Olympus Corporation (Tokyo, Japan), capable of precise reflectivity measurement at the micro-spot level. The lenses were mounted on a tilt stage to ensure perpendicular light incidence relative to the lens surface by fine-tuning x, y, and z positioning.

Our results indicated intra-lens NU of ≤ 1.2% within the optimally coated regions of the batch. Across the entire batch, NU was maintained at ≤ 5.0%. The findings underscore the capability of the Picosun® downflow thermal ALD system to achieve uniform coatings suitable for small to mid-sized batch production and represent a substantial advancement towards commercialization.

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AA-TuP-75 Enhancing the Stability of p-Type Tin Monoxide Thin Film Transistor Through 2D Structure Optimization via Discrete Feeding Method*, Haklim Koo*, *H. Kim, S. Choi, W. Lee, S. Kim, J. Park,* Hanyang University, Korea

Oxide semiconductors have a wide range of applications in electronics, including displays, semiconductors, and sensors, due to their exceptional electrical properties. These properties include high mobility, low off-current, and excellent uniformity. However, achieving high electrical performance in p-type oxide semiconductors is challenging due to the delocalized hole conduction path and difficulty in carrier formation mechanisms. Tin monoxide (SnO) is a promising p-type material among several candidates. This is due to its low formation energy of tin vacancies (V_{Sn}) and high hole mobility resulting from the delocalization of the hole conduction path. However, the SnO structure has low thermal stability, and it can easily undergo a phase transition to n-type tin dioxide (SnO_2). Therefore, it is important to study fabrication methods to obtain stable SnO. Several studies have reported the formation of SnO through sputtering. However, fabricating stable SnO thin films is challenging due to the narrow process window and occurrence of phase mixing. Recently, ALD has gained attention in research due to its advantages. ALD is preferred over sputtering methods due to its highly conformal growth in high aspect ratio structures and low damaging effects, making it suitable for 3D stacked devices.

In this study, we suggested that the 2d structure of c-axis aligned tetragonal SnO could be improved by controlling the precursor feeding process by evaluating water contact angle and grazing-incidence wide-angle X-ray scattering (GIWAXS) (Figure 1). Through controlling the precursor feeding method, which divides the dosing step into several stages, surface coverage was improved, and c-axis crystallinity was enhanced, which has fewer structural defects by optimizing horizontal crystal growth. As a result, it was confirmed that excellent reliability characteristics were obtained, and the thermal reliability of SnO-TFT, which had never been previously reported, was also confirmed to have outstanding characteristics. SnO-TFT we manufactured has an excellent reliability of +0.33 V and -0.25 V in P(N)BS (±2 MV/cm, 3,600s, RT), +0.47 V and -0.11 V in P(N)BTS (±2 MV/cm, 10,000s, 60℃). In addition, we have successfully fabricated a flexible SnO-TFT with a Vth change of only 0.06V even after 10,000 cycles of bending test with a curvature radius of 0.5cm (Figure 2). Through this process optimization research, we will be able to secure the stability of the SnO thin film and realize stable operation of the p-type oxide semiconductor, thereby promoting the application of oxide semiconductors to various industries such as displays.

AA-TuP-76 Resistive Switching in Hafnium-Titanium-Oxide Thin Films Grown by Atomic Layer Deposition*, Toomas Daniel Viskus,* *J. Merisalu, A. Kasikov, L. Aarik, K. Kukli,* University of Tartu, Estonia

Resistive switching has been previously studied in both titanium oxide [1] and hafnium oxide[2] metal-insulator-metal (MIM) structures. Devices utilizing TiO_2/HfO_2 bilayers have also been studied [3].

We investigated resistive switching properties of devices where $TiO_2:HfO_2$ mixed oxide dielectric layers were grown by ALD on RuO_2 bottom electrode with Pt top electrodes. The electrodes were deposited using magnetron sputtering. ALD was carried out at 350 °C. The precursors used were $HfCl_4$, $TiCl_4$, H_2O. Multiple samples with a varying ratio of TiO_2 to HfO_2 deposition cycles were prepared. For each ratio, both an as-deposited sample and a sample annealed for 30 minutes at 400 °C were evaluated.

GIXRD measurements showed that, as the HfO_2:TiO_2 ALD cycle ratio grew, one could at first observe the transition from the TiO_2 rutile phase to the $HfTiO_4$ orthorhombic ternary phase, followed by further transition the monoclinic HfO_2.

Electrical measurements were carried out using a Cascade Microtech EPS-150 probe station and a Keithley 2636A source-meter. All studied samples showed resistive switching properties. As-deposited devices with the $HfTiO_4$ orthorhombic phase and a HfO_2:TiO_2 ratio of 1:3 demonstrated ratio between the low resistance state (LRS) and high resistance state (HRS) about 10, with an endurance measurable up to thousands of cycles. Retention measurements were carried out at variable temperatures, up to 140 °C, for 6 hours and showed good stability for both LRS and HRS. Preliminary device-to-device repeatability tests were also carried out and showed that annealed devices demonstrated better repeatability when compared with non-annealed devices.

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AA-TuP-78 Comparative Study of $ZrAl_xO_y$ - based MIM Decoupling Capacitors with high-κ Dielectric Grown by 3 Generations of Metalorganic ALD Zr-precursors*, Konstantinos Efstathios Falidas*, *K. Kühnel, A. Viegas, M. Czernohorsky,* Fraunhofer Institute for Photonic Microsystems (IPMS), Germany

Decoupling capacitors provide stable capacitance over voltage, allowing good voltage regulation and noise immunity. Typically placed in BEoL, these MIM capacitors rely on high-κ dielectrics deposited through ALD. Zirconium oxide, a well-established oxide since DRAM times, is commonly doped with Al in alternating laminates. This doping strategy aims to control crystallization, minimize leakage, and enhance capacitor’s operational lifespan. The selection of appropriate metal precursors becomes pivotal in achieving optimal electrical properties that align with strict industrial standards.

This study presents a comparative analysis of 3 "generations" of metalorganic Zr-precursors employed in planar MIM capacitors. The explored Zr-precursors include 1st generation TEMAZr, 2nd generation Air Liquide ZyALD™ and the recently synthesized 3rd generation Air Liquide Kaze. Ozone serves as reactant agent and Ar as purge gas. Given the novelty of Kaze’s various ALD parameters, such as deposition temperature (T_D), purge time, oxidant time are systematically adjusted to achieve stable performance and properties comparable to existing precursors in BEoL (T_D≤400°C). Additionally, the step coverage of the last 2 generations is compared to facilitate Kaze’s application in deep 3D capacitors. Kaze exhibits coverage slightly better than its predecessor.

For $ZrAl_xO_y$ stacks, Al is introduced using Trimethylaluminum. Kaze’s uniformity and carbon impurities saturate at T_D≤400°C. Therefore, 2 T_D (350°C, 400°C) were further examined. Beyond chemical and structural analysis, MIM stacks are fabricated on 300 mm wafers incorporating TiN electrodes on both sides. Their electrical characteristics are scrutinized, considering parameters such as capacitance density and field linearity (α) across varying temperatures and frequencies. Across all 3 generations, C_0 exhibits stability over frequency (1-100 kHz). Higher T_D for Kaze$_{400°C}$ demonstrates a 62.5% lower α compared to Kaze$_{350°C}$. In comparison to TEMAZr, Kaze showcases a notable 93.7% improvement in α. Given the paramount importance of α for decoupling purposes, the decrease in C_0 is considered negligible. Moreover, studies are conducted on leakage, breakdown, and reliability. Both J-E curves and E_{BD} reveal for all 3 generations consistent and analogous behavior over a broad temperature window (25-125°C). The extrapolated lifetime of Kaze at T_D=400°C and under maximum temperature stress, exceeds the performance goal of 10 years under operating field conditions, indicating Kaze as a competitive precursor for Zr-based decoupling capacitors.

AA-TuP-79 ALD Capping Layers for Copper Redistribution Lines*, Ritwik Bhatia,* Veeco*; E. Chery,* imec, Belgium*; G. Sundaram,* Veeco*; N. Pinho, E. Beyne,* imec, Belgium

Chiplet based architectures have enabled integration of diverse chips (memory, logic, AI accelerators etc) into a high-performance package. Copper redistribution lines (RDL) enable connections between chiplets by moving power and signal lines to locations better suited for inter-chip bonding. One of the most promising approaches relies on the patterning of copper lines embedded in a polymer matrix [1]. Unfortunately, polymers are generally not good barriers against oxygen and moisture diffusion [2]. This makes the copper lines prone to oxidation (Figure-1, 3a) which is especially problematic as the width of the copper line becomes smaller [2].

In this study, ALD thin films, deposited at 100 °C, are evaluated as an oxidation barrier via high temperature storage (HTS) - 150°C for 1000 hours. Al2O3 is shown to be as good a barrier at 15nm as it is at 50nm (Figure-2). Thin capping layers are of primary importance, as they allow connections to the above metal layer through a simple sputter etch process to reopen the ALD film and land a via. ALD HfO2 is also found to be a good barrier, while TiO2 is not. Long term reliability testing (HTS for more than 2000 hours, corrosion testing (85-85 humidity + HTS) and temperature cycling) of daisy chained copper lines with ALD Al2O3-TiO2 as a barrier layer show no change in the resistance value (Figure-3b) confirming the ability of the ALD layer to fully block the oxidation of the copper lines. This indicates a very high quality of barrier performance.

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AA-TuP-80 Incipient Ferroelectric Properties in as-Deposited Hafnium Zirconium Oxide for BEoL Applications*, Alison Erlene Viegas,* Fraunhofer Institute for Photonic Microsystems (IPMS) - CNT, Germany*; K. Kuehnel,* Fraunhofer Institute for Photonic Microsystems (IPMS)- CNT, Germany*; S. Yang, K. Falidas,* Fraunhofer Institute for Photonic Microsystems (IPMS) - CNT, Germany*; M. Czernohorsky,* Fraunhofer Institute for Photonic Microsystems (IPMS)- CNT, Germany

The discovery of ferroelectric properties in doped hafnium oxide in 2011, has driven forward the research in the development of ferroelectric hafnium oxide devices. The ferroelectric phase can be stabilized by dopants, mechanical strain and annealing conditions. For application such as ferroelectric memories, a key issue is the wake-up effect, which means that the device has to be pre-stressed before the actual operation. Doping hafnium oxide with zirconium, makes it possible to fabricate devices in the Back-End-of-Line (BEoL), as the crystallization and annealing conditions are well within the BEoL restrictions.

In this paper, we report the development of the ferroelectric properties with as deposited hafnium zirconium oxide (HZO) using a new generation of metalorganic precursors, Air Liquide’s Kahe and Kaze for hafnium and zirconium respectively, designed to be operated at higher temperatures. With higher deposition temperatures, and a slow growth rate, the deposited HZO samples are crystallized in the metastable ferroelectric phase during deposition. Different ratios of hafnium to zirconium are deposited under varying deposition temperatures, to determine the optimum concentration for ferroelectricity. Higher deposition temperatures could also provide the possibility to deposit in high aspect ratio structures with good step coverage. The films are characterized by ellipsometry, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and X-ray photon spectroscopy (XPS) for the material properties. The XRD patterns show that the as deposited samples, for different ratios of Hf:Zr (deposited at 350°C), are already crystalline in the ferroelectric orthorhombic phase, without any signatures of monoclinic phase. The electrical properties were tested by depositing the material between two sandwiched titanium nitride electrodes in the form of a metal-insulator-metal capacitor. Initial testing reveals a wake-up free HZO samples with good memory window of 29.8 μC/cm^2 at 10^5 cycles.

AA-TuP-82 Exploring Brookite Phase Formation in Vanadium Oxides by Atomic Layer Deposition for Uncooled Infrared Sensor Applications*, **Hyeonho Seol**, S. Lee,* Kyung Hee university, Republic of Korea*; W. Jeon,* Kyung Hee University, Republic of Korea

Vanadium oxide has been extensively studied as a material for the microbolometer of uncooled infrared sensors. Previous research has highlighted its high reactivity, as evidenced by the high temperature coefficient of resistance (TCR) value at room temperature [1]. Vanadium dioxide (VO_2) exists in various crystalline phases, including monoclinic, brookite, and rutile phases [2]. The monoclinic phase, which is the most stable phase of vanadium dioxide, undergoes a semiconductor-to-metal transition known as the Mott transition at 67℃, rendering it unsuitable for use as an infrared detection layer for microbolometers over a wide temperature range [2]. In contrast, the brookite phase does not exhibit the Mott transition over a wide range around room temperature, making it suitable for use in infrared detection sensors.

In this study, we developed an atomic layer deposition (ALD) process for VO_2 with a brookite crystal structure, which is a metastable phase among its polymorphs. We investigated the characteristics of vanadium oxide thin films under various process conditions, including deposition temperature, using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence (XRF). TCR evaluation was conducted through resistance measurements at temperatures ranging from 30℃ to 100℃. The brookite phase was predominantly obtained at higher deposition temperatures, and it was revealed that the formation of the brookite phase was attributed to the presence of excess oxygen in the vanadium oxide thin film [3].

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AA-TuP-83 In-Situ ALD Fabrication of Heterogeneous Gate Insulators for Improved Reliability in High-Mobility IGZO Transistors*, T. Hwang, Y. Kim, H. Oh, **Jin-Seong Park**,* Hanyang University, Korea

Since their 2004 introduction by the Hosono group, oxide semiconductors (OS) represented by IGZO have revolutionized thin film transistor (TFT) technology, favored in the display industry for their transparency, uniformity, cost-effectiveness, low processing temperatures, high mobility, and extremely low off current. Atomic layer deposition (ALD) plays a key role in improving OS device characteristics by offering precise control over film thickness and composition of complex 3D structures, and the deposition of high-quality films. Yet, the high mobility of OS TFTs presents reliability challenges because OS is sensitive to impurities and defects like hydrogen and CO-related impurities. To fabricate a high-mobility and high-reliability OS device, not only the design of the active layer but also the process design surrounding the active layer must be followed. Inspired by the idea that internal defects in gate insulators and donor-induced species have opposite effects on threshold voltage shifts, we propose a novel approach to improve device reliability by in situ ALD stacking two gate insulators, each corresponding to one mechanism, with the reliability compensation that cancels out the two mechanisms. This strategy significantly enhances device reliability, mitigating the adverse effects of impurities and defects, and represents a significant breakthrough in semiconductor technology.

In this study, we enhance the reliability of high-mobility (>50 cm^2/Vs) ALD-IGZO top-gate transistors by employing a meticulously designed heterogeneous gate insulator, using an in-situ ALD process. We developed a heterogeneous (SiO_2/Al_2O_3) gate insulator, exploiting the distinct reliability mechanisms of opposing threshold voltage shifts in Al_2O_3 and SiO_2 to neutralize the net reliability change within the transistor. Aimed at minimizing the impact of opposing charges, this method has been applied to high-mobility ALD-IGZO transistors, achieving significant improvements in positive-bias-temperature-stability (ΔV_{th} = -0.02 V) and constant-current-stability (ΔI_D = 100.49 %). In conclusion, our investigation into reliability compensation, characterized by electron trapping in the gate insulator and compensation of shallow donor generation in the active layer with hydrogen defect passivation, provides profound insights into overcoming the reliability challenges typically associated with high-mobility ALD-OS TG transistors. This innovative, heterogeneous gate insulator design, rooted in an in-situ ALD process, offers a significant advancement in addressing the reliability issues of high-mobility ALD-OS TG transistors.

AA-TuP-84 Broadband Anti-Reflective Coatings with Graded Refractive Index on Plastic Optics*, **Philip Klement**, M. Zscherp, H. Spielvogel, A. Henss, S. Chatterjee,* Justus Liebig University Giessen, Germany

Plastic optics made from acrylic glass or polycarbonate are widely utilized in various applications such as eyeglasses, cell phone cameras, windows, and displays due to their light weight, cost-effectiveness, and ease of manufacturing. However, achieving broadband, omni-directional, and durable anti-reflective (AR) coatings for these plastics poses challenges with conventional deposition methods. These challenges include limitations in process temperatures, damaging surface modifications induced by process plasma, and the absence of robust chemical bonding between the coating and the plastic.

