ALD Applications
Room On Demand - Session AA1
Energy: Catalysis and Fuel Cells

AA1-1 High-crystalline RuO_2based on Atomic Layer Deposition for Oxygen Evolution Catalyst*, Jaehyeok Kim*, *D. Kim, J. Park, H. Kim,* Yonsei University, Korea

To alternate carbon-based energy source to protect the nature, hydrogen is widely researched worldwide. Electrochemical water splitting is the promising method that produces no pollutant, only $H_2$and O_2. However, Oxygen Evolution Reaction (OER) is sluggish, which determines the overall efficiency of electrocatalyst, so that water splitting is limited in industrial field.

RuO_2has been researched as efficient catalyst for oxygen evolution. The crystallinity of the RuO_2affects the efficiency. Therefore, synthesis of high-crystalline $RuO_2$is important. To enhance the efficiency of RuO_2, large surface-to-volume ratio and controllability of the crystallinity are the key factors in synthesis method.

Atomic Layer Deposition (ALD) has advantages of excellent conformality, large-area uniformity, and precise controllability of the thickness. For efficient catalyst, large surface area is helpful because it is directly related to the reaction sites. ALD is suitable fabrication process for electrocatalyst.

In this report, RuO_2film was synthesized based on ALD on Carbon Fiber Paper (CFP) at different growth temperature, which has large surface-to-volume ratio with high conductivity. It can be directly used for OER catalyst with enlarged active sites of OER. For the analysis, material properties of ALD RuO_2 such as X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, SiO_2substrate was prepared as reference. Electrochemical properties was measured in 3-electrode system consists of working electrode, reference electrode, and counter electrode. It showed low overpotential and Tafel slope, which imposes promising candidate for OER catalyst.

References

[1]Ya Yan, Bao Yu Xi, Bin Zhao, and Xin Wang, “A review on noble-metal-free bifunctional heterogeneous catalysts for overall electrochemical water splitting,” J. Mater. Chem. A, 2016, 4, 17587–17603, DOI: 10.1039/c6ta08075h

[2] Kelsey A. Stoerzinger, Liang Qiao, Michael D. Biegalsk, and Yang Shao-Horn “Orientation-Dependent Oxygen Evolution Activities of Rutile $IrO_2$and RuO_2, ,” J. Phys. Chem. Lett. 2014, 5, 1636−1641

doi: 10.1021/jz500610u

AA1-2 Atomic Layer Deposition of Pt@Pd Core-Shell Structure Electrocatalyst for Carbon Dioxide Reduction*, Ming Li,* Delft University of Technology, China*; R. Kortlever, R. van Ommen,* Delft University of Technology, Netherlands

Using electrocatalysts to convert CO_2 into chemicals or fuels through electrochemical reactions is an attractive approach to reduce CO2 emissions and decrease the greenhouse effect. However, existing electrocatalysts have several technological limitations, such as low selectivity, poor stability, low conversion rates of the feedstock, and high overpotential which will lead to energy losses. Most of the electrocatalyst improvement strategies focus on catalyst structure and composition optimization such as nanostructuring, doping and alloying, etc. However, the widely used catalyst fabrication methods, like impregnation, colloidal, ion-exchange methods are tough to tailor the morphology of the catalyst down to the atomic scale, let alone other delicate structures like nano-sized core-shell particles. One promising solution is to use the atomic layer deposition method to fabricate electrocatalysts with well-defined nanostructure. It is reported that Pd-Pt bimetallic catalyst can reduce CO_2 toward formic acid and achieve a high faradic efficiency at room temperature and atmospheric pressure. We investigate whether the performance of this catalyst could be further improved by tuning the nanostructure of the catalyst with ALD. We studied how to use fluidized bed ALD to synthesize core-shell structure bimetallic electrocatalysts, and synthesized the Pd-Pt bimetallic catalyst with core-shell structure on carbon black substrate in this work. The metal loading of the catalyst is precisely controlled. TEM, XPS, XRD, SEM, and ICP-OES were used to characterize the catalyst structure and metal loading. Electrochemical measurements were carried out in a custom-made H-cell using a three-electrode assembly at room temperature. This gives us a better understanding of the effect of the catalyst structure on carbon dioxide reduction, helping us to come to an optimized structure and the corresponding ALD strategy to make it.

AA1-3 Understanding Metal-Support Interactions in Model Pd/ALD-Al_2O_3/SiO_2 Catalysts*, Arun Asundi*, *E. Goodman,* Stanford University*; A. Hoffman,* SLAC National Accelerator Laboratory*; K. Bustillo,* Lawrence Berkeley Lab, University of California, Berkeley*; J. Stebbins,* Stanford University*; S. Bare,* SLAC National Accelerator Laboratory*; S. Bent, M. Cargnello,* Stanford University

The synergy between coexisting metal and metal oxide phases is critical in determining the reactivity of many supported heterogeneous catalysts. The interaction between the active metal and the support is one example of this synergy and can be controlled to modulate catalyst performance. ALD offers a unique opportunity to study metal-support interactions by enabling support modification one atomic layer at a time. Metal-support interactions are readily apparent in Pd methane combustion catalysts, where support properties can affect reaction rate by several orders of magnitude. Previous work has shown that the methane combustion rate is significantly higher for Pd/Al_2O_3 than Pd/SiO_2, but the nature of the metal-support interaction that determines this reaction rate is not well-understood. In this work, we study the effects of support chemical properties and morphology on the methane combustion reactivity of Pd supported on ALD Al_2O_3-modified SiO_2.

Catalysts were prepared through a combined ALD and colloidal synthesis method. Uniform SiO_2 nanospheres were modified with different thicknesses of Al_2O_3 films deposited by ALD. Colloidal Pd nanocrystals were then deposited on the ALD-Al-$_{2}$O$_{3--}$/SiO_2 supports. This synthesis method enabled independent control over the Pd nanocrystal size, Pd loading, and chemical nature of the support. The transition of the support properties from SiO_2 to Al_2O_3 results in two regimes of improved reactivity as a function of Al_2O_3 ALD cycle number: the reaction rate increases rapidly at low Al_2O_3 coverage and increases gradually at high Al_2O_3 loading. The two stages of promotion show that both surface and bulk properties of Al_2O_3 are important factors in controlling the reaction rate. At sub-monolayer alumina coverage, the reaction rate is determined by the number of Pd/Al interface sites. Through infrared spectroscopy we show that a monolayer of Al_2O_3 is deposited during the first three ALD cycles, leading to a linear increase in reaction rate as a function of ALD cycle number as the support surface transitions from SiO_2 to Al_2O_3. At high Al_2O_3 loadings, bulk properties of Al_2O_3 such as purity and crystallinity also affect reaction rate. ^{27}Al nuclear magnetic resonance spectroscopy reveals intermixing between Si and Al and crystallization of the Al_2O_3 for sufficiently thick coatings, both of which modulate the methane combustion rate. This work demonstrates the many support characteristics that influence catalyst reactivity through metal-support interactions. The controlled ALD-colloidal synthesis method used in this work can be applied to fundamental studies of metal-metal oxide interactions in many catalyst systems.