In this study, we introduce nanoporous alumina coatings with a graded refractive index on plastic optics to address these challenges. By employing Atomic Layer Deposition (ALD) of alumina on poly (methyl methacrylate) or polycarbonate followed by immersion in hot water, we fabricate grass-like alumina structures. This approach yields outstanding AR-performance, achieving a remarkable reduction of the residual reflectance to 0.3% in the visible range (400–900 nm) for a single-sided coating. Angular spectral reflectance measurements (0–70°) confirm the omni-directional nature of the AR coating with minimal residual reflectance across all angles of incidence.

Furthermore, the infiltration of trimethylaluminium and water into the polymer substrate during the ALD process forms rigid chemical bonds between the polymer and alumina, resulting in durable coatings. We investigate the depth of Al infiltration into the polymer as a function of process time and find an enhancement in AR performance attributed to the formation of an additional graded refractive index at the coating-substrate interface.

The exceptional AR performance, ease of processing, strong adhesion to various optical plastics, and compatibility with commercial deposition systems make this AR technology highly promising for practical applications.

AA-TuP-86 Effect of Sn-doping on Atomic-Layer-Deposited Ultrathin In-Sn-O Thin-Film Transistors*, **Binbin Luo**, S. Ding,* Fudan University, China

Indium oxide (In_2O_3) thin film transistors (TFTs) have attracted much attention for back-end-of-line (BEOL) compatible logic and memory applications towards monolithic 3D integration. Despite its excellent device performance, some challenges still exist for In_2O_3 TFTs such as high off-current (I_{OFF}), easy crystallization (cubic structure) and instability. Doping with metal cations (e.g., Ga, Zn, Al, W, Ti, Si) is an effective method to resolve these issues in the sputtering-derived In_2O_3-based TFTs. Compared to other elements, Sn with tetragonal structure (SnO_2), similar radius, and high binding energy with oxygen (531.8 kJ/mol) is a promising candidate, which is expected to not only inhibit crystallization but also enhance stability and mobility. In addition, InSnO (ITO) exhibits a lower permittivity of around 4 compared with IGZO (~16), which effectively reduces short-channel-effect (SCE). The atomic layer deposition (ALD) technique enables precise control of both the thickness and wafer-scale uniformity of the In_2O_3-based thin films. Besides, ALD can conformally deposit ultrathin films in nanoscale on three-dimensional (3D) structures such as sidewalls and deep trenches, which is a key technology for downscaling devices and monolithic 3D integration. This work focuses on the fabrication of high-performance ultrathin amorphous ITO TFTs using plasma-enhanced ALD (PEALD). Firstly, we obtained the temperature window and growth rate of PEALD In_2O_3 and SnO_2 films, where $In(CH_3)_3$ (TMIn) and $Sn(N(CH_3)_2)_4$ (TDMASn) were used as metal precursors for In and Sn. Then, we systematically investigated the effects of Sn-doping on the crystal structure of ITO films and the electrical performance of ultrathin (~3 nm) ITO TFTs. The compositions of ITO thin films were tuned by changing the cycle ratio of In_2O_3 to SnO_2 (In:Sn). It is found that Sn is an effective dopant to inhibit crystallization of In_2O_3, decrease V_O and increase mobility, but excessive Sn doping degrades the electrical performance of TFT. Among the various compositions, the TFT with In:Sn=7:1 channel demonstrated optimal electrical characteristics(μ_{FE} =54.8 cm^2/Vs, V_{th} = -0.67 V, SS = 91 mV/dec, I_{ON}/I_{OFF} = ~10^9). Our work provides a promising candidate for BEOL compatible transistors in monolithic 3D integration.

AA-TuP-87 Processing and Performance of Piezoelectric Lead Hafnate-Titanate Thin Films Grown by Atomic Layer Deposition for 3D MEMS Actuators*, Nicholas Strnad,* DEVCOM Army Research laboratory*; R. Knight, R. Rudy,* DEVCOM Army Research Laboratory*; A. Parrish, D. Wang, A. Shkel,* University of California, Irvine*; J. Pulskamp,* DEVCOM Army Research Laboratory

Lead hafnate-titanate ($PbHf_xTi_{1-x}O_3$, PHT) is a ferroelectric and piezoelectric ceramic that is a structural isomorph of lead zirconate-titanate (PZT), a well-studied and commercially relevant multifunctional material, and exhibits very similar electromechanical properties. Thin film PZT has been implemented commercially in MEMS printheads and in ferroelectric random-access memory (FRAM). PZT is also utilized for MEMS actuators, MEMS sensors, and energy harvesters. 3D implementation of either ALD PZT or PHT can offer functional thin films with 200x+ material volume fill per unit area that scales with the device surface-area (e.g., trench or nanopore depth and pitch), offering larger piezoelectric or ferroelectric energy densities in a small footprint. Alternatively, 3D implementation of ALD PZT or PHT can be used to fabricate actuators on sidewalls or curved surfaces where they may deliver forces more effectively or enable new axes of motion for MEMS. Despite the large technological potential of 3D piezoelectric films, there are few reports of ALD processes for piezoelectric thin films and scant reports on applications or prototypes. Here, we present results of a novel ALD process for PHT using oxygen as a co-precursor on platinized silicon wafers and implement the PHT as a 3D actuator on curved glass-blown micro-scale hemispherical resonators. The resonators are a fundamental component of micro-scale hemispherical resonating gyroscopes (µHRGs) which are being explored as a high performance and low-cost alternative to traditional navigation-grade inertial sensors. (1) We will present precursor dose saturation curves for the PHT process, PHT thin film material characterization, and piezoelectric characterization of the 3D actuator using laser doppler vibrometry (LDV) measurements of the resonator displacement. Equally important, the PHT also displayed excellent ferroelectric properties, and exhibited a 2Pr of 68 $\mu C/cm^2$ and a max polarization of +/- 78 $\mu C/cm^2$ at +/- 8V, respectively.

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AA-TuP-88 Stacked ALD Deposited Metal Oxide Films as Reliable Sensing Films for Organic Semiconductor-Based LAPS*, Chia-Ming Yang,* *Y. Yang,* Chang Gung University, Taiwan*; B. Jiang, C. Chen,* Ming-Chi University of Technology, Taiwan

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Light-addressable potentiometric sensor (LAPS) had been proven for chemical and bio sensing with ability of 2D imaging and easy fabrication. Recently, organic semiconductor had been proposed for the semiconductor layer of LAPS with advantages of high absorption, low-temperature process, capability of flexible substrates. However, restrictions are the stability and lifetime due to the electrolyte environment degraded the insulator/sensing membrane of LAPS. This research focuses on fabricating stacked aluminum oxide (Al_2O_3) and hafnium oxide (HfO_2) using an atomic layer deposition (ALD) system for sensing membrane to improve the stability and lifetime of organic semiconductor-based of LAPS.

A zinc oxide (ZnO) layer was applied to serve as the electron transport layer by spin coating on indium tin oxide (ITO)/glass. An organic material layer with composition of PTB7-Th and $PC_{71}BM$ were mixed then deposited on the ZnO using a spin coater. Different metal oxide including Al_2O_3 and HfO_2 with thickness of 6 nm for each layer to total thickness to be 24 nm were deposited by ALD to function as sensing films. The standard photocurrent versus bias voltage (PC-V) curves triggered by red laser (e.g., 658 nm wavelength) were collected in various sensing requirements including sensitivity, hysteresis and drift measurements for LAPS. In pH range from 2 to 10, the linearity and sensitivity of stacked ALD LAPS device is 99.7% and 50.7 mV/pH, respectively. The hysteresis width was -13.2 mV. Stacked ALD structure makes organic semiconductor-based LAPS can survive for whole drift measurement for 12 h and owns a drift coefficient of 3.26 mV/h, which approaches to basic requirement of inorganic semiconductor-based LAPS.

The employment of a multilayered configuration does offer a significant electrolyte-proof improvement, contributing to the device's overall durability and extending the possibility of 2D chemical imaging of organic semiconductor-based LAPS. This technique could ensure that organic materials to be utilized and maintained in LAPS structure and similar field-effect sensing devices for extended durations, thereby increasing their longevity and reliability.

AA-TuP-89 Effects of TiO_2 Incorporation via Atomic Layer Deposition on Yttria-Stabilized Zirconia Electrolyte for Energy Storage*, Jorge Luis Vazquez Arce,* El Centro de Investigación Científica y de Educación Superior de Ensenada, Baja California, Mexico*; C. Bohórquez Martinez,* UNAM, Mexico*; A. Bahrami,* Leibniz Institute for Solid State and Materials Research, Germany*; E. Blanco,* Universidad de cadiz, Spain*; M. Dominguez,* Universidad de Cadiz, Spain*; K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany*; G. Soto Herrera, H. Tiznado,* UNAM, Mexico

Electrolyte material optimization is crucial for electrochemical energy storage devices. The specific composition and structure have an impact on conductivity and stability, both of which are essential for efficient device performance. The effects of controlled incorporation of TiO_2 into Yttria-Stabilized Zirconia (YSZ) electrolyte using the atomic layer deposition (ALD) technique are investigated in this study. The surface chemical composition analysis reveals variations in the Ti oxidation state and a decrease in the O/(Zr+Y+Ti) ratio as TiO_2 concentration increases. The formation of acceptor states near the valence band is proposed to reduce the bandgap with the Fermi Level. The structural properties indicate that as TiO_2 concentration increases, surface homogeneity and crystallite size increase. The contact angle with water indicates a hydrophobic behavior influenced by surface morphology and potential oxygen vacancies. Finally, electrical properties, measured in Ru/TiO_2-doped YSZ/Au capacitors operated at temperatures between 100 and 170 °C, showed that the TiO_2 incorporation improved the ionic conductivity, decreased the activation energy for conductivity, and improved the capacitance of the cells. This study highlights the importance of the ALD technique in solid-state electrolyte engineering for specific applications such as energy storage devices.

AA-TuP-90 Dynamic Color Shifting of Green Organic Light-Emitting Diodes Utilizing Distributed Bragg Reflector Mirror Fabricated via Atomic Layer Deposition*, Junbeom Song*, *J. Bi,* Korea University, Republic of Korea*; Y. Park,* Sun Moon University, Republic of Korea*; B. Ju,* Korea University, Republic of Korea

Organic Light-Emitting Diodes (OLEDs) have garnered considerable interest owing to their benefits such as easy manufacturing process, wide viewing angle, low unit price and energy consumption, and thin and flexible form factor compared to liquid crystal displays (LCDs). However, a notable drawback of blue OLEDs is their shorter lifetime compared to green or red OLEDs, primarily due to their higher energy consumption. To address this issue, researchers are exploring various methods involving both materials and structural modifications.

Among these approaches, there is ongoing research aimed at leveraging the longer lifespan and higher stability of green OLEDs to generate other colors. In this study, we focus on modeling and fabricating OLEDs using a distributed Bragg reflector (DBR) model, utilizing atomic layer deposition (ALD). DBR involves depositing alternating layers of high and low refractive index thin films, exploiting total internal reflection (TIR) at each interface to achieve high reflectivity. By using DBRs, composed of Al_2O_3 and TiO_2, which exhibit high reflectivity due to their difference in refractive index, we could adjust the number of pairs to model specific spectral light.

Through comprehensive simulation, we verified that Alq_3, a green, fluorescent material with a peak emission wavelength at 564 nm (Fig 1a), could effectively shift green to a blue component with a peak emission wavelength at 478 nm by employing a 2-pair DBRs (Fig 1b). Additionally, in Figure 2, we verified that reducing the full width at half maximum (FWHM) from 182 nm to 42 nm enables the extraction of a highly pure blue color. Based on these simulation results, we are conducting experimental design and characterization to ensure the fabrication of devices matching the simulated properties. The electroluminescence (EL) characteristics of the device without a DBR show a peak wavelength at 554 nm (Fig. 4), which is similar to the simulation results. This indicates that including a DBR in the device is expected to result in a shift towards the blue wavelength region. This research contributes to advancing the understanding and utilization of novel techniques in OLED technology, paving the way for enhanced performance and longevity in display applications.

AA-TuP-91 Ultrathin TiN/TiO_2/Ti Solar Absorbers Enabled by Atomic Layer Deposition*, **Luca Mascaretti**,* Czech Technical University in Prague, Czech Republic*; A. Naldoni,* University of Turin, Italy*; L. Kalvoda, I. Richter,* Czech Technical University in Prague, Czech Republic

Solar-thermal conversion is an attractive strategy to collect sunlight and transform it into heat that is directly utilized or further transformed into electricity.$^{(1)}$ Depending on the specific route, solar absorber materials must be carefully designed to achieve the highest solar absorptance and to withstand severe thermal cycling. For example, metal-insulator-metal (MIM) metasurfaces based on titanium nitride (TiN) demonstrated nearly unitary absorption and stability under annealing and focused light irradiation.$^{(2)}$ In this contribution, we discuss a simple continuous and scalable MIM absorber based on TiN/TiO_2/Ti. We first discuss the optimization of optical absorption by numerically computing optical spectra for different values of the TiN and TiO_2 thickness in the ranges 0–35 nm and 0–75 nm, respectively. As a result, the optimized structure TiN (10 nm)/TiO_2 (50 nm)/Ti exhibits ~ 60% optical absorption in the 250–2000 nm range, outperforming a counterpart based on Au. Such optimized structure is then experimentally realized by the atomic layer deposition (ALD) technique by using the $TiCl_4$ precursor combined with H_2O (thermal process for TiO_2) and N_2 plasma (for TiN). We further discuss additional effects that can additionally increase the optical absorption up to ~75%, such as surface oxidation of the ultrathin TiN layer, which affects its permittivity.$^{(3)}$ Therefore, the combination of such Ti-based materials allows the realization of a solar absorber without further need of surface patterning, highlighting the potential of ALD for solar energy applications.

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AA-TuP-92 Simultaneous Enhancement in Performance and Stability of LSCF Air Electrode of Reversible Solid Oxide Cell by Atomic Layer Deposited CeO_2 Coating*, **Sung Eun Jo**, K. Ju, H. Kim, W. Park, J. An,* Pohang University of Science and Technology (POSTECH), Republic of Korea

Atomic layer deposition(ALD) offers the ability to conformally coat intricate structures at atomic level. Widely adopted in the semiconductor industry, ALD stands out as a beneficial technique for enhancing the performance and durability of electrochemical devices(battery, fuel cells) Surface engineering via protective, catalytic nano-layer by ALD, durability and performance of electrochemical devices increases.

Reversible solid oxide cells(rSOSs) are energy conversion devices between chemical energy(hydrogen) and electrical energy, which operate both in fuel cell mode(solid oxide fuel cell : SOFC) and in electrolysis mode(solid oxide electrolysis cell : SOEC). rSOCs show high thermodynamic efficiency, fuel flexibility, and scalability; however, their high operation temperature, typically exceeding 800°c, causes rapid degradation at the electrode surface which is usually composed of perovskite materials. Particularly in rSOCs, the thermal degradation of air electrode by A-site dopant material(Sr) segregation on the surface of perovskite electrode(e.g. lanthanum strontium cobalt ferrite(LSCF)) and formation of an insulating secondary layer is dominant surface degradation mechanism.

In this research, the focus is on enhancing the performance and stabilization of LSCF air electrodes in rSOCs through ALD CeO_2, which is well known for its exceptional ionic conductivity and surface exchange activity. Its potential for enhancing the oxygen evolution reaction(OER) and oxygen reduction reaction (ORR) in rSOCs has been investigated. Electrochemical characterizations were carried out to compare bare LSCF(without ALD) with ALD CeO_2-coated electrodes. Interestingly, the initial electrochemical performance with ALD CeO_2-coated(10nm) sample showed 30% increase in maximum power density on SOFC mode and 10% increase in current density in SOEC mode. During long-term rSOCs operation at 750°c for over 100 hrs, the thermal stability of the ALD CeO_2-coated cell improved by 100% compared to the bare LSCF cell.