AA1-4 Size Control of Gold Nanoparticles Using Sequential Atomic Layer Deposition of Gold and Titanium Dioxide*, Saeed Saedy*, *R. Baaijens,* Delft University of Technology, Netherlands*; E. Goodwin, M. Griffiths, S. T. Barry,* Carleton University, Canada*; J. van Ommen,* Delft University of Technology, Netherlands

Gold nanoparticles (AuNPs) supported on metal oxides exhibit exceptional catalytic activities in several processes, especially oxidation reactions. The performance of AuNPs strongly depends on size. Large gold particles do not show notable catalytic activity; the lack of efficient synthesis and stabilization methods of AuNPs resulted in gold being considered a catalytically inactive metal for decades. Additionally, due to weak interaction with the supports, the supported GNPs usually are not stable enough and tend to agglomerate, again resulting in activity loss.

This strong dependency of catalytic activity imposes a significant obstacle in developing supported AuNPs as catalysts, especially when the AuNPs with an average size smaller than 5 nm are desired. This challenge becomes more significant when the preparation of large amounts of supported AuNPs is the final goal, which is the prerequisite of practical applications. For such applications, the supported AuNP synthesis method needs to be capable of controlling the AuNPs size, scaling to large-scale production, and reproducibility. The conventional AuNP syntheses are a variety of liquid phase methods, which have been widely studied for decades; however, they still suffer from poor size control, contamination of the final product with residual solvents/co-reactants, reproducibility issues, and high sensitivity to operating conditions.

Atomic layer deposition (ALD) has proven successful for the synthesis of supported metal NPs for various applications, especially as catalysts. ALD makes it possible to synthesize supported NPs with controlled size, shape, and morphology. Recently we reported ALD synthesis of supported AuNPs on TiO-$_2$ in a fluidized bed reactor, with the minimum average particle size of 4 nm. In this work, we report a modification to our previous synthesis, enabling us to attain Au/TiO$_2$ with an average particle size of 2.8 nm. In this method, a sequential ALD of metallic gold (using trimethylphosphinotrimethylgold(III)), TiO$_2$ (using isopropoxytitanium (IV)), and ozone (as an oxidizer) at 105°C were used to confine the ALD deposited AuNPs with a TiO$_2$ over-coat. Different TiO$_2$:Au pulse ratios from 1 to 4 were used. An analysis by inductively coupled plasma optical emission spectrometry of the resulting samples showed a gold loading of about 0.8% in samples. Transmission electron micrographs indicated a decrease of AuNP average size from 3.7 nm to 2.8 nm. Interestingly, the particle size distribution became narrower with increasing the TiO$_2$:Au pulse ratio. The standard deviation of AuNP size decreased from 1.4 nm to 0.8 nm.

AA1-7 Atomic Layer Deposition for Improved Biomass Conversion Catalysts, ***Wilson McNeary***, *S. Tacey, G. Lahti, D. Conklin,* National Renewable Energy Laboratory; *K. Unocic,* Oak Ridge Natinal Laboratory; *E. Tan,* National Renewable Energy Laboratory; *E. Wegener,* Argonne National Laboratory; *T. Eralp Erden,* Johnson Matthey, UK; *S. Moulton, C. Gump, J. Burger,* Forge Nano; *M. Griffin, C. Farberow,* National Renewable Energy Laboratory; *M. Watson, L. Tuxworth,* Johnson Matthey, UK; *K. van Allsburg,* National Renewable Energy Laboratory; *A. Dameron, K. Buechler,* Forge Nano; *D. Vardon,* National Renewable Energy Laboratory

Heterogeneous catalysts are a key enabler of the transition towards a sustainable, bio-based economy for fuels and chemicals. However, the harsh conditions in many biomass conversion processes lead to nanoparticle sintering, support collapse, and metal leaching in conventional PGM catalysts. Next-generation catalysts must be developed to address these stability challenges. This presentation will discuss ongoing work between the Catalytic Carbon Transformation and Scale-Up Center at NREL and various industrial partners to develop scalable and cost-effective atomic layer deposition (ALD) coatings for improving the performance of biomass conversion catalysts.

The substantial focus will be devoted to the benefits of TiO$_2$ ALD coatings on supported Pd hydrogenation catalysts. Ten cycles of TiO$_2$ ALD were found to dramatically improve the activity of a conventional Pd/Al$_2$O$_3$ catalyst towards aromatic hydrogenation, despite partial coverage of the Pd sites by the ALD layer. Subsequent advanced characterization and atomic-scale computational modeling revealed that the ALD coating weakened the adsorption strength of hydrogenation surface intermediates, leading to higher reaction rates. Reaction testing after exposure to sulfur impurities, high temperature oxidation, and hydrothermal treatment demonstrated the improved stability of the ALD-coated catalyst. Additionally, the ALD synthesis process was found to be scalable over two orders of magnitude with minimal deviation in synthesized catalyst properties. These results were contextualized with cost models of industrial ALD coating and aromatic hydrogenation processes to further refine the value proposition of ALD coatings. Given the demonstrated improvements in hydrogenation, TiO$_2$ ALD coatings have also been applied to supported Pt catalysts for use in other biomass conversion reactions, such as hydrodeoxygenation for the production of sustainable aviation fuel (SAF) and the oxidation of glucose to bio-derived gluconic acid. Recent findings from these experimental campaigns will also be shared. ALD technology holds great potential in the development of next-generation catalysts for biofuels and bioproducts, and this work constitutes an important examination of the impact of ALD coatings in a variety of reaction environments.