AA-TuP-93 Comparison of Thermal and Remote-Plasma ALD to Prepare Schottky Diodes to Gallium Nitride*, **Suzanne Mohney**, J. Clark, C. Chiu, T. Larrabee, N. Banner, N. Redwing, J. Gray,* Penn State University

We have explored the use of atomic layer deposition for creating Schottky diodes to *n*-type GaN, which is an important wide-bandgap semiconductor for power electronics. For high-temperature applications, we wanted to deposit a metallization that is unreactive with GaN. There are conductive metal nitride candidates in thermodynamic equilibrium with GaN, including Mo_2N, [1] but we did not want to prepare layers by sputter deposition due to electrically active defects that can be introduced in the GaN by the plasma. Instead, we prepared diodes using thermal ALD and compared them to diodes we reported previously using ALD with a remote plasma. [1] With bis(tertbutylimido)bis(dimethylamino)molybdenum as the precursor, the co-reactants were NH_3 or a remote N_2-H_2 plasma. Thermal ALD was performed with the stage at 250 °C and walls of a Lesker LX reactor at 200 °C using a stop-flow process, while the remote-plasma process was performed in a Veeco Gen II reactor at 200 °C. In both cases, the layers contained carbon, similar to other reports using this precursor, [2, 3] but fortunately Mo_2N can dissolve MoC, [1] and the films were good conductors. Thermal ALD resulted in diodes with a Schottky barrier height of 0.69 eV and an ideality factor of 1.06 before annealing, while the remote-plasma process created non-ideal diodes that initially exhibited high reverse currents. After annealing in N_2 at 600 °C, however, the diodes prepared by both methods offered similar Schottky barrier heights of 0.84 eV by thermal ALD and 0.87 eV by remote-plasma ALD. Moreover, the diodes prepared with the remote-plasma process were ideal after annealing. At room temperature, an ideality factor of 1.02 is expected due to image force lowering and was measured after annealing the diodes prepared using the remote-plasma process. After annealing the diodes prepared by thermal ALD, the ideality factor became 1.04. Cross-sectional transmission electron microscopy suggests a very thin interfacial layer in the diodes prepared by thermal ALD, which may be the origin of the slight non-ideality after annealing. The authors gratefully acknowledge the support of ONR through N00014-22-1-2462 (Approved, DCN# 543-1698-24).

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AA-TuP-94 Y_2O_3 Thin Film Deposition Via Atomic Layer Deposition Utilizing Y(EtCp)2(iPr-amd)And O_3*, S. Cho, **Seunghwa Choi**,* Sungkyunkwan University (SKKU), Republic of Korea

These days there are many microstructures in semiconductor equipment. Especially equipment using plasma-enhanced deposition has narrow and complicated structure peripheral parts. These parts need to be stable with plasma damage. So, these parts need to be coated with material, which can protect the parts from plasma damage. Y2O3 is well-known for plasma passivation material. In this study, a study was conducted to coat Y2O3 thin films with atomic layer deposition (ALD) method for this purpose. Since the structure of the parts used in semiconductor processing equipment is becoming more complex, ALD is the most suitable method for uniformly coating parts that have complex structures. Y2O3 ALD thin films were deposited using Y(EtCp)2(iPr-amd) for Y precursor, and ozone for oxygen. The material characteristics and plasma stability of the deposited Y2O3 thin films were evaluated.

AA-TuP-95 Microstructure and Environmental Stability of Plasma-Enhanced ALD TiO_2/SiO_2 Multilayer Anti-Reflective Films on PMMA Substrates*, D. Cu, J. Ho,* Department of Optics and Photonics, National Central University, Taiwan*; W. Cho, C. Kei,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan*; **Chien-Cheng Kuo**,* Department of Optics and Photonics, National Central University, Taiwan

In this study, plasma-enhanced atomic layer deposition (PE-ALD) technology was used to coat an anti-reflective (AR) film on a PMMA substrate using TDMAT and 3DMAS precursors for TiO_2 and SiO_2 films, respectively, at a low temperature of 70℃. The plasma mode introduced a mix of oxygen and argon for oxidation. The refractive index (n) and extinction coefficient (k) trends in the single-layer film were examined to determine optimal process parameters and conditions. Due to the soft nature of the plastic substrate, a 50-watt setting was chosen for AR film deposition to avoid substrate surface damage and crack formation caused by ion bombardment at higher power settings.

The structures of single and multi-layer films were analyzed using various measurement instruments. X-ray diffraction confirmed the composition of the TiO_2 film structure, revealing an increase in crystallization strength from 82 to 117 as the number of ALD cycles (indicative of film thickness) increased from 200 to 1200. Atomic force microscopy showed a film surface roughness of approximately 0.28 nm, indicating a notably flat surface and a microcrystalline state for the single-layer TiO_2 film. Transmission electron microscopy verified that the multi-layer film structure matched the layer count predicted by Macleod simulation software.

Incorporating an inhibition layer within the nano-composite layer of a single film can effectively reduce the crystallization phenomenon and subsequently lower the stress on the film. The film's changes and durability under harsh conditions (85°C and 85% humidity) were observed using a constant temperature and humidity machine. AR films without the inhibition layer lasted up to 998 hours, while those with four inserted layers of 1.5nm SiO_2 only persisted for 209 hours. The results suggest that increasing the number of insertion layers does not significantly improve the stress on TiO_2. Instead, the thickness of TiO_2 decreases, causing the film to become less dense and more susceptible to erosion by moisture in high humidity conditions. In contrast, the relatively thicker TiO_2 film in non-inserted layers is denser, resulting in a lower water vapor transmission rate (WVTR) and better durability for the AR film.

AA-TuP-96 Optimization of Atomic Layer Deposition Process for Tin Oxide Thin Films at Low Deposition Temperatures for Halide Perovskite Solar Cells*, **Saurabh Gupta**, L. Laxmi, A. Paul, V. G. Chityala, S. Nayak, M. Misra, D. Kabra,* Indian Institute of Technology Bombay, India

Tin oxide (SnO_X) thin film, having properties such as high transparency, conductivity, higher electron mobility, band alignment with halide perovskite materials, and high mass density has potential to be employed in optoelectronic devices. Halide perovskite solar cells (PSCs) with high power conversion efficiency and low-cost of fabrication are promising candidates for next-generation tandem photovoltaics. However, tandem configuration requires to deposit sputtered transparent electrodes. This sputtering process damages the underneath organic and perovskite layers. Atomic layer deposited SnO_X thin film is capable to protect the damages and is compatible with electron transport layers for NIR-transparent PSCs. Thin films via Atomic Layer Deposition (ALD) process are pin-hole free, dense, uniform, conformal and deposited at lower temperatures. This study focuses on the optimization of ALD recipe parameters for the deposition of SnO_X thin films at low temperatures.This work investigates the effects of deposition temperature, precursor exposures, and purge times on the growth behaviors and on structural, optical, and electrical properties of SnO_X thin films. Our ~20 nm SnO_X films are having high average transmittance (>94.8 %), varied refractive index (1.78 to 1.95), negligible extinction coefficient, stoichiometric ratio of O/Sn (1.69 to 1.95), and mass density (>5.6 gm/cm^3) are suitable to be employed as functional layers in NIR-transparent PSCs. We successively applied the optimized SnO_X film in NIR-transparent PSCs as a protecting layer. We further explored annealing treatment of these films which enhances transmission (>95.6 %) and resistivity (min. 1.79E-2 Ohm-cm) properties. These enhanced-quality films show potential as other forms of functional layers in optoelectronic devices.

AA-TuP-97 Atomic Layer Deposition for Proton-exchange Membrane Water Electrolyzers*, **Bhavesh Chavan**, A. Tzavara Roussi, V. van Steijn, R. Kortlever, R. van Ommen,* Delft University of Technology, Netherlands

Proton-exchange membrane (PEM) water electrolyzers represent the forefront of hydrogen production through water electrolysis. However, they heavily rely on platinum group catalysts and titanium structures, which constitute a significant portion of the total electrolyzer costs *Babic et al.(2017)*. The emergence of atomic layer deposition (ALD) technology offers a promising solution to address these challenges by providing precise control over film thickness, maximal material utilization, and excellent conformality.

In this poster, we explore the versatile applications of ALD in both catalyst coated membrane (CCM) and porous transport electrode (PTE) configurations. In CCM, platinum group catalysts can be efficiently coated on carbon powder using fluidized bed reactor ALD (FBR-ALD) and subsequently applied to membranes *Lee et al.(2020)*. In PTE, ultrahigh mass activities are achieved by atomically depositing Pt and Ir nanoclusters on titanium and graphite felts for anode and cathode sides, respectively *Laube et al.(2021)*. Moreover, porous transport layers and bipolar plates, typically made from titanium and stainless steel, are coated with ultrafine Pt, Au, or nitride coatings to withstand high acidic and oxidation potentials *Woo-Lee et al.(2020)*. Additionally, ALD is explored for fabricating support materials and providing porous and protective coatings in the form of oxides and metal- organic frameworks (MOFs) and so on *Li et al.(2024)*; *Xiao et al.(2024)*.

This poster will comprehensively discuss various literature studies and propose the best possible options for utilizing ALD in fabricating various electrolyzer components. Such advancements highlight the potential of ALD in revolutionizing the efficiency, cost-effectiveness, and durability of PEM water electrolyzers, thus paving the way for scalable hydrogen production with sustainability.

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AA-TuP-98 Mitigating Competing Reactions: Atomic Layer Deposition of Ultrathin Overlayers for Anode Protection in Direct Seawater Electrolysis*, **Katherine Encalada**, J. van Ommen, R. Kortlever,* Delft University of Technology, Netherlands

Direct seawater electrolysis is a promising technology for green hydrogen generation. Nonetheless, technical challenges arise due to seawater's complex chemical composition. Specifically in acidic media, the problematic competition at the anode between the undesired chlorine evolution reaction (CER) and the targeted oxygen evolution reaction (OER). Previous studies showed that permeable overlayers like MnOx and SiOx can selectively suppress the CER. However, the overlayer´s liquid deposition techniques resulted in non-uniform thickness and poor stability [1,2]. This work explores the effectiveness of an ALD-deposited SiO_2 overlayer on a GC-supported IrO_2 catalyst to suppress competing reactions at the anode during water electrolysis in an acidic chloride-containing electrolyte.

The methodology to quantify the competing OER vs. CER consists of a Rotating Ring Disk Electrode (RRDE) setup that simultaneously measures the oxidation (disk) and reduction (ring) currents within a potential range. Both competing reactions are promoted at the disk (IrO_2|GC) by sweeping the potential from 1,1 V to 1,55 V vs RHE. In this first step, water molecules and chloride ions oxidize, forming O_2(g) and Cl_2(g). The second simultaneous step involves reducing at the ring (Pt) the previously formed Cl_2(g), for which the ring is kept at 1,09V vs. RHE. This way, measuring how much Cl_2(g) evolved at the disk is possible. The SiO_2 overlayer was built by atmospheric ALD using $SiCl_4$ and water as reactants at 100 °C reaction temperature. Comparative measurements were conducted with and without the SiO_2 overlayer on the IrO_2|GC catalyst.

The preliminary results show that a thin layer of 25 cycles of SiO_2 by ALD gives a promising suppression of CER over OER. However, after subjecting the system to 20 cyclic voltammograms, the electrochemical behavior of the anode reverts to the one obtained with bare IrO_2. This observation suggests a SiO_2 overlayer's instability, presumably arising from a physical detachment of the overlayer from the substrate. Despite this setback, some strategies to improve the anchoring of the coating are to be yet explored, like pre-activation of the substrate or the usage of more reactive precursors like O_3.

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AA-TuP-99 Monolayer Engineering and Novel Annealing Techniques to Enhance the Ferroelectricity of HfO_2-Based Thin Films with a Low Thermal Budget

***Ting-Yun Wang**, C. Mo, C. Chuang, Y. Yin, M. Chen,* National Taiwan University, Taiwan

HfO_2-based ferroelectric thin films have emerged as promising materials for a wide range of applications, including non-volatile memory and neuromorphic computing. Consequently, intensive research efforts have been made to develop and optimize various film compositions and processing techniques to enhance their ferroelectric properties. However, a notable challenge is the high annealing temperature requirement for HfO_2-based ferroelectric thin films, which conflicts with the low thermal budget constraints (<400°C) of the back-end-of-line process in advanced semiconductor technology nodes. In this study, we present two novel approaches to overcome this limitation and enable pronounced ferroelectric performance of HfO_2-based thin films with a low thermal budget. The first approach introduces the concept of "monolayer engineering" by exploiting the layer-by-layer growth of atomic layer deposition (ALD). A significant remnant polarization ($2P_r$) ~ 30 μC/cm^2 was achieved in ~ 4 nm thick $Hf_{0.5}Zr_{0.5}O_2$ thin films by replacing the HfO_2 monolayer with the ZrO_2 monolayer in the vicinity of the bottom electrode. In particular, the sub-5 nm $Hf_{0.5}Zr_{0.5}O_2$ thin films exhibited pronounced ferroelectric behavior in their pristine state, even at the relatively low annealing temperature of 370°C. This is noteworthy because it is typically difficult to achieve ferroelectricity in HfO_2-based thin films with thicknesses below 5 nm. This result highlights the distinguished capability of monolayer engineering to precisely tailor materials at the atomic scale, leading to exceptional functional properties in nanoscale ultrathin films. In addition, the second technique involves the development of "large-area electron beam annealing (EBA)" to obtain highly crystalline Al-doped HfO_2 (HAO) thin films deposited by ALD. The EBA treatment produces a highly localized annealing region within approximately 20 nm below the sample surface, which effectively mitigates the inherent thermal budget constraints imposed by the high annealing temperatures typically required for HAO thin films. As a result, an impressive ferroelectricity of $2P_r$ ~ 29 μC/cm^2 and high crystallinity of the orthorhombic phase were achieved in HAO thin films by EBA with a low thermal budget. In summary, both techniques provide innovative ways to achieve significant ferroelectric performance of nanoscale HfO_2-based thin films with low thermal budgets.

AA-TuP-100 2D Transition Metal Chalcogenide Films Synthesized by ALD as Diffusion Barriers in Interconnects

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For the continuous miniaturization of nanoelectronics, the conventional TaN/Ta barrier, preventing Cu diffusion in interconnect structures, needs to be scaled down below the current thickness limit of 3 nm[1]. Replacing the conventional barrier with a two-dimensional transition metal chalcogenide (2D-TMC) offers the opportunity to reduce the thickness of the barrier. Atomic layer deposition (ALD) provides the conformality and suitable process temperatures required for back-end-of-line application of the 2D films. In this work we will demonstrate the performance of various 2D-TMCs synthesized by ALD as Cu diffusion barrier.

Previously, we showed that ALD-MoS--$_2$ of various thicknesses is an effective Cu diffusion barrier[2]. In addition, other 2D-TMCs deposited by ALD, such as WS_2, TaS_x and NbS_2, were tested by time-dependent dielectric breakdown measurements. These materials show differences in barrier performance. Highly crystalline MoS_2, specifically, showed superior blocking with respect to the other TMC films, as the median time to failure is $(3.2\pm0.1)\cdot10^3$ s for 2.2 nm MoS_2 versus $(5.3\pm0.1)\cdot10^2$ s for 10 nm TaS_2. All 2D-TMC films deposited by ALD result in relatively small grains (~10 nm)[3]. However, the degree of crystallinity differs per film as it is strongly affected by the process conditions, mainly by temperature and plasma composition (e.g., H_2S/H_2 flow ratio). Furthermore, some of the films show out-of-plane oriented growth besides the in-plane crystal growth, resulting in a mixed morphology. The combination of grain size, degree of crystallinity and morphology leads to different barrier performances, where a higher degree of crystallinity generally results in better Cu diffusion blocking.