AA1-10 Electrochemical Activation of Atomic Layer Deposited Cobalt Phosphate Electrocatalysts for Water Oxidation, ***Gerben van Straaten***, *R. Zhang, V. DiPalma,* Eindhoven University of Technology, Netherlands; *G. Zafeiropoulos,* Dutch Institute For Fundamental Energy Research, Netherlands; *E. Kessels,* Eindhoven University of Technology, Netherlands; *R. van de Sanden, M. Tsampas,* Dutch Institute For Fundamental Energy Research, Netherlands; *A. Creatore,* Eindhoven University of Technology, Netherlands

Storage of electricity into chemicals is the most viable answer to the intermittency of renewable sources and the most investigated example this is water splitting. For the O$_2$ evolution half reaction (OER), cobalt phosphate-based electrocatalysts (CoPi) are interesting as they are made of earth-abundant elements and their catalytic activity scales with film thickness. In parallel with others[1], we have demonstrated synthesis of amorphous CoPi films by ALD [2]. CoPi is prepared by combining ALD of CoO$_x$ from cobaltocene (CoCp$_2$) and O$_2$ plasma, with cycles of TMP ((CH$_3$O)$_3$PO) and O$_2$ plasma, according to an ABCD recipe scheme [2,3]. We have also shown that tuning the Co-to-P ratio, by combining this recipe with extra cycles of CoO$_x$, enhances the OER performance [3], beyond that achieved by traditional electro-deposited films.

In the present contribution we focus on the mechanism behind the enhancement of the catalytic activity of CoPi when tuning the Co-to-P ratio. We show that ALD CoPi thin films undergo activation with increasing number of cyclic voltammetry (CV) cycles. During this activation process, the current density increases in parallel with a progressive leaching of phosphorous out of the electrocatalyst and the shift of the oxidation state of Co from Co^{2+} to a mixture of Co^{2+} and Co^{3+} [4]. This induce structural changes in the electrocatalyst: CV combined with Rutherford backscattering indicate that after activation, for the best performing CoPi film, as much as 22% of all Co atoms become accessible to the electrolyte. Measurements of the electrochemical surface area (ECSA) reveal that during activation, the ECSA of this film increases by a factor 30. However, this increase in ECSA is strongly dependent on the initial composition of the CoPi films. While the aforementioned increase holds for CoPi films with a Co-to-P ratio of 1.6, for films with a Co-to-P ratio of 1.9 the ECSA only increases by a factor 3.6. We find that for all investigated Co-to-P ratios, after activation the electrochemical activity scales linearly with ECSA. Thus, the initial composition affects the activity of the catalyst indirectly by guiding the restructuring of the catalyst during potential cycling and the ECSA is a critical parameter in determining the activity of CoPi-based and related electrocatalysts. Thus, next to the well-established control over film properties ALD of CoPi enables to disclose the mechanisms behind its electrochemical activation.

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

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

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

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

ALD Applications
Room On Demand - Session AA10
Memory Applications: RRAM & Neuromorphic, MIM Capacitors

AA10-1 Li-Nb-O Family Deposited by Atomic Layer Deposition (ALD) for Artificial Neuron and Synapse, ***Hyun Seung Choi***, *H. Kim, S. Park, T. Park,* Hanyang University, Korea (Republic of)

Neuromorphic computing, consisting of artificial neurons and synapses, is one of the most promising candidates to resolve the von-Neumann bottleneck because of its in-memory-computing attributes, high efficiency, and parallel signal processing. Recently, artificial neurons and synapses have been studies using the variety of materials to improving device properties. The lithium niobium oxide (Li-Nb-O) family have many desirable multifunctional properties including memory, TS behavior, ferroelectric effect, etc. [1-2] Among these properties, niobium oxide (NbO$_2$) is well known as metal-insulator-transition selector, and lithium niobate (LiNbO$_x$) as memristor. [3] Especially, lithium niobate can represent superior characteristics due to small ion size of lithium (Li) ion enabling low energy consumption, high mobility, and high endurance. Despite the potential for new and enhanced functional devices and materials, this Li-Nb-O multifunctional family remains relatively unexplored due to the difficulty of precise composition control.

In this study, niobium oxide and lithium niobate deposited by Atomic Layer Deposition (ALD) are proposed for artificial neuron and synapse. Controllable memory and TS behaviors are confirmed by adjusting the composition of Li-Nb-O compound. Niobium oxide represented the volatile property as reported, and lithium niobate showed analog switching memory applicable to artificial synapse. Especially, by understanding the effect of Li-ion concentration on synaptic properties such as potentiation/depression, an optimal composition of lithium niobate is achieved. Consequently, our work can provide an easy yet effective way to construct functional neuromorphic devices by using similar materials in same family.

References [1] IEDM (2013) 268–271 [2] APL Mater. 7, 071103 (2019) [3] Nanotechnology 2020, 31(23):235203

AA10-2 Li Compound-Based Two-Terminal Artificial Synaptic Devices via Atomic Layer Deposition*, **Hye Rim Kim**, H. Choi, S. Park,* Hanyang University, Korea (Republic of)*; G. Kim ,* Korea Research Institute of Chemical Technology (KRICT), Korea (Republic of)*; T. Park,* Hanyang University, Korea (Republic of)

Brain-inspired neuromorphic computing is considered a novel computing paradigm that mimics the human brain, capable of parallel data processing and low power consumption. [1] Memristor devices are potential candidates as a synaptic component for neuromorphic computing especially towards spiking neural networks (SNN) due to their inherent nature. [2] Lithium titanate ($Li_4Ti_5O_{12}$, LTO) as a proposed anode material of lithium (Li) ion batteries, is a zero-strain material capable of reversible Li ion migration. Also, the feasibility of synaptic characteristics in lithium titanate based device has been confirmed through the metallic and insulating phase separation by an electric field. [3] The behavior of Li ions, a key component of synaptic properties, is highly dependent on the Li concentrations inside the LTO active layer [4], but related studies are still insufficient.

In this research, the lithium titanate active layers were grown through atomic layer deposition (ALD) and fine composition control was achieved using super-cycle method. Sequentially, the Li concentration-dependent resistive switching characteristics of the LTO based memristor devices were confirmed. Also, synaptic properties including potentiation and depression were confirmed by applying the identical neuronal spikes. Consequently, we derived an optimized Li concentration of the lithium titanate materials suitable for synapse devices using atomic layer deposition and pulse engineering. The detailed experimental results will be presented.

References list: [1] IEEE Nanotechnol. Mag., Sep., 36-44 (2018). [2] Nat. Commun., 9, 2514 (2018). [3] Adv. Mater., 32, 1907465, 1-12 (2020). [4] Chem. Mater., 27, 1740-1750 (2015)

ALD Applications
Room On Demand - Session AA11
Memory Applications: Other Non-Volatile Memories (MRAM, FeRAM, Phase Change,...)