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AA-TuP-101 Rational Design of a Full Plasma-Enhanced ALD Super-Cycle Process for Indium Gallium Zinc Oxide Based on in-Situ Characterization

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Transparent conducting oxides are a promising materials class for applications in the field of photovoltaics and thin film transistors. For the latter, indium gallium zinc oxide (IGZO) can be an enabler for the next generation of flexible electron devices and organic light-emitting diode displays due to its high optical transparency and electron mobility. In the past, IGZO was usually deposited by radio-frequency magnetron sputtering, solution processing, and pulsed laser deposition. More recently, atomic layer deposition (ALD) has shown the potential to overcome limitations of the other deposition methods allowing low-temperature processing and uniform depositions on 3D structures.

This work presents a bottom-up approach for the deposition of IGZO layers by a super-cycle ALD process using a SENTECH plasma-enhanced ALD (PEALD) reactor. Initially, a super cycle combining a thermal process (TALD) for zinc oxide (ZnO) and plasma-enhanced processes for gallium and indium oxide (Ga_2O_3, In_2O_3) was developed. The growth mechanisms of the individual processes within the super-cycle have been thoroughly investigated and monitored by in-situ ellipsometry (i-SE, SENTECH ALD Real-Time-Monitor). A nucleation delay for the thermal ZnO process was found, making it challenging to properly adjust the elemental composition by the sub-cycle ratio. Hence, the thermal ZnO cycle has been replaced by a plasma-enhanced ZnO process, which shows no nucleation delay, thus enabling a full PEALD super-cycle at low temperature (150°C).

X-ray photoelectron spectroscopy, grazing-incidence X-ray diffraction, and scanning electron microscopy in combination with energy-dispersive X-ray fluorescence analysis were used to investigate the elemental composition and morphology of the ALD films. Our results demonstrate that the elemental composition can indeed be precisely adjusted by varying the sub-cycle ratio within the super-cycle. Furthermore, metal/insulator/semiconductor (MIS) layer stacks were built to measure the electrical performance of the oxide films. This showed that the conductivity of films prepared using the full PEALD super-cycle is significantly higher than that of the layers deposited by the mixed TALD/PEALD process.

Therefore, this approach allows the preparation of ultra-thin IGZO layers with controlled thickness, composition, and electrical properties, while thermally induced segregation is largely prevented.

AA-TuP-102 Fabrication of ZnO Metal-Semiconductor-Metal Photodetectors on Cotton via Thermal-ALD

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Studies on electronic textiles have continued to increase in recent years and some applications have begun to find a place in daily life. Various flexible devices fabricated on textiles have been developed, including sensors, solar cells, and energy storage devices. In particular, wearable photodetectors (PDs) have attracted the attention of researchers due to their possible contributions to security, health, and communication applications. Zinc Oxide (ZnO) is one of the most suitable materials for textile-based PDs due to its wide bandgap, stability under long-term light exposure, and high sensitivity to UV/visible radiation. However, integrating thin film devices on textiles often affects their mechanical properties such as flexibility, durability, and washability. This work presents an approach that leverages low-temperature atomic layer deposition (ALD) of ZnO on cotton to achieve flexible PDs while preserving the inherent properties of cotton.

ZnO was deposited on cotton (woven bleached, 98 gsm) substrates using diethylzinc (DEZ) and H_2O as Zn precursor and co-reactant respectively in a thermal ALD reactor at 120 °C. The unit ALD cycle in which 20 sccm N_2 is used as the carrier gas consists of 0.5s DEZ pulse, 30s purge, 0.5s H_2O pulse, 30s purge steps. Following the deposition of ZnO layers on cotton, interdigitated electrodes consisting of 25/150 nm Ti/Al layers were evaporated by e-beam deposition to create the metal-semiconductor-metal (MSM) structures.

The resulting ZnO films on cotton are characterized in terms of their structural, morphological, compositional, and photo-response properties. X-ray diffraction analysis revealed the polycrystalline nature of the as-grown ZnO layer on cotton. SEM and EDX analyses showed that ZnO is uniformly synthesized on cotton. The photo-response characteristics of the fabricated MSM-PD device structures were examined by placing a visible light source at a distance of 30 mm. The bias voltage was scanned from –1 to 1V in a 50-mV step under dark and illuminated conditions. The resulting photo-current at 1V bias showed ~2.5-fold increase when compared to dark current (from 57 to 130 µA). Our study displays an effective ZnO-based photodetector on cotton at low bias voltages highlighting the potential for low-power wearable sensing applications. Future studies could focus on further characterizing the spectral photo-response under various environmental conditions and optimizing the device architecture by exploring different doping strategies, or composite structures that can enhance light absorption.

AA-TuP-103 Enhancing Charge Trapping Performance of Hafnia Thin Films by using Sequential Plasma Atomic Layer Deposition*, SoWon Kim, J. Yu, W. Park, H. Lee,* Tech University of Korea

HfO_2, as a high-k dielectric material, holds promise for replacing silicon nitride-based charge trapping layers (CTL) in traditional NAND flash memory. This is due to its high trap densities, significant conduction band offset with respect to the tunneling oxide (TO), and thin equivalent oxide thickness (EOT).

The Direct Plasma (DP) ALD process offers advantages such as higher film density and lower process temperatures compared to thermal ALD processes. However, because the plasma discharge happens within the chamber, it risks damaging the substrate through ion bombardment, potentially degrading device characteristics.

In Remote Plasma (RP) ALD, the plasma discharge occurs in a separate space, with thin film progress achieved by supplying radicals. However, it suffers from low productivity due to longer cycle times. By carefully considering the pros and cons of both plasmas, it is possible to mitigate device damage and cycle time simultaneously.

This study employed a Sequential Plasma ALD process to deposit HfO_2 films. Sequential RP and DP-ALD processes were utilized, allowing for thickness variation in each layer during deposition. Thin films of HfO_2 deposited by RP-ALD on the substrate ranged from 0 nm to 7 nm, forming a total of 10 nm HfO_2 thin films. Additionally, a Charge Trapping Memory (CTM) with an $Au/Al_2O_3/HfO_2/SiO_2$/p-Si (MAHOS) structure was fabricated using the deposited film to analyze RP-ALD thickness effects and assess memory operational characteristics degradation.

The HfO_2 film with a 4-nm-thick RP-ALD exhibited a significant memory window of over 7 V across a gate voltage range of ± 10 V, along with a relatively low interface trap site of 1.3×10^{12} $eV^{-1}cm^{-2}$ or less. As the thickness of the RP-ALD-deposited HfO_2 increased, both memory window and time-dependent dielectric breakdown (TDDB) endurance improved, while interface trap sites and V_{FB}(flat band voltage) shift with read/write repetition decreased.

In conclusion, the methodology proposed in this study is promising for future implementations of multi-level charge-storage nonvolatile memories or synaptic devices requiring numerous states.

AA-TuP-104 Atomic Layer Deposition of Self-Healing Protective Coatings for Stone Cultural Heritage Conservation*, Aranzazu Sierra Fernández,* CIC nanoGUNE, Donostia-San Sebastián, Spain*; M. Knez,* CIC nanoGUNE, Donostia-San Sebastián and IKERBASQUE, Basque Foundation for Science, Spain

The development of protective coatings for the construction industry and cultural heritage (CH) applications with combined strength, toughness, and compatibility remains a long-standing challenge. Applying a hybrid coating system to building components before the onset of severe damage could effectively increase longevity and reduce maintenance demand. This study introduces a novel self-healing coating, deposited via Atomic Layer Deposition (ALD), to advance the protection of porous stone substrates. The ALD layers incorporated metal oxides that trigger a self-healing mechanism, including passivation processes aimed at autonomously repairing micro-damages, thusextending the durability of the material.The ALD process was precisely tailored to facilitate the formation of metaloxide interfaces,whichwere key to the self-healing functionality. A comprehensive evaluation of their mechanical properties on stone substrates is presented to validate the self-healing capabilities of the coatings after exposure to simulated environmental conditions such as variations in relative humidity, temperature, and UV light. This characterization approach involved both nanoindentation, assessing the hardness and elastic modulus at the nanoscale, and microindentation, determining the mechanical integrity at a larger scale. This method enabled us to capture the responses of the coatings to external mechanical stimuli across different scales, thereby providing detailed insights into the effectiveness of the self-healing process. Preliminary results indicate a promising enhancement in the resistance of the coatings to mechanical stresses and microfracture propagation. Through meticulous design and characterization, this research endeavors to develop a self-healing coating system that not only protects, but actively maintains the integrity of CH stone materials. The implementation of such technology stands to redefine conservation methodologies, offering a sustainable and efficient approach to CH preservation.

ALD Applications
Room Hall 3D - Session AA1-WeM
Flash and Ferroelectric Memories

Moderators: Haripin Chandra, EMD Electronics, USA, **Matti Putkonen**, University of Helsinki

8:00am **AA1-WeM-1 Ferroelectric Doped HfO_2: From Ald Processing to Device Applications*, Uwe Schroeder,*** Namlab, Germany **INVITED**

Extensive research and development have been conducted on doped HfO_2 or ZrO_2-based ferroelectric materials [1]. These unique fluorite-structured ferroelectrics have outstanding potential for commercial applications due to their scalability, CMOS compatibility, and ease of fabrication. Ferroelectric HfO_2 is particularly attractive for semiconductor memory applications because of its advantageous properties. The scientific community has made great efforts to improve and optimize the ferroelectric properties using a variety of approaches due to the wide range of conditions under which ferroelectricity can occur in thin films. Consequently, thin-film ferroelectric capacitor and memory array technologies are advancing quickly. But, researchers are still trying to elucidate the various causes of ferroelectricity in doped HfO_2 and ZrO_2 thin films in order to improve device performance.

Different chemical precursors for HfO_2 and ZrO_2 are compared for the best ALD process window [2]. The doping and oxygen content of the film are important for both the formation of the crystal phase and the performance of HfO_2-based devices [3]. It is crucial to consider all of these factors when designing and optimizing HfO_2-based devices. Other factors, such as interaction with electrode materials, crystallization anneals, and stress in the resulting film, can also significantly affect the ferroelectric properties. Once a ferroelectric phase is reached in thin films, it can be influenced by further thermal treatments and the application of an electric field. Recent piezo-force microscopy studies have confirmed a nanoscale electric field-induced phase transition from a non-polar tetragonal to a polar orthorhombic phase. This knowledge of phase transitions in doped HfO_2- and ZrO_2-based films is essential for the development of future ferroelectric devices.

The recently discovered properties of HfO_2, even at film thicknesses below 10 nm, have enabled a growing number of applications, such as high aspect ratio ferroelectric capacitors (FeCap) and field-effect transistors (FeFET) [4]. Additionally, other applications, such as ferroelectric tunnel junctions, neuromorphic, piezo-, and pyroelectric devices, are being discussed [4]. Many devices can now be realized on smaller technology nodes and in larger memory arrays. At the end of 2023, non-volatile FeCap based memory chips have been presented at conferences [5].

This review will cover recent results and provide an overview of the subject, starting with a discussion of the causes of ferroelectric properties and experimental reports on phase stabilization in doped HfO_2, as well as an introduction to recent semiconductor applications.

8:30am **AA1-WeM-3 Interfacial Layer Engineering by Tungsten Oxide for Ferroelectric La-Doped $Hf_{0.5}Zr_{0.5}O_2$ Layer*, Dae Seon Kwon,*** *M. Popovici, J. Bizindavyi,* imec, Belgium*; G. De, A. Delabie,* KU Leuven, imec, Belgium*; A. Belmonte, G. Sankar Kar,* imec, Belgium*; J. Van Houdt,* KU Leuven, imec, Belgium

In this work, the electrical performance of the ferroelectric La-doped $Hf_{0.5}Zr_{0.5}O_2$ (La:HZO) layer was optimized by interfacial engineering employing tungsten oxide with back-end-of-line (BEOL) compatibility, and the effect was investigated in detail. A major problematic issue arising when scaling down the physical thickness of the HZO for industrial applications is undesirable stabilization of non-ferroelectric tetragonal phase, especially at the interface between the TiN electrode and HZO layers due to a high defect level such as oxygen vacancy. This phenomenon was attributed to the oxygen scavenging effect by the TiN electrode, leading to the formation of oxygen vacancies throughout the HZO layer, and especially at the interfaces. In this study, to stabilize the ferroelectric orthorhombic phase, tungsten oxide was adopted as an oxygen donor for the HZO layer.

Tungsten oxide has numerous advantages, ranging from high compatibility with complementary metal-oxide-semiconductor (CMOS) technology to its various oxidation states, which can control the oxygen vacancy level in the HZO layer when used as an interfacial layer between the TiN electrode and HZO layer. First, the atomic layer deposition (ALD) process of the tungsten trioxide (WO_3) was established, and the characteristics as a potential interfacial layer were examined. Subsequentially, all layers in metal-insulator-metal (MIM) capacitor were deposited via ALD. The oxygen supply from reducible tungsten oxide, transitioning from WO_3 to WO_{3-x}, effectively annihilated oxygen vacancies in the HZO, leading to the promotion of the orthorhombic phase. Additionally, the possible distribution of the oxygen vacancies induced by the interfacial tungsten oxide layer and its effect was investigated depending on the device cycling through the imprint of the polarization-electric field (P-E) loop and the depth profile of the oxygen element. Appropriate control of oxygen vacancies via interfacial engineering with various seed and capping layer materials enabled the stabilization of the orthorhombic phase, thereby increasing the two remanent polarization ($2P_r$) value. Finally, the superior electrical performance of the improved $2P_r$ value with an endurance cycle number over 10^9 cy was achieved with an optimized tri-layer stack consisting of seed TiO_2/La:HZO/capping WO_3. This interfacial engineering work is anticipated to provide a guideline for further engineering involving thickness, dopant, and functional layer in FeRAM capacitor.

8:45am **AA1-WeM-4 Ultrathin HfO_2–ZrO_2 Multilayers Structures by ALD for Embedded Ferroelectric Non-Volatile Memories*, Amanda Mallmann Tonelli,*** *J. Mercier, N. Vaxelaire, Y. Mazel, Z. Saghi, N. Gauthier, S. Martin, L. Grenouillet, V. Jousseaume, M. Bedjaoui,* CEA-Leti, France

The rapid progress of nanoelectronic systems and miniaturized portable devices has increased the urgent demands for miniaturized and integrated circuit. Recently, the developedhafnium-oxide (HfO_2)basedferroelectric filmswith CMOS-compatible process shows a great potential for advanced low-power device technology [1]. However, ultrathin HfO_2-based ferroelectric films are still in the risk of device failure due to the large leakage current, which makes it unstable and limits the device service life [2], [3]. On the other hand, a significant effort has been made to lower the ferroelectric film thickness below 10 nm while maintaining good ferroelectric properties. The multilayer approach can provides solutions to the problems of leakage current and endurance by blocking the electrons injected from the electrode, which provides a promising idea for the application of HfO_2 in electronic devices [4].

The aim of this study is to develop ultrathin ferroelectric layers by ALD for MFM (Metal-Ferroelectric-Metal) capacitors based non-volatile memories. Within this work, HfO_2-ZrO_2 multilayers consisting of stacked HfO_2 and ZrO_2 were developed and investigated. The objective of this project is i) to investigate the intrinsic characteristics of the material and its evolution at each stage of the MFM fabrication through different structural, physicochemical and image analyses and ii) correlate the structural properties to the electrical characteristics.

The experimental analysis of the 10 nm thick nanolaminates films allowed some preliminary conclusions. The x-ray diffraction results presented in (Fig. 1) reveal that the films are already crystalline after deposition of the TiN/W top electrodes, carried out at 380°C. The diffraction peaks around 30.5° stand for a mixture of tetragonal and orthorhombic phase and could be evidence of the beginning of crystallization of a ferroelectric material. Furthermore, after dry plasma etching of the top electrode, the chemical state of material was analyzed using x-ray photoelectron spectroscopy. In addition to the composition of the material, an estimation of the oxygen vacancies (V_o) was made, as V_o is supposed to play a crucial role in the ferroelectricity of HfO_2-based films (Fig. 2). After annealing, through electrical positive-up-negative-down (PUND) measurement, it was possible to obtain evidence of ferroelectricity of the structure (Fig. 3) The preliminary findings showed in this work seems favorable for the implementation of FE HfO_2-ZrO_2 multilayers in non-volatile memory devices.

9:00am **AA1-WeM-5 Effects of Gamma Radiation on the Electrical and Structural Properties of Ferroelectric Hafnium Oxide-Based Capacitors*, Samantha Jaszewski,*** *M. Henry,* Sandia National Laboratories

Ferroelectric hafnium oxide (HfO_2) presents opportunities for technological developments in microelectronics, such as scaling of ferroelectric random-access memory (FeRAM) and new devices such as ferroelectric field-effect transistors (FeFETS) and ferroelectric tunnel junctions (FTJs), that were not previously possible with conventional ferroelectrics. This is due to its compatibility with silicon and ability to exhibit a ferroelectric response in films as thin as 1 nm.Understanding the interaction between radiation and HfO_2-based ferroelectrics is necessary before this material can be utilized in devices facing radiation-hostile environments. In this work, the effects of varying doses of gamma radiation (1 to 8 Mrad) on the structural and electrical properties of metal-ferroelectric-metal capacitors fabricated with 17 nm thick hafnium zirconium oxide (HZO) layers is investigated.

Additionally different electrode materials, titanium nitride and tungsten, will be compared. Polarization-electric field, capacitance-voltage, and leakage current measurements were made after electric field cycling with voltages ranging from 2.6 to 4 V. It will be shown that the devices experience decreased endurance and a shift in the coercive voltage that scales with the applied gamma dose and depends on the electrode material. This work advances the understanding of the interaction between radiation and HfO_2-based ferroelectrics in order to probe the fundamental limits of radiation tolerance in this material.

9:15am **AA1-WeM-6 Enhancement of Ferroelectric Phase Formation of HfO_2/ZrO_2 Nanolaminate Films by Tuning HfO_2 and ZrO_2 Thicknesses Using Atomic Layer Deposition*, Takashi Onaya,*** *Y. Sakuragawa, K. Kita,* The University of Tokyo, Japan

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) thin films are typically fabricated by forming HfO_2/ZrO_2 nanolaminate films deposited by alternately depositing HfO_2 and ZrO_2 layers using atomic layer deposition (ALD). It has been reported that the remanent polarization of HfO_2/ZrO_2 nanolaminate films changed depending on each HfO_2 and ZrO_2 thickness [1]. However, it is still unclear how each HfO_2 and ZrO_2 thickness affect the formation of ferroelectric orthorhombic (O) phase. In this work, we studied the crystal structure of HfO_2/ZrO_2 nanolaminate films with various conditions using ALD.

A 10-nm-thick HfO_2/ZrO_2 nanolaminate film was deposited on a TiN/p-Si substrate by alternately depositing HfO_2 and ZrO_2 layers using ALD at 300°C. $Hf[N(C_2H_5)CH_3]_4$ and $Zr[N(C_2H_5)CH_3]_4$ precursors were used for HfO_2 and ZrO_2, respectively, and H_2O was used for an oxidant. The ALD cycle ratio was varied from HfO_2/ZrO_2=1/1 to 60/60 so that each HfO_2 and ZrO_2 thickness would be varied from 0.08 to 5 nm while keeping the total thickness of the nanolaminate film to 10 nm. Finally, post-deposition annealing was performed at 600°C for 1 min in a N_2 atmosphere. A 10-nm-thick HZO solid-solution film was also fabricated by ALD using a $Hf/Zr[N(C_2H_5)CH_3]_4$ cocktail precursor as a reference.

In grazing-incidence X-ray diffraction (GIXRD) spectra, all samples clearly showed the diffraction peak at ~30.7°, attributed to either O(111), tetragonal (T) (101), or cubic (C) (111) (O/T/C) phases. The peaks for HfO_2 and ZrO_2 are not distinguishable due to almost the same lattice constant. The O/T/C peak areas of the HfO_2/ZrO_2=6/6 and 12/12 films were ~1.4 times larger than that of the HZO solid-solution film, where each HfO_2 and ZrO_2 thickness was 0.5−1 nm (1−2 monolayers). On the other hand, the HfO_2/ZrO_2=1/1 and HZO solid-solution films showed similar O/T/C peak area, because Hf and Zr atoms could be uniformly mixed in the HfO_2/ZrO_2=1/1 film. In addition, the O/T/C peak area decreased by increasing ALD cycle ratio, such as the HfO_2/ZrO_2=20/20 and 60/60. We also found that the as-grown ZrO_2 film was already crystallized in O/T/C phases even without annealing, whereas the most of as-grown HfO_2 and HZO solid-solution films was amorphous [2]. Therefore, the ZrO_2 layers in HfO_2/ZrO_2 nanolaminate films should play a role to provide nuclei efficiently to enhance the O/T/C phase formation in the HfO_2/ZrO_2=6/6 and 12/12 films.

In conclusion, the O/T/C phase formation can be prompted by using HfO_2/ZrO_2 nanolaminate films with each HfO_2 and ZrO_2 thickness of 1−2 monolayers.

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9:30am **AA1-WeM-7 Investigating the Impact of Process Parameters on the In-plane Strain of Ultra-Thin $H\text{-}f_xZr_{1-x}O_2$ Films*, Florian Wunderwald,*** Namlab, Germany*; B. Xu,* Namlab, China*; P. Vishnumurthy,* Namlab, India*; S. Enghardt,* TU Dresden, Germany*; K. Holsgrove,* Queen's University Belfast, UK*; A. Kersch,* University of Applied Sciences Munich, Germany*; T. Mikolajick, U. Schroeder,* Namlab, Germany

Since the development of Atomic Layer Deposition (ALD) 50 years ago, the technique has improved the deposition of thin films [1]. The first hafnium oxide processes were developed in the mid-1990s, and the material has been in mass production for semiconductor devices since 2007 [2, 3]. Interestingly, in the same year, T. Boescke discovered ferroelectricity in doped hafnium oxide thin films [4]. The finding of ferroelectricity in a fluorite-structured material, which is simultaneously compatible with semiconductor processing, has generated significant interest in their use for cutting-edge technologies such as non-volatile memory applications, neuromorphic computing, and AI applications [5]. To achieve the desired industrial properties of the material, which include high remnant polarization, high endurance, and high retention, understanding the impact of ALD processing on the later properties is crucial. In addition to that, the thickness scaling and behavior of ultra-thin $Hf\text{-}_xZr_{1-x}O_2$films are receiving more attention from the industry [5]. However, there is a lack of studies that review the impact of the single-stack engineering steps, such as atomic layer deposition (ALD), interface engineering, and annealing conditions, on one of the key factors: biaxial in-plane strain and its influence on ferroelectric phase formation in ultra-thin $H\text{-}f_xZr_{1-x}O_2$ films.

This study fills this gap and investigates the shortcomings mentioned above. To determine the biaxial in-plane strain, the lattice spacing was measured using the $\sin^2\Psi$-method [6]. The results in Figure 2 show a clear increase in in-plane strain for thinner films, indicating a stronger impact of interfacial crystal lattice misfits, which can be confirmed by TEM measurements. Changes in strain lead to phase transitions for thinner films. To determine the different phases Gracing Incidence XRD (Figure 3) and EBSD (Figure 4) has been performed. For a deeper understanding and correlation, bipolar electric field cycling measurements were carried out to set the strain results in correlation with the electric switching field.

This study aims to enhance the knowledge of the influence of ALD process parameters on the in-plane strain in thin and ultra-thin $Hf\text{-}_xZr_{1-x}O_2$films. The findings will provide a better understanding of processing and, thus, the establishment of $Hf\text{-}_xZr_{1-x}O_2$films in non-volatile memory storage applications.

9:45am **AA1-WeM-8 Thermal ALD IGO Channel Layer with High-thermal Stability (> 800 ^{o}C) for New Hybrid (Poly-Si/IGO) Vertical 3D NAND Application*, Su-Hwan Choi,*** *J. Sim,* Hanyang University, Korea*; C. Park,* Hanyang University, Korea, Republic of Korea [], Republic of Korea*; Y. Song, J. Park,* Hanyang University, Korea

The oxide semiconductor (OS) channel materials represented by IGZO have been attracting attention from memory devices such as DRAM and NAND flash applications because of their outstanding properties, such as high mobility, low off-current, and excellent uniformity. Especially for the NAND flash memory, high field-effect mobility OS is proposed as the channel layer. However, OS channel NAND has problems, such as the inability to erase operations and poor thermal stability. To improve the disadvantages of OS channel NAND, we proposed a hybrid channel (HC, Poly-Si/OS) for V-NAND flash memory in which a poly-Si and an OS channel coexist for the remaining gate-induced-drain leakage (GIDL) erase scheme and high mobility, respectively. In this study, we adopt the atomic layer deposition (ALD) method for depositing the OS channel. The ALD has great advantages, such as excellent step coverage and sub-nanometer-scale thickness control. Especially for hybrid channel structures, high step coverage properties of OS deposition are crucial because the aspect ratio is increased by Poly-Si channel deposition. This is because the hole diameter of the V-NAND string is decreased by poly-si thickness, whereas the hole height is similar.

In this study, we adopt the IGO for the hybrid channel structure (poly-Si/IGO). The DBADMIn was adopted to deposit the InO, the mother material of IGO. As shown in **Fig 1 (a) and (b)**, the 250 ^{o}C deposited InO using ozone as a reactant easily crystallizes even at 3 nm thick with highly c-axis aligned Cubic (222) orientation, exhibiting superior electrical and stability properties. The TMGa was adopted to gallium doping for the InO channel using the super-cycle method. A thickness of IGO above 10 nm is needed to achieve high thermal stability after the post-annealing process at 800 ^{o}C for 3 hours because the thermal stability of IGO is related to crystallinity (**Fig 1 (c)**). The vertically structured HC NAND flash was successfully fabricated, as shown in **Fig 2**. The Schematic of the V-NAND flash memory structure for illustrating conventional poly-Si and the purpose of the hybrid-channel (HC) structure are summarized in **Fig 2(a)**. As shown in **Fig 3 (a)**, the GIDL current of HC channel NAND flash was achieved and confirmed as successfully operating the program and erase operation after the post-annealing process at 800 ^{o}C for 3 hours. We easily understand the conventional program, however, in the case of GIDL erase, through **Fig. 3(b)**, the proposed HC structure generates a band to band tunneling generation through a poly-Si channel, therefore the GIDL-assisted increasing channel potential can be confirmed through hole current generation.

ALD Applications
Room Hall 3D - Session AA2-WeM

Memory Applications: RRAM & Neuromorphic, MIM Capacitors

Moderators: Uwe Schröder, Namlab, **Seung-Yeul Yang**, Samsung

10:45am **AA2-WeM-12 Towards Neuromorphic Computing Using ALD Grown HfO₂ Based Memristive Devices***, **Christian Wenger**,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany **INVITED**

Due to its advantages of massive parallelism, high energy efficiency, and cognitive functions, brain-inspired neuromorphic computing is attracting immense interest. As the basic unit cell for learning algorithms, the implementation of synaptic behavior into memristive devices is the key step toward neuromorphic computing.

Recent advances in the performance of resistive random access memory (RRAM) acting as memristive devices have led to a significant interest in neuromorphic applications. Although RRAM based memory arrays demonstrated excellent performance parameters, the variability is still a critical issue. Controlling this intrinsic phenomenon requires employing program-verify schemes. In this talk, an optimized scheme to minimize resistance state dispersion and to achieve reliable multi-bit operation is evaluated.

However, statistical variations can be tolerated in computing applications like neuromorphic networks. The synaptic behavior memristive devices can be evaluated by applying successive algorithms consisting of set or reset pulses. These algorithms can be used to study the synaptic functionality of memristive arrays.

Nevertheless, there is still a huge gap between the physical implementation and the verification of circuits and systems proposed for memristive devices. The first step, required to fill the gap, is the development of analog simulation tools, which are the base for the successful implementation of digital CMOS circuits with memristive elements. New designs and concepts need to be supported up by physical implementation and verification to be reliable. That means, new simulation tools for memristive devices have to address the following issues: device variability, cycling variability, data endurance, data retention as well as device switching speed. Meaning that memristive device models still have a long way to be completed.

11:15am **AA2-WeM-14 Novel Carbon-Doped HfO$_x$ Memristor with Born-ON Characteristics Synthesized via ALD/MLD Combined Technique***, **Minjong Lee**, Y. Hong, J. Kim, D. Le, D. Kim,* University of Texas at Dallas*; R. Choi,* Inha university, Republic of Korea*; J. Rohan, G. Yeric,* Cerfe Labs*; J. Kim,* University of Texas at Dallas

Transition metal-oxide (TMO) materials are recognized as the most promising for memristive devices. The majority of TMO memristors require a one-time initialization step, during which a relatively large voltage induces filamentary switching. This forming process introduces challenges, including large overshoot currents under high voltage conditions [1]. Beyond typical memristive operations, including the initial forming process, the novel concept of a born-ON memristor generates universal non-polar switching in carbon-doped TMO films deposited by spin-on fabrication [2]. The introduction of additional defects to the pristine TMO film results in born-ON characteristics accompanied by excellent device yield and reliability. However, spin-on fabrication has a significant limitation as it is not compatible with CMOS process. In our previous presentation at the ALD/ALE 2023 conference, we demonstrated feasible born-ON characteristics by using a carbon-composited oxidant during the ALD process [3].

Herein, we extend the technical feasibility of previous work to demonstrate a super-cycle approach generating controllable HfOx film density and carbon concentration. Beyond typical HfOx film deposition using TDMA-Hf and H2O, we used ethylene glycol (EG) as an additional reactant for carbon doping. Within the super-cycle framework, we varied the 'm' cycles of the ALD process (TDMA-Hf/H2O) and the 'n' cycles of the MLD process (TDMA-Hf/EG). Notably, adjusting the ratio between the ALD and MLD processes resulted in HfOx film densities ranging from 4.5 to 9.4 g/cm3 (Fig. 1a). Furthermore, leveraging this super-cycle approach of ALD and MLD cycles provides control over the carbon rate, evident from the XPS profiles (Fig. 1b). The electrical characteristics of HfOx memristors were comprehensively investigated across various carbon concentrations (Fig. 2a). With an increase in carbon concentration to 10%, the set voltage decreases, and the initial leakage current closely aligns with OFF current, indicating a forming-free memristor. In devices with 15% carbon, we achieved born-ON memristive behavior. This device ensures reliable non-volatile memory operation with excellent endurance and retention properties (Fig. 2b). Our work marks a significant advance towards the development of novel forming-free TMO memristors within this controllable film density paradigm using super-cycle approach of ALD and MLD processes.

This research is supported by Cerfe Labs and KIAT granted by MOTIE Korea (P0017303).

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11:30am **AA2-WeM-15 Evolution of Structural Order in Doped Hafnia Thin Films by Atomic Layer Deposition for Emerging Device Applications***, **Mohammad Hassan Sultani**, F. Cüppers,* Forschungszentrum Juelich GmbH, Germany*; A. Dippel, O. Gutowski,* Deutsches Elektronen Synchrotron DESY, Germany*; A. Besmehn, D. Müller, S. Hoffmann-Eifert,* Forschungszentrum Juelich GmbH, Germany

HfO_2-based thin films by atomic layer deposition (ALD) are widely used in emerging electronic devices. Monoclinic and tetragonal structures serve as high-k dielectric in field effect transistors (FET). Films with ferroelectric orthorhombic structures, often achieved by doping, enable ferroelectric FETs. Further, thin films of HfO_2 form the switching layer in resistive random-access memories (ReRAM) for new neuromorphic computing architectures. Due to limitation of the thermal budget in back-end-of-line to about 450°C, an amorphous state of the HfO_2 layer after full chip fabrication is essential for high device-to-device reproducibility. For a deeper understanding of the optimum design of emerging devices based on ALD HfO_2 films, it is crucial to describe the nature of the amorphous material and to control the crystallization process and the resulting phase by heterovalent and homovalent doping.