AA11-1 Fabrication of Vertical-Type Phase-Change Memory Leveraging Atomic Layer Deposition*, **Jeong Woo Jeon**, C. Yoo, E. Park, W. Kim, W. Choi, B. Park,* Seoul National University, Korea (Republic of)*; Y. Lee,* Jeonbuk National University, Korea (Republic of)*; C. Hwang,* Seoul National University, Korea (Republic of)

Storage Class Memory (SCM) is a new hybrid storage/memory tier to achieve high speed, low power computing using a nonvolatile and byte-accessible memory denser than DRAM and faster and more durable than flash memory.[1] Intel and Micron Technology recently commercialized the SCM using chalcogenide-based phase-change memory (PCM) that utilizes resistance contrast between the amorphous and crystalline states for data storage. It has stacked memory cell arrays that alternately share either wordlines or bitlines between the different memory layers. This structure inevitably requires lithography and patterning steps proportional to the number of layers, resulting in high production costs. For the commercial success of PCM-based SCMs, it is important to achieve high density and low cost per bit, which requires the development of a novel three-dimensional (3-D) architecture similar to the 3-D vertical-NAND device.

This report demonstrates the vertical-type PCM (V-PCM) enabled by atomic layer deposition (ALD) of $Ge_2Sb_2Te_5$ (GST-225), as shown in Fig. 1.[2] SiO_2 was used for interlayer dielectric (ILD) separating each memory layer, and TiN was used for the bottom electrode (BE). Fig. 1(b) shows an ALD GST-225 films conformally grown on vertically etched sidewalls, in which ILD and BE are alternately stacked. The switching region is defined by the patterned width and thickness of the BE, equivalent to the structure of a mushroom type cell vertically erected. In this work, the contact area was as high as 0.02 mm^2 due to the limited lithography capability of university scale research. The electrical characteristics of the fabricated device can be seen in Fig. 2. The SET and RESET characteristics of the V-PCM device are shown with a threshold voltage of 1.4 V and a RESET current of 4 mA, which corresponds to a RESET current density of 20 MA/cm^2. The cyclic endurance was more than 10^8 cycles, which is sufficiently high compared with the planar type PCM devices, showing the feasibility of the ultra-high density V-PCM.

References

[1] S. W. Fong *et al.*, *IEEE Trans. on Electron Devices*, **2017**, 64, 11, 4374-4385.

[2] E.-S. Park et al., Chem. Mater., **2019**, 31, 21, 8752-8763

AA11-2 Effect of Ti Scavenging Layer on Ferroelectricity of $Hf_xZr_{1-x}O_2$ Thin Films Fabricated by Atomic Layer Deposition using Hf/Zr Cocktail Precursor*, **Takashi Onaya**,* Meiji University/National Institute for Materials Science/JSPS Research Fellow, Japan*; T. Nabatame,* National Institute for Materials Science, Japan*; N. Sawamoto,* Meiji Renewable Energy Laboratory, Japan*; A. Ohi, N. Ikeda, T. Nagata,* National Institute for Materials Science, Japan*; A. Ogura,* Meiji University/Meiji Renewable Energy Laboratory, Japan

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) films have attracted a lot of attention for ferroelectric field-effect transistor (FeFET) applications. Numerous papers have reported that an annealing process at > 300°C is required to obtain the ferroelectric orthorhombic (O) phase. [1] However, an interlayer such as SiO_x between an HZO film and a Si substrate was typically formed during the fabrication process of metal-ferroelectric-semiconductor (MFS) structures and an annealing process. To understand how the fabrication process affects the interlayer formation is important because the interlayer can cause reliability problem and reduction in remanent polarization ($2P_r$). We employed a Ti layer deposited on an HZO film because Ti can scavenge oxygen from a SiO_x interlayer. [2] In this work, we studied the effect of an annealing temperature on the interlayer formation and ferroelectricity of HZO-based MFS capacitors with a Ti layer.

A 10-nm-thick HZO film was deposited on a p^+-Si substrate by atomic layer deposition at 300°C using $(Hf/Zr)[N(C_2H_5)CH_3]_4$ (Hf:Zr = 1:1) cocktail precursor and H_2O gas. Next, a 1-nm-thick Ti layer was deposited on an HZO film by DC sputtering. A 100-nm-thick TiN top-electrode was then fabricated by DC sputtering. Finally, a post-metallization annealing (PMA) was performed at 300 or 400°C for 1 min in N_2 ambient. TiN/HZO/p^+-Si capacitors were also fabricated as references.

For the MFS capacitor without a Ti layer, the SiO_x interlayer could be formed between an HZO film and a Si substrate after the PMA at 400°C while the formation of the interlayer was found to be negligible, evaluated by X-ray photoelectron spectroscopy. The 300°C-PMA-treated MFS capacitors showed almost the same capacitance (C) of 0.8 μF/cm^2 regardless of the presence of a Ti layer. After the PMA at 400°C, on the other hand, the higher C was obtained because HZO films were crystallized with the ferroelectric O phase. Moreover, the MFS capacitors with a Ti layer exhibited slightly higher C of 1.5 μF/cm^2 than that (1.3 μF/cm^2) without a Ti layer. This might be attributed to the reduction of the interfacial SiO_x layer due to the scavenging effect of a Ti layer. [2] Therefore, the higher $2P_r$ value (33 μC/cm^2) of the MFS capacitor with a Ti layer was achieved compared to that (26 μC/cm^2) without a Ti layer. Based on these results, inserting a Ti layer could be one of the pathways to improve ferroelectricity of HZO films in MFS structures.

This work was partially supported by JSPS KAKENHI (JP18J22998 and JP20H02189).

[1] T. Onaya et al, Microelectron. Eng. 215, 111013 (2019).

[2] H. Kim et al., J. Appl. Phys. 96, 3467 (2004).