The present study investigates the structural properties of thin films from HfO_2 doped with Al, Si, and Ti. The films at a total thickness of 30 nm were grown in a FlexAL^{TM} system at 250°C heater temperature using oxygen plasma as the counter reactant. Tetrakis(ethylmethylamido)hafnium, trimethylaluminium, Bis(tertiary-butylamino)silane, and tetrakis(dimethylamino)titanium served as metal precursors. Effective dopant concentrations between 2 and 10 at% were realized by the growth of nanolaminates of n-times (x cycles HfO_2 - y cycles MO_x – x cycles HfO_2)(with M=Al, Si, Ti). The laminate structures after growth and crystallization were characterized by X-ray reflectivity and by time-of-flight secondary ion mass spectroscopy. The local structure of the amorphous layers was probed by high-energy X-ray scattering at grazing incidence and pair distribution function analysis. Further, in-situ thermal treatment in vacuum allowed to study the crystallization process of the different films in detail. Crystallized films were analyzed by high-resolution grazing-incidence X-ray diffraction. The measurements were performed at PETRA-III storage ring at DESY

The results will be discussed with special emphasis on the effects of the dopant element, the laminate sequences, the effective doping concentration on the local structure of as-grown films, on the crystallization behavior, and on the crystalline phase obtained after annealing. Results of this study can enhance the understanding of the thin films' local structure and the crystallization process and thereby can support the optimization of material's and process' design for the various applications of HfO_2 thin films in emerging devices for energy-efficient next-era computing applications.

11:45am **AA2-WeM-16 ALD HfZrO2 Films from Ferroelectric to High-k Applications***, **Alessandra Leonhardt**,* ASM, Finland*; R. Ramachandran,* ASM, Belgium*; M. Surman,* ASM, Finland*; R. John, F. Tang, M. Balseanu,* ASM*; A. Illiberi,* ASM, Belgium

HfO2 based ferroelectric (FE) materials have gained tremendous attention as a potential candidate for memory applications such as FeFET and FeRAM. Since its first demonstration as a FE material [1], immense research has been done to circumvent the challenges such as scalability, increasing the remnant polarization (Pr), and improving endurance. Among others, Zr-doped HfO2, $HfZrO_2$ is being intensively studied due to its compatibility with complementary metal oxide semiconductor (CMOS) processing and excellent scalability. ALD has been the technique of choice for the deposition of those films, due to the high conformality, high film quality and simplicity of tuning the composition. $HfZrO_2$ has excelled in this field, with high polarization, high endurance and retention. Those properties were still further improved by the addition of dopants such as La, which resulted in the record high 2Pr for films fabricated by ASM and imec using metalorganic precursors [2].

In this presentation we take ALD $HfZrO_2$ one step forward, and describe how, with the addition of suitable dopants, the ferroelectricity can be modulated in a broad range, and how this can be incorporated in applications where high dielectric constants are desired. We discuss the use of Al dopants in $HfZrO_2$ and explore the relationship between film composition and electrical properties, discussing the physics of ferroelectricity and high dielectric constant. Thin Al:$HfZrO_2$ films show significant modifications in their dielectric properties with respect to pure $HfZrO_2$. Low Al doping levels initially boost the capacitance, while higher levels results in CV peak shifting which leads to a quasi-flat CV behavior at 5% Al doping. This is consistent with the model of dopants with small atomic radius promoting tetragonal phases inside the (initially orthorhombic) $HfZrO_2$ lattice [3]. This results in high dielectric constant at relevant operation voltages e.g. k>40 @ -1.2V for 6-7nm films, which is in line with future high-k applications.

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ALD Applications
Room Hall 3E - Session AA3-WeM
Other Emerging Applications

Moderators: Sumit Agarwal, Colorado School of Mines, **Parag Banerjee**, University of Central Florida

10:45am **AA3-WeM-12 Tunable Superconducting $Nb_xTi_{1-x}N$ by Fast Plasma-enhanced ALD for Quantum Applications***, **Silke Peeters**, L. Nelissen,* Eindhoven University of Technology, Netherlands*; D. Besprozvannyy,* Oxford Instruments Plasma Technology, UK*; M. Verheijen,* Eindhoven University of Technology, Netherlands*; M. Powell, L. Bailey,* Oxford Instruments Plasma Technology, UK*; E. Kessels,* Eindhoven University of Technology, Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, UK

Superconducting films ranging from a few to hundreds of nanometers are at the basis of a wide range of quantum devices, and are therefore key in advancing quantum technology to an era of widespread utility. The further development of quantum technologies hinges on improvements in materials and their interfaces. With its atomic-scale growth control, plasma-enhanced ALD (PEALD) could become an enabling technique for the growth of superconducting thin films with high-quality interfaces. High-throughput processes will facilitate the growth films beyond 100 nm, broadening the application perspective for ALD of superconducting films.

We demonstrate PEALD of superconducting $Nb_xTi_{1-x}N$ films ranging from 5 to 100 nm thickness at a high throughput of >50 nm/hour on the Plasma Pro ASP system. The depositions consist of NbN and TiN supercycles using the TBTDEN and TDMAT precursors and an $Ar/H_2/N_2$ plasma at a table temperature of 320 °C. The RF-driven remote capacitively coupled plasma source is combined with RF substrate bias functionality allowing for ion-energy control.

The $Nb_xTi_{1-x}N$ films show critical temperatures of superconductivity from 3 K at *x=0* to 13 K at *x=1* for 25 – 50 nm films. High film quality is confirmed by low O impurity contents ~ 5 at.% or lower and room-temperature resistivities increasing with Nb content from 160 μΩ cm (41 nm TiN) to 284 μΩ cm (25 nm NbN). Accurate composition control of $Nb_xTi_{1-x}N$ is demonstrated from *x=0* to *x=1*, with the C content increasing from 5 at.% to 16 at.% and the N content correspondingly decreasing from 48 at.% to 36 at.%. EDX mapping confirms homogeneous mixing of Ti and Nb, and XRD measurements show all prepared films are fcc polycrystalline. Tuning of the ion energy indicates a stable composition, while the crystallinity and conductivity can be influenced. TEM imaging of the most conductive 49 nm $Nb_{0.5}Ti_{0.5}N$ film reveals a disordered polycrystalline film in agreement with XRD measurements. A relatively high sheet kinetic inductance of 24 pH/sq is found for 38 nm film thickness. In addition to lowering resistivity, substrate biasing provides the ability to enhance film disorder, making these films attractive for applications such as microwave kinetic inductance detectors. The high throughput and tunability of the $Nb_xTi_{1-x}N$ deposition process puts forward PEALD as a promising technique to tackle material challenges in quantum technologies.

11:00am **AA3-WeM-13 Atomic Layer Deposited Metal Nitrides (TiN and InN) and Metal Semiconductor Heterojunctions for Quantum Applications***, **Neeraj Nepal**, J. Prestigiacomo, M. Sales, P. Litwin, T. Growden, V. Wheeler,* US Naval Research Laboratory

Direct integration of III-N semiconductors with superconductors are beneficial for quantum technologies such as superconducting qubits, secure quantum communications, and superconducting radio-frequency circuits [1]. To-date direct integration has been achieved using III-N/NbN grown at >600 °C [1]. Atomic layer deposition (ALD) provides a path towards integration at lower temperatures with wafer scale uniformity, conformality and subatomic thickness control. Titanium nitride (TiN) is a favorable, superconductor (T_c ~5.6 K [2]) to integrate with III-N materials. In fact, ALD TiN has been used as a Schottky gate metal in III-N devices for improved electrical and thermal performance [3]. Also, kinetic inductance is one of the highest in TiN [4] and increases with decreasing thickness. High quality InN semiconductor with high carrier concentration has been demonstrated by ALD [5]. Thus, integrating high quality, crystalline ALD deposited TiN metal with InN semiconductor could provide metal-semiconductor heterojunctions (HJ) for various quantum applications.

ALD TiN and InN films (40 nm), were deposited as single and bilayer structures on resistive Si and c-sapphire in a Veeco Fiji Gen2 ALD reactor. TDMAT and TMI precursors were used to grow TiN and InN, respectively. An Ar/N_2 plasma at 300W was used for both layers. ALD process windows were monitored and optimized on Si substrates using *in-situ* ellipsometry and *ex-situ* characterizations. Both materials were determined to have a common ALD window at 250 °C allowing bilayers to be deposited at these temperatures with abrupt interfaces.

40 nm TiN films grown on c-sapphire and resistive Si(100) exhibited a T_c of 3.85 K and 3.45 K, respectively. This is similar to previously reported 50 nm TiN films on resistive Si with a T-$_c$of 4.05 K [4]. XRD revealed a more crystalline TiN film on sapphire than Si, which could account for the higher T_c measured. ALD InN films exhibited a high electron carrier concentration of ~4x10^{20} cm^{-3}. Bilayer semiconductor-superconductor HJ of 40 nm TiN/40 nm InN on and 40 nm InN/40nm TiN were then deposited on sapphire at 250 °C. XRD shows that individual layers in these HJ are crystalline with both InN (0002) and Ti(111) peaks present. Detailed ALD growth and characterization results will be presented for all layers and discussed in context of use in quantum applications.

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11:15am **AA3-WeM-14 Ceramic Thin-Film Composite Membranes with Tunable Subnanometer Pores for Molecular Sieving by Atomic Layer Deposition***, X. Zhou,* Yale University*; R. Shevate, A. Mane, **Jeffrey Elam**,* Argonne National Laboratory*; J. Kim, M. Elimelech,* Yale University

Membranes with tunable, sub-nanometer pores are needed for molecular separations in applications including water treatment, critical mineral extraction, and recycling. Ceramic membranes are a promising alternative to the polymeric membranes typically used in such applications due to their robust operation under harsh chemical conditions. However, current fabrication technologies fail to construct ceramic membranes suitable for selective molecular separations. In this presentation, we describe a ceramic thin film composite (TFC) membrane fabrication method that achieves sub-nm pore size control using atomic layer deposition (ALD) by incorporating a molecular-scale porogen. By co-dosing alkyl alcohols along with the H_2O coreactant during Al_2O_3 ALD, we incorporate alkoxide species in the film which create a continuous network of pores upon calcination. Varying the alkyl alcohol (methanol, ethanol, isopropanol) tunes the pore size. We use Fourier transform infrared absorption spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy to elucidate the surface chemistry and growth during the alcohol-modulated ALD as well as the subsequent pore formation. We evaluate the transport and separations properties of the ALD TFC membranes using a two-chamber diffusion cell with aqueous salt solutions. We measured a remarkable enhancement in the transport of Cl^- compared to SO_4^{2-} (8.6 times faster) matching the selectivity of state-of-the-art polymer membranes. We attribute this selectivity to the dehydration of the large divalent ions within the subnanometer pores. In addition, permeation studies using neutral adsorbates revealed average pore sizes of ~7Å, 13Å, and 19Å for ALD TFC membranes prepared using methanol, ethanol, and isopropanol, respectively. This work provides the scientific basis for the design of ceramic membranes with subnanometer pores for molecular sieving using ALD.

11:30am **AA3-WeM-15 Recent Developments and Emerging Applications in Atmospheric-Pressure Atomic Layer Deposition of High-Porosity Materials***, M. Chen,* TU Delft, China*; M. Nijboer, A. Kovalgin, A. Nijmeijer,* University of Twente, The Netherlands*; F. Roozeboom,* University of Twente and Carbyon B.V., Netherlands*;* ***Mieke Luiten-Olieman****,* University of Twente, The Netherlands

Atomic layer deposition (ALD) is a widely recognized technique for depositing ultrathin conformal films with excellent thickness controlat Ångström or (sub)monolayer level. Atmospheric-pressure ALD is an upcoming ALD process option with a potentially lower reactor ownership cost.

We will present a comprehensive overview of the recent applications and development of ALD applications exclusively working at atmospheric pressure [1]. Spatial ALD (sALD) has been recently introduced for the commercial surface passivation and encapsulation in the large-area production of solar cells, and for the production of 2D displays, in particular organic light-emitting diode (OLED) displays. Atmospheric-pressure temporal ALD (tALD) has found its route for new emerging applications such as high-porosity particle coatings, functionalization of capillary columns for gas chromatography, and membrane modification in water treatment and gas purification. The challenges and opportunities in achieving highly conformal coatings on porous substrates by atmospheric-pressure ALD will be discussed.

Typically, each application often requires its own optimized reactor design [1]. For the application of tuning and functionalizing nanopores in tubular ceramic nanofiltration membranes, we will present a new tubular reactor design [2]. In this design, the reactor wall is formed by the industrial tubular ceramic membrane itself, and carrier gas flows are employed to transport the precursor and co-reactant vapors to the reactive surface groups present on the membrane surface, see Fig. 1. The layer growth for atmospheric-pressure ALD, in this case, proceeds similarly to that for state-of-the-art vacuum-based ALD. Moreover, for membrane preparation, this new reactor design has three advantages: i) monolayers will be deposited only at the outer pore mouths rather than in the entire bulk of the porous membrane substrate, resulting in reduced flow resistances for liquid permeation; ii) an *in-line* gas permeation method was developed to monitor the layer growth in the pores during the deposition process, allowing more precise control over the finished membrane (see Fig. 2), and iii) expensive vacuum components and cleanroom environment are avoided. This opens up a new avenue for commercial ceramic membrane functionalization with nano-scale precision by using ALD at atmospheric pressure.

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11:45am **AA3-WeM-16 Modulation Acceptor Doping of Silicon Nanowires using a SiO_2-shell doped with ALD Metal Oxide Monolayers***,* ***Daniel Hiller,*** Institute of Applied Physics (IAP), TU Bergakademie Freiberg, Germany*; S. Nagarajan,* Nanoelectronic Materials Laboratory (NaMLab) gGmbH, Dresden, Germany*; I. Ratschinski, S. Shams,* Institute of Applied Physics (IAP), TU Bergakademie Freiberg, Germany*; M. Venzke,* Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany*; P. Hönicke,* Helmholtz-Zentrum Berlin (HZB), Berlin & Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany*; T. Mikolajick,* Nanoelectronic Materials Laboratory (NaMLab) gGmbH, Dresden & Institute of Semiconductors and Microsystems, TU Dresden, Germany*; J. Trommer,* Nanoelectronic Materials Laboratory (NaMLab) gGmbH, Dresden, Germany*; D. König,* Integrated Materials Design Lab (IMDL), Australian National University (ANU), Canberra, Australia

Silicon nanowires (Si NWs) or nanosheets are the building blocks for future transistors and efficient doping processes are inevitable for conductivity. Yet, NWs suffer from severe difficulties with efficient impurity doping due to a multitude of physical and technological problems when the diameters are reduced to a few nanometers: diffusion, dielectric and quantum confinement, statistics of small numbers, etc. Junctionless NW-transistors (JNTs) in particular require high conductivities. However, high impurity dopant concentrations are accompanied by a severely decreased mobility, which in turn implicates the need for higher operation voltages and increased electrical energy dissipation into heat. Therefore, alternative doping methods are desirable to separate the dopant atoms from the doping-induced free carriers.

Here, we present a novel modulation doping approach for Si NWs. According to results from density functional theory (DFT) calculations [1,2], we use Al- or Ga-doped SiO_2 as a shell around Si NWs. The trivalent group-III impurities incorporated into the tetravalent SiO_2 network form unoccupied acceptor states with an energy level located below the Si valence band edge (cf. Fig. 1). Such induced acceptor states can capture electrons from Si, creating free holes as majority charge carriers in the process [1-5].

Experimentally, the Al- or Ga-doping of SiO_2 is realized by ALD to form (sub-)monolayers of Al_2O_3 or Ga_2O_3 on an ultra-thin tunnel-SiO_2 and a subsequently deposited capping layer of SiO_2 or HfO_2. Crucial details of the Al/Ga-deposition on a dry-thermal oxide surface during the initial ALD-cycles are obtained via synchrotron-based reference-free grazing incidence X-ray fluorescence spectrometry (GIXRF) [6].

In this presentation, we furthermore demonstrate that Si NWs with modulation-doped SiO_2 shells exhibit up to 6 orders of magnitude lower electrical resistances as compared to NWs with undoped SiO_2-shells, as shown in Fig. 2 [7,8].

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ALD Applications
Room Hall 3D - Session AA1-WeA
More than Moore Applications

Moderators: Benjamin Greenberg, Naval Research Laboratory, **Sami Sneck**, Beneq

1:30pm **AA1-WeA-1 ALD Solutions for Compound Semiconductor Devices***, **Mikko Söderlund**, A. Voznyi, T. Ivanova, A. Perros, P. Rabinzohn,* Beneq Oy, Finland **INVITED**

Among the wide bang gap (WBG) WBG semiconductors, SiC and GaN offer attractive performance over Silicon-based devices for the realization of high-voltage switches to be used in power converters and have been widely adopted for many applications.Tesla's adoption of SiC in 2017 for the onboard, or traction, inverters for its Model 3 was an early and major win. EV traction inverters typically range from about 35 kW to 100 kW for a small EV to about 400 kW for a large vehicle.On the other hand, AlGaN/GaN High-Electron-Mobility-Transistors (HEMTs) have allowed realization of low on-resistance and high-switching frequency transistors, enabling GaN-based power FETs rating 650 V with preferred normally-off device performance achieved using a p-GaN gate stack.

However, both SiC and GaN-based power transistors face challenges with defectivity of the semiconductor-dielectric interface, reducing the device electrical performance and especially on-resistance to less than ideal. In particular, low electron mobility at the SiO2/SiC interface due to carbon-related interface defects resulting from thermal oxidation remains the number one challenge for SiC devices and is associated with hysteresis of threshold voltage. Thus, a clear industry trend is to eliminate oxidation from the SiO2 formation process. The formation/deposition of highest-quality gate dielectric stacks (including SiO_2 and high-k) by atomic layer deposition (ALD) with the capability to control the dielectric/SiC interface by in-situ surface treatment and plasma enhanced atomic layer deposition (PEALD) Interfacial Layers (IL) are expected to play a significant role in the manufacturing of high performance SiC MOSFETs.

This paper presents an industrially proven three-step PEALD/thermal ALD cluster tool approach to engineer and perfect the semiconductor/dielectric interface quality and deposition of dielectric stack applicable to both GaN and SiC power devices. Characteristics of capacitance voltage (CV) and current density voltage (JV) for 4H-SiC MOS capacitors that utilize either ALD SiO_2 only, or ALD SiO_2 after plasma preclean (PP) or ALD SiO_2 with IL, are measured and presented. Overall, all devices demonstrate high-breakdown, low leakage current and negligible CV hysteresis indicating high-quality of ALD SiO_2 film and low-density of traps at the SiC/SiO_2 interface. In the best condition with PP/SiO2, nearly ideal SiC-SiO2 interface with hysteresis of less than 20 mV is achieved while demonstrating very low trapped charges. Improvement of p-GaN gate HEMT dynamic Rds on-resistance by ALD passivation layer will also be presented.

2:00pm **AA1-WeA-3 Plasma Effects on the Epitaxial Growth of Aluminum Nitride Thin Films on (0001)4H-SiC by PE-ALD***, **Bruno Galizia**, P. Fiorenza, C. Bongiorno,* Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica e Microsistemi (CNR-IMM), Italy*; B. Pécz, Z. Fogarassy,* Centre for Energy Research, Institute of Technical Physics and Materials Science, Hungary*; G. Greco, F. Giannazzo,* Consiglio Nazionale delle Ricerche - Istituto per la Microelettronica e Microsistemi (CNR-IMM), Italy*; F. Roccaforte,* Consiglio Nazionale delle Ricerche - Istituto per la Microelettronica (CNR-IMM), Italy*; R. Lo Nigro,* Consiglio Nazionale delle Ricerche - Istituto per la Microelettronica e Microsistemi (CNR-IMM), Italy

Aluminum Nitride (AlN) is considered a suitable candidate for the replacement of SiO_2 as gate dielectric in 4H-SiC based power MOSFETs because of its high permittivity constant (~9.1), large bandgap and good band-offset with 4H-SiC. Moreover, epitaxial growth and good interface quality could be favored by its low in-plane lattice mismatch with 4H-SiC (~0.9%) and because of their similar thermal expansion coefficients. Several deposition techniques such as molecular beam epitaxy, metal-organic chemical vapour deposition or physical vapour deposition have been used as AlN thin film synthesis technique, but they all suffer from high temperature processing.In this work, we investigated lower temperature PE-ALD processes, depositing AlN thin films on (0001)4H-SiC substrate at 300°C and we studied the effects of NH_3 plasma pulse time on crystalline quality, structural and electrical properties. Precursor nucleation and plasma effects have been monitored via *in-situ* ellipsometric spectroscopy half-cyle and end-cycle measurements and it has been observed that different AlN cristallyne phases have been formed as a function of plasma time pulsing. In particular, the wurtzite AlN structure is always present at the interface with the 4H-SiC substrate, while upon increasing thickness a poly-crystalline wurtzite phase was obtained by short-pulse NH_3-plasma, whereas longer plasma exposure resulted in a mixture of wurtzite and zincblende defective phases. The different phase formation has been also related to electrical properties by nanoscopic characterization using conductive atomic force microscopy (C-AFM). The C-AFM characterization, in fact, demonstrated that zincblende defective AlN layer resulting in poorer insulating properties while the totally wurzite AlN (0001) oriented films can be considered good insulator materials. This work has been supported by the European Union (NextGeneration EU), through the MUR-PNRR projects SAMOTHRACE (ECS00000022).

2:15pm **AA1-WeA-4 Novel Low Temperature Thermal ALD of Aluminum Nitride Utilizing a Non-Metal Catalyst***, **Sara Harris**, M. Weimer, D. Lindblad, A. Dameron,* Forge Nano

Quality aluminum nitride (AlN) with conformal step coverage is crucial for the performance of current and next-generation microelectromechanical (MEMS) and microelectronic devices, including energy harvesters, ultrasonic transducers, high-frequency wide band communications, and power semiconductors.[1] AlN is widely utilized due to a unique combination of high piezoelectric quality factor (Q=5000 at 10 MHz),[2] high thermal conductivity (up to 320 W/m·K)[3] and a high dielectric constant (k= 9.0).[3] State of the art technology relies on AlN deposited via physical vapor deposition (PVD) or metal organic chemical vapor deposition (MOCVD); techniques unable to deliver the step coverage over high aspect ratio features necessary for device miniaturization. AlN deposited via ALD typically requires plasma or elevated temperatures (>350 °C) affecting process scalability and thermal budget, ultimately disincentivizing industry adoption.[4] In this work, AlN was grown at 285 °C via thermal ALD through the addition of a novel nonmetal catalyst during the nitride conversion step, referred to as a CRISP process. We demonstrate the power of CRISP on two different AlN processes: trimethylaluminum (TMA)/hydrazine (HZ) and TMA/monomethylhydrazine (MMH) and report a 15 % increase in refractive index (RI) for the TMA/HZ-CRISP process and binary off/on growth for the TMA/MMH-CRISP process. Normal ALD AlN films grown using TMA/HZ in the absence of a catalyst have an RI of 1.65 and GPC of 1.17 Å/cy. In comparison, AlN films grown via the novel TMA/HZ-CRISP process, using the nonmetal catalyst, have an RI of 1.95 and GPC of 1.50 Å/cy, as measured via spectroscopic ellipsometry. The partial pressure ratio between HZ and the nonmetal catalyst must be finely tuned to maximize AlN RI. To enhance understanding of the catalytic reaction pathways accessed by the CRISP process, ALD of TMA and MMH was conducted at 285 °C where the process is not kinetically favorable [4]. The absence of TMA/MMH film growth in traditional ALD fashion at 285 °C was confirmed, then a CRISP-based catalysis was introduced to facilitate proton transfer [4] and AlN was grown with RI of 1.62 and a GPC of 0.92 Å/cy. While under these conditions the TMA/MMH-CRISP film is of lower quality than those deposited with HZ/CRISP, this result highlights the ability of the nonmetal catalyst to enhance surface reactivity. GPC and RI improvement between a standard ALD process and the CRISP process is shown in Figure 1 for TMA/HZ and TMA/MMH. Additional characterization of the density and crystallinity of AlN films grown via the CRISP process will be discussed.

2:30pm **AA1-WeA-5 Thermal and Plasma Enhanced ALD growth of functional Al_2O_3/AlN dielectric stacks for silicon carbide MOSFETs***, **Raffaella Lo Nigro**, B. Galizia, P. Fiorenza, E. Schilirò, F. Roccaforte,* Consiglio Nazionale delle Ricerche – Istituto per Microelettronica e Microsistemi (CNR-IMM), Italy

Over the last years, silicon carbide (4H-SiC) semiconductor has become suitable for high-power applications due to its superior properties compared with silicon, such as lower intrinsic carrier concentration, higher breakdown field, saturation velocity, and thermal conductivity. Nevertheless, there are still some open topics related to the exploitation of the full potentiality of this material and among them, the nature of the gate dielectric in metal-oxide-semiconductor-field effect-transistors (MOSFETs) is a crucial issue to be faced. In fact, the traditionally used SiO_2 dielectric suffers from low dielectric constant (≈3.9) compared to the one of 4H-SiC (≈9.7), so that, according to Gauss' law, the high breakdown field of 4H-SiC (3 MV/cm) cannot be fully exploited because of the earlier breakdown of SiO_2 layer. Consequently, high dielectric constant, large band-offset and good thermal stability as well as low density of defects are the ideal properties for gate dielectric in 4H-SiC power devices.

Aluminum oxide (Al_2O_3) possesses most of the ideal dielectric properties, nevertheless, did not demonstrate a better interface quality than SiO_2 layers. In this context, another high-κ insulator of interest is the aluminium nitride (AlN) having not only high dielectric constant, but also a low lattice mismatch to 4H-SiC (~0.9%).These properties make it promising for a very good interface quality if epitaxially grown on (0001)4H-SiC.

In this work, a new solution is proposed: Al_2O_3/AlN bilayers were fabricated on 4H-SiC via ALD methods. In particular, thermal-ALD and PE-ALD processes of Al_2O_3 layers on AlN thin interfacial layer have been compared. Structural and electrical characterization of the two Al_2O_3/AlN bilayers obtained by T-ALD or PE-ALD depositions of the Al_2O_3 layers, are reported. Poor electrical behavior of the PE-ALD Al_2O_3/AlN bilayer has been correlated to its structural characteristics. In particular, the presence of degradation at the interface between plasma-deposited Al_2O_3 and AlN has been detected probably due to an oxidation interaction caused by oxygen plasma even at deposition temperature as low as 250°C.

By contrast, the structural and electrical properties of the T-ALD Al_2O_3/AlN bilayers showed promising characteristics such as a reduction of the oxide trapped charges (almost one order of magnitude down to 10^{11}-10^{12}), as well as of the interface traps density and an increase of dielectric constant (from 7.5 to 8.5) compared with a single Al_2O_3 reference layer. These preliminary results encourage the investigation of Al_2O_3/AlN bilayers as a candidate for future 4H-SiC power applications.

2:45pm **AA1-WeA-6 Reduction of Defects at or Near ALD-Al_2O_3/GaN Interfaces for Improved Electrical Performance of GaN Power Devices***,* ***Caleb Glaser****, B. Rummel, J. Klesko, M. Meyerson, P. Dickens, A. Binder, R. Kaplar,* Sandia National Laboratories*; D. Feezell,* University of New Mexico

Wide bandgap (WBG) semiconductors, such as gallium nitride (GaN) and silicon carbide (SiC), are ideal candidates for high-power switching applications due to their high electron saturation velocity, lower conduction losses, and higher operating temperature capabilities compared to traditional silicon-based devices. GaN power devices often demonstrate clear technological improvements over their silicon counterparts and are competitive with SiC products in many high-power application spaces. However, there exist significant manufacturing challenges and reliability concerns associated with the complex architectures utilized by GaN-based designs, including the lack of a dependable thermally grown oxide. Atomic layer deposition (ALD) provides the opportunity to form reliable films for gate dielectrics or passivation layers in GaN structures. Electronic traps at or near the semiconductor/dielectric interface in MOS structures severely impact gate and channel performance by introducing leakage current pathways and threshold voltage instabilities as well as reduced channel mobilities. In addition, the formation of Ga_xO_y interlayers during the ALD formation of oxides like Al_2O_3 or HfO_2 may create additional defect sites leading to further deterioration of device performance.

This study explores the defect distributions at or near the ALD-Al_2O_3 interface in MOS gates and their impact on the electrical performance of GaN MOSCAPs and MOSFETs. Relative improvements to dielectric leakage, D_{IT} distributions, and capacitance-voltage hysteresis in MOSCAP structures have been analyzed to understand how the elimination of native oxides and reduction of potential defect sites improve electrical characteristics. Characterization of observable chemical bonds and surface morphology via XPS and AFM imaging and mapping shows the reduction of native oxide interlayers when exposed to precursor TMA cycling prior to Al_2O_3 film growth by ALD. The optimized deposition techniques and early detection methods for defect sites show an observable reduction of interface trap states, mid-gap trap states, and hysteresis measured by quasi-static C-V. Initial findings for improved semiconductor/dielectric interfaces on GaN MOSCAP devices were implemented into vertical GaN power MOSFETs and show significant improvements to device leakage currents and breakdown voltage. This marked increase in device performance follows the optimized ALD procedure that includes TMA cycling and reduces the calculated defect densities at or near the Al_2O_3/GaN interface through quasi-static C-V analysis.

3:00pm **AA1-WeA-7 Fabrication of RuS2 Photodetector Via Post Sulfurization of Atomic Layer Deposition Ru Thin Film***,* ***Jaehyoek Kim,*** Yonsei University, Korea*; N. Tatsuya,* TANAKA Kikinzoku Kogyo K.K, Japan*; D. Kim,* Samsung Advanced Institute of Technology, Republic of Korea*; K. Yohei,* TANAKA Kikinzoku Kogyo K.K, Japan*; S. Chung,* Yonsei University, Korea*; S. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; H. Kim,* Yonsei University, Korea

Near Infrared (IR) photodetectors are essential for many emerging applications in machine vision, health imaging, consumer electronics, and optical communications. Especially spectral responses of the photodetector at 940 nm are required for daylight applications due to the low interference intensity of the sunlight near that wavelength. Compound semiconductor materials have been mainly used in NIR photodetectors, but the exploration of novel semiconductor materials for excellent performance and effective fabrication processes continues to date.

Among the various emerging materials, the pyrite group semiconductors are promising candidates for optoelectronics. It belongs to the transition metal dichalcogenides (TMDs) family, and due to high absorption coefficient, extensive research on photovoltaic applications is being carried out to explore. In the case of Ru chalcogenides, RuS_2 is n-type semiconductor with suitable bandgap (0.8~1.4 eV) for NIR wavelength ranges and was identified as an optical and photoelectrode material with excellent environmental resistance and long lifespan. However, NIR photodetector studies based on RuS_2 to fabricate devices and measure photocurrent has not been conducted due to the difficulty of the RuS_2 thin film synthesis method.

In this report, RuS_2 film was synthesized based on Ru thin film deposition using atomic layer deposition (ALD) and post sulfurization process. Compared to sputtered Ru film, ALD of Ru film can be expected to improve the electrical and optical properties because ALD process provides uniform surface control and accurate thickness due to layer-by-layer deposition. Ru thin films with a thickness of 2, 4, and 6 nm were produced through ALD cycle control and post sulfurization were performed,and it was confirmed that 4 nm was optimized for RuS_2. After that, the RuS_2 characteristics of ALD Ru and Sputtered Ru were compared through several analyses such as XRD and XPS. The results suggest that the surface morphology of Ru thin film was important during sulfurization process, indicating that ALD Ru was excellent. We also fabricated RuS_2 photodetector with interdigitated comb-structured electrodes and measured at 940 nm NIR light. In this work, RuS_2 is proposed as a candidate material for the NIR photodetector and was the first to fabricate RuS_2 photodetector.