AA11-3 Atomic Layer Deposition of Antiferroelectric La-Doped $Hf_{0.5}Zr_{0.5}O_2$ Thin Film and Its Electrical Behaviors*, **Yong Chan Jung**, J. Kim, S. Hwang, J. Mohan, H. Hernendez-Arriaga,* University of Texas at Dallas*; W. Maeng, K. Im,* SK hynix Inc, Korea (Republic of)*; J. Kim,* University of Texas at Dallas

Recently, the ferroelectricity and antiferroelectricity of doped Hf-based fluorite-structured ferroelectric thin films have been extensively investigated. In particular, it has been reported that La-doping for $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films can be applied to stabilize the ferroelectric orthorhombic (O) phase ($Pca2_1$) if the low doping concentration is precisely controlled.[1] On the other hand, ferroelectric-antiferroelectric transition is shown when the amount of La doping is relatively large due to its amorphizing characteristic for HfO_2,i.e. increase of crystallization temperature.[2] For the antiferroelectricity of HZO, it is known as the nonpolar tetragonal ($P4_2/nmc$) is contributed, however, it is less clear than the ferroelectric O phase.

In this study, we investigated the doping effects of La on the antiferroelectric properties of the HZO film. The HZO film as a reference was deposited on the TiN bottom electrode by atomic layer deposition (ALD) using TDMA-Hf, TDMA-Zr, and O_3 as the precursors of Hf, Zr, and oxidant, respectively. To dope the HZO film with La, $La(^iPr_fAMD)_3$ and O_3 were used as the La precursor and oxygen source, respectively. The 10-nm thick La-doped HZO film (LHZO) growth was proceeded with 6 super cycles consisting of 8 (Hf-purge-O_3-purge-Zr-purge-O_3-purge) and 1 ($La(^{i}P_{r}fAMD)_3$-purge-O_3-purge). In Figure 1, the Hf, Zr, and La concentration of the LHZO film is 48, 48, and 4 at. % as confirmed by XPS depth profiling. After the TiN top electrode was deposited on HZO and LHZO films, rapid thermal annealing was done, and metal-insulator-metal capacitors were fabricated using a Pd/Au hard mask and wet etch process.

In Figure 2(a) and 2(b), the small-signal dielectric constant of LHZO film at 0 MV/cm was increased to 69 compared to 48 of HZO film and the leakage current density of LHZO film at 1 MV/cm was approximately 2 order magnitude lower than HZO film, respectively. We suspected that the higher dielectric constant and lower leakage current is caused by tetragonal phase in the LHZO film. In Figure 3(a), the ferroelectric-antiferroelectric transition of the LHZO film was proved by the polarization-electric field curves, the remnant polarization ($2P_r$) of HZO and LHZO devices is 56 and 5 µC/cm^2, respectively. As shown in Figure 3(b), interestingly, after 10^8 and 10^9 endurance cycling, the $2P_r$ of the LHZO film is recovered to 13 and 26 µC/cm^2, respectively. It is plausible to suggest that this phenomenon is occurred due to the field-induced ferroelectric phase transition[3] or the effect of domain unpinning after longer switching cycles with high electric field (2.5 MV/cm).

This work is supported by SK hynix Inc.

AA11-4 Metal-insulator Transition in ALD VO_2 using VCl_4 and H_2O as Precursors*, **Jeya Prakash Ganesan**, D. Dev, A. Krishnaprasad,* University of Central Florida*; D. Moser, R. Kanjolia,* EMD Electronics*; T. Roy,* Nanoscience Technology Center, University of Central Florida*; P. Banerjee,* University of Central Florida

Vanadium dioxide (VO_2) undergoes a reversible transition between the semiconducting (monoclinic) and metallic (tetragonal) state at 68 °C, thus making VO_2 a perfect candidate for electrical/optical switches, thermal sensors, metamaterials, and oscillators. Atomic Layer Deposition (ALD) of VO_2 has been reported with different metalorganic and halide-based vanadium precursors. Out of these, the halide-based precursors have the advantage of a simpler chemistry, high vapor pressure and ease of delivery, little or no potential carbon residue and use of milder oxidants such as, H_2O.

In this talk, we demonstrate the ALD of VO_2 using VCl_4 and H_2O in a VEECO® FIJI Gen2 ALD system. The as-deposited films are amorphous and turn crystalline VO_2 only after a post-deposition anneal at 550 °C, 60-minute using forming gas. Raman spectroscopy is used to confirm the amorphous nature of the film pre-anneal, and its conversion to monoclinic VO_2 post-anneal. X-ray photoelectron spectroscopy suggests that the as-deposited film and the annealed film show vanadium oxides with mixed valence states on the surface and VO_2 in the bulk. Thus, despite using a V^{4+} precursor significant surface oxidation takes place during deposition to produce a multivalent oxygen-rich surface. The excess surface oxygen could result in an amorphous film. Temperature-dependent Raman spectroscopy and ellipsometric studies reveal the semiconducting to metallic transition (SMT) of annealed and crystallized VO_2 thin film. The transition temperature is recorded at 68 °C for a 30 nm film. Optical constants (*n, k*) from ellipsometry suggests that beyond 68 °C, significant free carrier absorption in the near infrared results in higher *k*. Electrical measurements performed on a fabricated device showed SMT behavior at 68 °C with a resistance high (semiconducting) : low (metallic) ratio of 66.

In conclusion, we have deposited 30 nm VO_2 via ALD using VCl_4 and H_2O at 350 °C. Contrary to a past report,[1] the VO_2 deposited in the current work is amorphous and must be annealed at 550 °C for 60 minutes in forming gas to obtain VO_2 films with SMT properties. Experimental investigations are currently underway to understand the synthesis-structure-property relationship in this promising ALD chemistry such that as-deposited, crystalline VO_2 films can be reliably obtained.

References:

1. *Coatings* **2018,** *8* (12).

ALD Applications
Room On Demand - Session AA12
Display Applications: Thin Film Transistor, Diodes, Thin Film Encapsulation for OLEDs/QDs...