3:15pm **AA1-WeA-8 Spatial Atomic Layer Deposition: A New Revolution in Ultra-Fast Production of Conformal and High-Quality Optical Coatings***,* ***John Rönn****, P. Maydannik, S. Virtanen, K. Niiranen, S. Sneck,* Beneq, Finland

Since its invention 50 years ago, atomic layer deposition (ALD) has shown tremendous performance in depositing thin film structures for various applications in physical, chemical, biological, and medical sciences. Due to the unique layer-by-layer growth mechanism of ALD, thin films with exceptional uniformity, conformality and quality can be deposited not only on planar substrates, but also on the most complicated surfaces. Despite its superior advantages, traditional ALD, or temporal ALD, suffers from relatively low deposition rates (20-50 nm/h), which has greatly limited ALD's application in many systems where thin films with thicknesses of several hundreds or even microns are required. Such examples are often found in optical coatings that are widely used in our everyday lives in the form of self-driving cars, augmented reality goggles or mobile phones, to name a few.

In this work, we present our latest achievements with the novel C2R spatial plasma-enhanced rotary ALD system. The results include ultra-fast production of SiO_2, Ta_2O_5 TiO_2, HfO_2 and Al_2O_3 with deposition rates reaching up to 2 µm/h. In addition, we show that the deposition of these films can be controlled in such a way that no coating induced stress is obtained on the substrate, ultimately allowing extremely thick layer configurations to be deposited for optical applications. Finally, we show that these films exhibit low optical losses which make them very advantageous for novel optical applications where conformal, thick, and low-loss coatings are highly desirable.

ALD Applications
Room Hall 3D - Session AA2-WeA

Emerging: Optics/Optoelectronics

Moderators: Tero Pilvi, Picosun Oy, **Tania Sandoval**, Technical University Federico Santa Maria

4:00pm **AA2-WeA-11 Deposition and Characterization of Electro-Optic ALD K(Ta_x,Nb_{1-x})O_3 Films for Photonics***,* ***Eric Martin,*** Ohio State University*; J. Bickford,* Army Research Laboratory*; H. Sønsteby,* University of Oslo, Norway*; R. Hoffman,* Army Research Laboratory*; R. Reano,* Ohio State University

Electrooptic (EO) materials are critical for optics and photonics, enabling fast and dynamic control propagating light.In particular K(Ta_x,Nb_{1-x})O_3 (KTN) stands as a unique EO material in that it possesses an extremely high quadratic (Kerr) EO coefficient. KTN is a solid solution of $KTaO_3$ and $KNbO_3$ perovskites with a Curie temperature (T_c) that is defined by the Ta:Nb ratio.Bulk KTN crystals have shown record high Kerr nonlinearity of greater than 2.2 x 10^{-14} m^2/V^2 when thermally tuned near T_c.However, difficultly in fabrication of KTN crystals greater than $1cm^2$ in area has limited applications to small varifocal lens and beam deflectors.Recent advancements in ALD of KTN utilizing alkoxide precursors and O_3 as the oxidant has shown precise composition control and excellent crystallinity on both $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$ (LSAT) and $MgAl_2O_4$ (MAO) substrates.ALD KTN films open exciting new possibilities for both bulk and integrated optical building blocks, including tunable filters, reflectors, modulators, phase shifters, and grating emitters.In this work, we investigate the deposition of crystalline KTN on a variety of substrates including LSAT, MAO, MgO, and Si. Our approach encompasses several facets. We begin by depositing KTN thin films using alkoxide precursors and O_3 as the oxidant. The deposited films are characterized for their optical properties using spectroscopic ellipsometry. We determine the crystallinity of the films through x-ray diffraction (XRD) and evaluate the composition via x-ray fluorescence (XRF). We further probe the dielectric response of the films and determine T_c the through capacitance measurements. This includes utilizing interdigitated capacitors (IDCs) and metal-oxide-semiconductor (MOS) capacitors for precise temperature-dependent characterization. Additionally, we investigate the EO properties of KTN films as a function of temperature and composition. This is achieved using specialized silicon Photonic Integrated Circuit (PIC) test chips, comprised of a Mach-Zehnder interferometer trenched for KTN deposition with an integrated photodetector. For the first time, we report the optical, dielectric, and electrooptic properties of ALD KTN thin films.

4:15pm **AA2-WeA-12 Advances in Plasma-based Atomic Layer Processing of AlF_3 for the Passivation of FUV Mirrors**, ***Virginia Wheeler****, M. Sales, D. Boris,* Naval Research Laboratory*; L. Rodriguez de Marcos,* Catholic University of America and NASA Goddard Space Flight Center*; J. del Hoyo,* NASA Goddard Space Flight Center*; A. Lang, S. Walton,* Naval Research Laboratory*; E. Wollack, M. Quijada,* NASA Goddard Space Flight Center

Efficient ultraviolet mirrors are essential components for UV astronomy. While aluminum mirrors with stable and reliable fluoride-based passivation layers are commonly used, the optical performance is still insufficient for systems where several reflections are required. We previously demonstrated the feasibility of a new, room temperature plasma process based on a benign SF_6 electron beam (e-beam)-generated plasma to simultaneously remove the native oxide and form an AlF_3 layer with tunable thickness [1]. This produces Al-mirrors with high FUV reflectivity ($R\approx90\%$ at λ=121nm) and improved durability. Plasma-enhanced atomic layer deposition (PEALD) is a known low temperature, highly conformal coating process which has previously been shown to produce AlF_3 films [2], though little has been reported on their performance in FUV applications. In this work, we focus on optimizing a PEALD AlF_3 process using a remote ICP plasma and developing a new hybrid approach combining the e-beam-generated plasma and ICP processes. We will provide a detailed analysis of AlF_3 film materials properties and FUV optical performance produced by each approach individually and combined.

PEALD AlF_3 films were deposited using trimethylaluminum and SF_6 plasma precursors in a Veeco Fiji G2 reactor custom fitted with an on-axis cylindrical e-beam-generated plasma to replicate the self-fluorination process directly on an ALD reactor. ALD windows were optimized using *in situ* ellipsometery directly on Al substrates and supplemented with post-deposition x-ray photoelectron spectroscopy, atomic force microscopy, transmission electron microscopy and FUV measurements to elucidate process-structure-property relationships. Plasma diagnostics, including optical emission spectroscopy and Langmuir probe measurements, were also conducted on the reactor to correlate ion fluence and ion energy to resulting film properties. PEALD AlF_3 films with F/Al ratios of 2.92-2.97, < 2 at% oxygen, and surface roughness similar to starting Al-mirrors were attained at lower plasma power (100W), high SF_6/Ar ratios (≥ 0.5) and gas flows (> 30sccm). However, the FUV properties of these films are still inhibited by the native oxide interface that cannot be adequately treated with remote ICP plasma alone. Initial films combining an *in situ* e-beam-generated plasma for fluorine passivation of the Al mirror interface with the optimum PEALD produced better FUV performance in the 100-190 nm region. Full detailed characterization of this hybrid approach will be discussed.

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4:30pm **AA2-WeA-13 Plasma-Enhanced Atomic Layer Deposition with RF Substrate Biasing to Tune the Performance of Superconducting Nanowire Single-Photon Detectors in the Mid-Infrared**, ***Ciaran Lennon,*** Oxford Instruments Plasma Technology, University of Glasgow, UK*; D. Morozov,* University of Glasgow, UK*; Y. Shu,* Oxford Instruments Plasma Technology, UK*; H. Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands*; K. Hore,* Oxford Instruments Plasma Technology, UK*; R. Hadfield,* University of Glasgow, UK

Superconducting nanowire single-photon detectors (SNSPDs) offer field-leading time-correlated single photon detection in the infrared, with ultrafast timing jitter, near-unity internal detection efficiency and low dark count rates [1]. Extending the performance in the mid-infrared has been a focus in the field, potentially expanding the range of SNSPD applications in areas like exoplanet spectroscopy and LIDAR [2,3].

Previous work on mid-infrared SNSPDs has focused on amorphous superconducting materials (WSi) owing to their lower superconducting energy gap (Δ), demonstrating saturated internal detection efficiency up to 29 µm [4,5]. However, amorphous materials have lower T_c, requiring device operation at < 2K with bulky, energy-intensive cryocoolers. Crystalline metal nitrides, like NbN and NbTiN, are a promising alternative, with T_c > 10 K, enabling device operation at > 2 K, although with higher Δ. Lowering Δ has been shown to increase the detection efficiency in the mid-infrared [5]; therefore, tuning Δ for NbN and NbTiN could be a promising approach.

Controlling the ion energy in the plasma-enhanced atomic layer deposition (PEALD) process using RF substrate biasing can influence various material properties such as crystallinity, composition and stress [6]. Recent work has also shown that the superconducting properties of metal nitride thin films can be tuned using RF substrate biasing [7,8], as well as enhancing the uniformity, making it an ideal technique for the development of large-area SNSPD arrays. Consequently, we have used PEALD with RF substrate biasing to develop NbN and NbTiN thin films tuned for mid-infrared SNSPDs. We report on the electrical and superconducting properties of the ultrathin films and discuss the fabrication, electrical transport properties and optical testing of fabricated SNSPDs, with their performance benchmarked from 1.5-4 µm.

Overall, this study highlights the potential of PEALD with RF substrate biasing for developing NbN and NbTiN thin films for SNSPDs tuned for mid-infrared photon counting applications, with scope to develop large-area SNSPD arrays.

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ALD Applications
Room Hall 3E - Session AA3-WeA

Display Applications

Moderator: Marianna Kemell, University of Helsinki

4:00pm **AA3-WeA-11 Atomic Layer Deposition for Stable On-Chip Quantum Dot LEDs: Hybrid Quantum Dot Pockets**, ***Robin Petit****, R. Özdemir, H. Van Avermaet, J. Kuhs, A. Werbrouck, J. Dendooven, Z. Hens, P. Smet, C. Detavernier,* Ghent University, Belgium

The latest advancements in displays include micro-LEDs with chip sizes < 100 µm that are used as subpixels. To avoid color filters and bulky layers with separate color converter devices, the color converter is preferably deposited on-chip.

Their narrow emission spectrum and size-tunability make quantum dots (QDs) attractive as color converters in displays. The best alternative to Cd-based QDs are InP-based QDs, owing to their ability to emit the full spectrum of colors, their structural integrity and low toxicity[1]. However, non-radiative pathways from defect-related traps or interactions with the environment (H_2O, O_2) can be detrimental to the luminescence efficiency.

State-of-the-art hybrid barriers are explored to safeguard the QD luminescence. Metal oxides grown by atomic layer deposition (ALD) have shown potential when paired with organic layers, such as those deposited by molecular layer deposition[2]. The defect-free nature and conformality of the coatings is unique to ALD, making it an ideal technique for barrier applications.

This study investigates ALD for stable on-chip QD LEDs as follows: **(a) Understanding the optical response** of core/multi-shell InP/ZnSe/Zn(Se,S)/ZnS QDs to precursors (TMA, TDMAT, DEZ), reactants (H_2O, O_3), plasmas (Ar, H_2, O_2) and full ALD processes (Al_2O_3, TiO_2, ZnO) using a home-built in situ photoluminescence setup[3]. Results show that the QDs are highly susceptible to degradation during the ALD process (Fig. 1). **(b) Characterizing ALD growth** (Al_2O_3) **on polymer substrates** (Kraton) by spectroscopic ellipsometry and Fourier transform infrared spectroscopy. Island growth is identified as the dominant growth mode and is linked to the copolymeric structure of Kraton (Fig. 2). It is observed the stability of the QDs during ALD is vastly improved by polymer embedding. **(c) Fabrication of pick-and-place, hybrid QD pockets** using a digital light processing setup as a demonstrator for on-chip QD LEDs (Fig. 3)[4]. By combining the on-chip design of the QD pockets and seamless encapsulation of the QDs by a polymer (thiol:ene) with the barrier performance of ALD coatings, this work aims to contribute to the development of stable QD LEDs for displays. **(d) Examining the long-term stability** of (ALD coated) pristine QDs, polymer-embedded QDs, and QD pockets through accelerated aging tests using a humidity chamber. The hybrid QD pockets show superior stability demonstrating their potential for QD LEDs.

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4:15pm **AA3-WeA-12 A Comparative Study on Cation distribution effects in Heterogeneous channel IGZO TFTs via Atomic Layer Deposition Supercycle Design**, ***Hye-Jin Oh***, *H. Kim,* Hanyang University, Korea*; C. Park,* Hanyang University, Republic of Korea*; J. Park,* Hanyang University, Korea

Oxide semiconductors (OSs), known for their high mobility, large-area uniformity, low temperature processability, low off current, are garnering interest in display applications.[1] To apply in various fields, it is essential to enhance the electrical properties of OS thin-film transistors (TFTs). Atomic layer deposition (ALD) a-IGZO has been reported to exhibit improved electrical properties due to increased packing density compared to the conventional sputtering method.[2] Sputtering uses a target mixed with each element to form a homogeneous thin film, but supercycle-based ALD forms a relatively heterogeneous thin film. In this regard, it is crucial to consider the cation distribution resulting from the ALD supercycle configuration in multicomponent OSs.

In this study, we aimed to compare surface and bulk compositions based on cation distributions by reversing the supercycle sequence of the indium (In), gallium (Ga), zinc (Zn) elements in IGZO: **A (In (14) -Ga (3) -In (14) -Zn (4))**, **A'(Zn (4) -In (14) -Ga (3) -In (14))**. As a result, the surface composition (XPS) of channels A and A' was significantly higher for the element located in the last order of the supercycle sequence (A: Zn-rich surface, A': In-rich surface). However, the XRF analysis indicated a similar bulk composition for A and A', and notable distinctions in physical properties were not evident. Despite considerable differences in surface composition between A and A', the TFT electrical properties did not show substantial variation, but there was a significant distinction in reliability. The outcomes suggest that the bulk composition has a more pronounced influence on the electrical properties of the TFTs, and the composition ratio at the surface acting as the back channel has a significant impact on stability. The A' TFT, with an In-rich surface, experiences a hump phenomenon caused by the formation of a parasitic channel on the back channel, leading to performance degradation. Our research proposes that the cation distribution in ALD-based multicomponent heterogeneous channel TFTs can affect the electrical properties and reliability results, depending on the device structure.

References

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4:30pm **AA3-WeA-13 Characteristics of PEALD IGZO Films Using Tetrahydrofuran-Adducted In & Ga Precursors**, *S. Lee, S. Jeon, S. Lee, Y. Kwone, Y. Im, T. Byun,* ***Sungchul Kim,*** DNF Co. Ltd., Republic of Korea

As the down-scaling of semiconductor materials, silicon compatible emerging materials have extensively researched for next generation display and 3D structured devices. In particular, oxide semiconductors are considered a promising candidate for backplane applications in display. Among them, indium-gallium-zinc oxide (IGZO) using plasma enhanced atomic layer deposition (PEALD) has excellent properties, like high mobility, low leakage current, high transparency and low temperature processability. However, conventional precursors for IGZO still have some problems to solve such as low deposition rate, low thermal stability and high price.

In this study, we developed indium precursor (Trimethylindium Tetrahydrofuran, DIP-4) and gallium precursor (Trimethylgallium Tetrahydrofuran, DGP-2) to overcome the shortcomings of the conventional In & Ga precursors. ALD characteristics of the films deposited using the newly developed the precursors were confirmed through the source feeding time saturation and linearity. Furthermore, the incubation time of In, Ga and Zn oxide films according to the different bottom layer was respectively verified and calculated using the developed DIP-4, DGP-2 and commercially used DEZn. In order form a multilayer IGZO thin film, application of the incubation factors at IGZO process were experimentally demonstrated. Thickness of the IGZO films can be easily controlled through modulation of the incubation factors. The physical and chemical properties of the films were analyzed by X-ray diffraction, X-ray reflectrometer, X-ray photoelectron spectroscopy, transmission electron microscope.

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