AA12-1 Two-dimensional electron gas at atomic-layer-deposited ZnS/ZnO Heterostructure*, **Jae Hyun Yoon**, T. Seok,* Hanyang University, Korea (Republic of)*; Y. Liu,* Hanyang University, China*; J. Choi, S. Kim, T. Park,* Hanyang University, Korea (Republic of)*; S. Lee,* Ajou University, Korea (Republic of)

Recently, two-dimensional electron gas (2DEG) has attracted great attention due to its presence at various heteroepitaxial perovskite oxide interfaces. Typically, epitaxial LaAlO3/single-crystal SrTiO3 (LAO/STO) heterostructure shows high density of electrons (~10^13-10^14 cm^-2) confined at the oxide interface, where the density is about ~100 times higher than that of a typical semiconductor interface (~10^11-10^12 cm^-2).[1] Creation of 2DEG is conventionally defined on the basis of discontinuity in polarity linked with the difference in the charge of the atomic layers. Simply, it can be described as half an electron charge being transferred to the interface to avoid a potential divergence, 'polar catastrophe'.[2] Another mechanism is associated with the generation of oxygen vacancies (Vo) at the surface of the STO layer during LAO or Al2O3 layer deposition, acting as electron donor for the 2DEG formation. It provides an opportunity for 2DEG realization for various oxide heterostructures and fabrication processes. Recently, we reported Vo generation mechanism-based 2DEG formation process using atomic-layer-deposited (ALD) ultrathin (~10 nm) binary metal oxide heterostructure.[3] 2DEG layer can be formed at the interface of an ultrathin Al2O3/TiO2 heterostructure on standard SiO2 substrate at a low temperature

AA12-2 Three-Dimensional Multi-Stacked Field-Effect Transistor Using Two-Dimensional Electron Gas at the Interface ofAl_2O_3/ZnO Ultra-Thin Film Heterostructures*, **Ji Hyeon Choi**, T. Seok, J. Yoon,* Hanyang University, Korea*; S. Lee,* Ajou University, Korea (Republic of)*; T. Park,* Hanyang University, Korea

Two-dimensional electron gas (2DEG) has been realized with various fabrication process using diverse oxide heterostructure since epitaxial $LaAlO_3$/single-crystal $SrTiO_3$ (LAO/STO) heterostructure was reported as a typical 2DEG system, which shows high density of electrons (~10^{13}-10^{14} cm^{-2}) confined at the oxide interface. The origin of 2DEG created at the heterointerface is still controversial mainly between the discontinuity of polarity at the atomic layers, inducing electron charge reconstruction and the presence of oxygen vacancies (V_o) at the interface, widely known as electron donors. Recently, we reported V_o generation mechanism-based 2DEG formation process using atomic-layer-deposited (ALD) ultrathin (~10 nm) binary metal oxide heterostructure: amorphous Al_2O_3/polycrystalline TiO_2, whose electrical property is comparable with typical LAO/STO epitaxial 2DEG system at room temperature (sheet carrier density, n_{sh}= ~10^{14} cm^{-2}, electron mobility, μ_n= ~4 cm^{2}V^{-1}s^{-1}). To demonstrate V_o generation mechanism for 2DEG creation specifically, an *in-situ* resistance measurement was conducted to prove the presence and effect of V_o at the heterointerface. The resistance of the interface dropped significantly with the injection of trimethylaluminum (TMA) molecules, indicating that V_o were formed on the TiO_2 surface during the TMA pulse in the ALD of the Al_2O_3 film, such that they provide electron donor states to generate free electrons at the interface of the Al_2O_3/TiO_2 heterostructure, creating 2DEG. Being well-informed of this mechanism, ZnO as a different bottom material was applied for oxide heterostructure 2DEG system to improve electrical and structural property of TiO_2-based 2DEG due to its excellent intrinsic property. As expected, the Al_2O_3/ZnO heterostructure exhibited enhanced electrical properties (n_{sh}= ~10^{14} cm^{-2}, μ_n= ~15 cm^{2}V^{-1}s^{-1}), even at the lower thickness of bottom layer (~ 5 nm) and lower deposition temperature (150°C).

In this work, using ultrathin Al_2O_3/ZnO 2DEG layer as a channel, we succeeded to fabricate 2DEG field-effect transistors (FETs), achieving extremely low off-current (I_{off} ~10^{-9} A/m), high on/off current ratio (I_{on}/I_{off} > ~10^9), and low subthreshold swing (SS ~95 mV/dec.), which outperforms other oxide heterostructure-based FETs reported so far, including the previous work of TiO_2-based 2DEG system.Furthermore, due to facile film deposition with excellent thickness control of ALD, stacking 2DEG layers is possible to make three-dimensional multi-stacked 2DEG FETs, leading to great conductivity resulting from accumulated electron transport path. The detailed experimental results will be presented.

**AA12-3 Atomic Layer Deposited p-type SnO Thin Film Transistors*, Kham Niang*, *D. Gomersall,* Cambridge University, UK*; J. Parish, A. Johnson,* University of Bath, UK*; A. Flewitt,* Cambridge University, UK

In the past decade, extensive research has been carried out on p-type oxide semiconductor materials for realisation of complementary metal oxide semiconductor (CMOS) circuits. In particular, SnO is of great interest due to its disperse valence band maximum due to hybridization between O 2*p* and Sn 5*s* orbitals, allowing a relatively high hole mobility [1]. While sputtering method has been widely used for SnO, atomic layer deposition (ALD) has not been widely reported [2]. ALD is a very attractive technique due to its precision on stoichiometry arising from the self-limiting growth, its repeatability and its conformality over a large substrate area [3].

In this report, SnO thin films were deposited using a novel Sn precursor and H_2O in a cross-flow wafer scale ALD reactor. The precursor bottle was heated at 100°C and depositions were carried out at temperatures between 170 and 210°C. To achieve high quality films suitable for channel layers in thin film transistors (TFTs), we investigated three deposition modes: single pulse (SP), multiple pulses (MP) and multiple pulses and exposure (MP+E). The SP mode is the standard ALD process comprising of the Sn and H_2O half cycles. The pulse/purge times of 1s/15s and 0.03s/10s are used for the Sn and H_2O cycles respectively. In the MP mode, three consecutive Sn pulses are applied with 5 s delay between the pulses which is then followed by the H_2O half cycle. The MP+E mode is a combination of the MP mode and stopping of the gas flow for 10s to increase the residence time in the chamber.

P-type SnO thin films were then incorporated as a channel layer in TFTs. A field effect mobilities of 0.5 and 2.5 $cm^2V^{-1}s^{-1}$ were achieved for TFTs annealed at 250°C and 350°C respectively. We will discuss in detail the effect of different ALD deposition modes on the characteristic of the thin films and the performance of the TFTs.

[1] J. A. Caraveo-Frescas, P. K. Nayak, H. A. Al-Jawhari, D. B. Granato, U. Schwingenschlogl, and H. N. Alshareef, *ACS Nano,* vol. 7, no. 6, pp. 5160-5167, 2013.

[2] J. H. Han, Y. J. Chung, B. K. Park, S. K. Kim, H.-S. Kim, C. G. Kim, and T.-M. Chung, *Chemistry of Materials,* vol. 26, no. 21, pp. 6088-6091, 2014.

[3] S. George, Chem. Rev. **110**, 111 (2010).

**AA12-4 The Impact of PEALD InGaO TFT Performances on Paring In/Ga Precursor Structures*, TaeHyun Hong*, *H. Jeong, J. Park,* Hanyang University, Korea

Recently, ALD oxide semiconductor has been attractive as TFT material that has the potential for high mobility and stability compared to conventional method due to precisely controlled thickness and metal composition. However, multi-component deposition using ALD is difficult to control without understating growth mechanism according to precursor and reactant, it is necessary to study and library the adsorption and reactivity of the surface depending on various precursor. In this study, InGaO (IGO) semiconductors were deposited by plasma enhanced atomic layer deposition (PEALD) using two sets of In and Ga precursors, which one set is $In(CH_3)_3[CH_3OCH_2CH_2NHtBu]$ (TMION) and $Ga(CH_3)_3[CH_3OCH_2CH_2NHtBu]$]) (TMGON) and the other is $(CH_3)_2In(CH_2)_3N(CH_3)_2$ (DADI), $(CH_3)_3Ga$ (TMGa), as denoted as TM-IGO and DT-IGO, respectively. We changed the ratio of InO sub-cycles from 3 to 19 to control the chemical composition of ALD-processed films. The different growth properties are observed at different precursor set. This could be originated from the precursor structure and the density of adsorption sites. Despite this different growth behavior, it could set the IGO TFTs with the identical In/Ga ratio controlling each super-cycle. Interestingly, the both TFTs (TM-IGO and DT-IGO) showed different film properties and the associated TFT characteristics (TM-IGO: -5.5V, 36.7 cm^2/Vs, DT-IGO: -9.7V, 27.7 cm^2/Vs for the V_{th} and mobility respectively). This difference could be originated from not only the growth behavior but also the anion/cation ratio/binding states in the IGO thin films.

**AA12-5 Structural Modulation of ALD IGZO TFT for Controlling the Hydrogen Concentration*, Wan-Ho Choi*, *K. Kim, J. Park,* Hanyang University, Korea

Nowadays, a novel deposition technique for thin film transistor (TFT) application using atomic layer deposition (ALD) such as semiconductor, gate insulator (GI), and encapsulation has been studied extensively. Herein, we developed unified-ALD (U-ALD), which deposits buffer, semiconductor and GI by ALD and named this structure as sandwich structure. In U-ALD IGZO TFTs, material forming interfaces with the channel layer exhibited a critical role in the electrical performance of IGZO TFTs because of hydrogen (H) diffusion, which has a Janus-faced effect in IGZO. Through measurement of hydrogen permeability of ALD insulators and Secondary Ion Mass Spectroscopy of each sandwich structure after annealing, we found a hydrogen accumulation effect in the ALD IGZO layer like a dam, which caused degradation of TFT properties. In contrast, TFTs with ALD SiO_2, which has proper hydrogen diffusivity, chosen as the buffer and GI had favorable electric properties of 28.17 cm^2/Vs, 0.20 V/decade, 0.96 V, and 0.12 V for the mobility, V_{th}, SS, and hysteresis. In this regard, an optimized GI structure via the ALD SiO_2 and Al_2O_3 in situ process on the basis of excellent interface formation with the semiconductor and hydrogen barrier performance, respectively, was developed. This functional GI structure with SiO_2 and Al_2O_3 exhibited proper TFT characteristics (27.52 cm^2/Vs, 0.24 V/decade, and 1.07 V for the mobility, SS, and V_{th}, respectively) and improved stability against hydrogen annealing, which was used to examine the resistance to external hydrogen.

**AA12-6 Ultrathin Amorphous Titanium Oxide Field-Effect Transistors with Large Gate-Induced Electron Mobility Modulation*, Nikhil Tiwale*, Brookhaven National Laboratory*; A. Subramanian,* Stony Brook University*; Z. Dai,* Brookhaven National Laboratory*; S. Sikder,* Stony Brook University*; J. Sadowski,* Brookhaven National Laboratory*; C. Nam,* Brookhaven National Laboratory/Stony Brook University

Recent reports show a great promise of using ultrathin metal oxide films prepared by atomic layer deposition (ALD) for enabling high performance devices featuring ultra-sharp subthreshold swing and even the formation of two-dimensional electron gas (2DEG). A key characteristic of ultrathin metal oxide thin-film transistors (TFTs) is their very low off-state current with a sharp and high on off ratio. While the on-off operation in typical TFTs primarily results from the modulation of gate-dependent charge carrier density, recent reports suggest that the high on-off ratio in ultrathin oxide TFT operation can be associated with a large gate-induced carrier mobility modulation, which few reports provide a clear picture regarding its origin and implication. In this study, we study the 3.5 nm-thick amorphous-titania-based ultrathin TFT fabricated by low-temperature ALD, which exhibited six-decade on-off ratio predominantly driven by the same magnitude of gate-induced mobility modulation [Tiwale et al., *Commun. Mater.***1**, 94 (2020)]. We observe that the power law dependence of gate-dependent saturation mobility featured a very high exponent at low gate voltages, unprecedented for oxide TFTs reported so far. Drawing parallels from the disordered organic TFT that exhibits similarly high power law exponent, and by combining the physicochemical analysis of titania prepared under varying post-ALD thermal treatments and the accompanying TFT device characterization, we identify that the large gate-induced mobility modulation originates from the variable range hopping (VRH) transport of charge carriers through the band-tail states of ultrathin titania, with its bi-exponential density of states reflected on the observed two different power-law exponent regimes in the gate-dependent mobility. The results highlight rather unusual and counterintuitive roles of defect states within ultrathin metal oxides in possibly enabling some of the high performance parameters in associated TFT devices, as best exemplified by the increased off-state current accompanied by the reduced device on–off ratio upon the oxidative annealing of ultrathin titania, against the typical notion that such an oxidative annealing in metal oxide transistors would reduce the background carrier density while increasing the on–off ratio.

ALD Applications
Room On Demand - Session AA14
Emerging: Optics/Optoelectronics/Metamaterials/Plasmonics

**AA14-1 Optical Quantizing Structures in Al_2O_3/TiO_2 Heterostructures by Plasma Enhanced Atomic Layer Deposition*, Pallabi Paul*, *A. Szeghalmi,* Friedrich Schiller University Jena, Germany

Atomically thin heterostructures and superlattices are promising candidates for various optoelectronic and photonic applications. In this research, different combinations of Al_2O_3/TiO_2 composites are fabricated by plasma enhanced atomic layer deposition (PEALD). The growth, dispersion relation, optical bandgap and composition of such structures are systematically studied by means of UV/VIS spectrophotometry, spectroscopic ellipsometry (SE), x-ray reflectometry (XRR), scanning transmission electron microscopy (STEM) and x-ray photoelectron spectroscopy (XPS). Besides, an effective medium approximation (EMA) approach is applied to model the heterostructures theoretically. The refractive index and the indirect bandgap of the heterostructures depend on the ratio of the two oxides, while the bandgap is very sensitive to the thicknesses of the barrier and quantum well layers. A large blue shift of the absorption edge from 400 nm to 320 nm is obtained by changing the TiO_2 (quantum well) thickness from ~ 2 nm to ~ 0.1 nm separated by ~ 2 nm of Al_2O_3 (barrier) layers. PEALD unfolds the possibility of achieving optical quantizing effects within complex heterostructures enabling control of their structures down to atomic scale. It enables a path towards atomic scale processing of new 'artificial' materials with desired refractive indices and bandgap combinations by precise control of their compositions.

Selected compositions are identified for applications in antireflection coatings at 355 nm wavelength. Interference multilayers of TiO_2/Al_2O_3 composites as high refractive index material and SiO_2 as the low refractive index show low reflectance and optical losses at 355 nm wavelength with transmittance values of approximately 99%. Such heterostructures overcome the limitations of the low bandgap dielectric TiO_2 for optical applications in the UV spectral range.

AA14-2 Excellent Surface Passivation of Germanium by ALD Al_2O_3 with a-Si:H Interlayers, ***Willem-Jan Berghuis***, *J. Melskens, B. Macco, R. Theeuwes, K. Erwin,* Eindhoven University of Technology, Netherlands

After the adoption of ALD for the preparation of high-k gate oxides in field-effect transistors (FETs), the unique features of ALD have only become more important with the advancement of the technology nodes: precise and uniform thickness control, excellent conformality, and the ability to generate high-quality surfaces with well-passivated channel surface states. For the next-generation, multiple stacked nanosheet FETs, the requirements become even more stringent. Now the gate needs to be wrapped all around the channel while also both Si and Ge channel surface states need to be passivated. Similar challenges lie in the passivation of Ge and SiGe nanowire devices such as nanolasers, nano-LEDs, and solar cells.

The passivation of SiGe and Ge surfaces by ALD films has been a long-standing challenge which mostly has been addressed by examining FET-like structures. We have recently carried out an in-depth study of the passivation of Ge by ALD Al_2O_3 films. By measuring the carrier lifetime on passivated substrates we extracted the maximum effective surface recombination velocity $S_{eff,max}$. For Al_2O_3, we demonstrated that values as low as $S_{eff,max}$= 170 cm s^{-1} can be achieved after optimization of the ALD substrate temperature, film thickness, and post-deposition anneal temperature. It was moreover established that a GeO_x interlayer forms during ALD and that the GeO_x/Al_2O_3 stack on a Ge surface has a negative fixed oxide charge density ($Q_f = - 1.8 \cdot 10^{12}$ cm^{-2}).

In this work, we have systematically examined the surface passivation of Ge by thermal and plasma-enhanced ALD Al_2O_3 in combination with an amorphous silicon (a-Si:H) interlayer. For this purpose, we have grown a-Si:H/Al_2O_3 stacks on Ge substrates under various conditions using plasma-enhanced chemical vapor deposition (PECVD) for the a-Si:H layer (1-10 nm) and ALD for the Al_2O_3 (5-20 nm). We found an excellent surface passivation by an a-Si:H layer as thin as 1.7 nm ($S_{eff,max}$ = 6.8 cm s^{-1}). To better understand the role of the a-Si:H interlayer and its interaction with the ALD Al_2O_3 film, we have performed measurements of the interface defect density (D_{it}) and fixed charge density (Q_f) together with a Transmission Electron Microscopy study. We have found a remarkably high fixed charge ($Q_f = - 8.8 \cdot 10^{12}$ cm^{-2}) present in this passivation stack due to the interplay between the Si and PEALD Al_2O_3 leading to a SiO_x interlayer making it a Ge/a-Si:H/SiO_x/Al_2O_3 stack. Thermal ALD Al_2O_3 yields a lower $Q_f$in comparison, which is likely related to a less prominent SiO_x interlayer. The understanding of this material system is expected to be valuable for the design of well passivated Ge interfaces and devices.

AA14-3 Tunable and Scalable Fabrication of Plasmonic Dimer Arrays With Sub-10 nm Nanogaps by Area Selective ALD, ***Chengwu Zhang***, *B. Willis,* University of Connecticut

Plasmonic nanoantennas, especially with sub-10 nm nanogaps, can greatly enhance electric fields through excitations of surface plasmons, which are collective oscillations of electrons excited by light.Arrays of plasmonic nanoantennas can be designed to concentrate and manipulate light at the nanoscale, and have wide applications such as surface enhanced spectroscopy, photo-driven chemical conversion, and optical information processing.Atomic layer deposition (ALD) is a thin-film deposition technique capable of producing conformal thin films with precise control of thickness and composition at the atomic level.Area selective ALD (AS-ALD) provides a flexible way to precisely tune nanogaps to enhance their optical and electrical properties. In this work, we investigate the optical response of plasmonic nanoantenna dimer arrays with sub-10 nm nanogaps by AS-ALD.

We present a case study of Cu AS-ALD on Pd/Au layered nanoantenna dimers. Figure 1 shows a side view schematic diagram of AS-ALD to tune nanogaps. Pd layers are designed to promote Cu nucleation, and Au layers provide strong plasmonic resonances in the visible and near IR range. Arrays of Pd/Au layered nanoantenna dimers are fabricated on fused quartz substrates using electron beam lithography, followed by Cu AS-ALD to tune the inter-particle distances. Results show nanogaps can be well tuned to sub-10 nm. In figure 2, the nanogaps are measured by electron microscopy and the average post-ALD gap is 6.5 ± 2.2 nm. The inset shows an example dimer with a nanogap of 4.2 nm; each pixel in the SEM image is 0.9 nm. Optical extinction curves were measured to track the changes to the dipolar plasmonic resonances as the number of ALD layers was increased. Figure 3 shows the extinction measurements for light polarized along the axis of the dimer. The dipolar resonance initially blue shifts around 100 nm after 50 ALD cycles, and then red shifts back towards the pre-ALD peak location after more deposition cycles. Control experiments show that the initial blue-shift is largely due to heating, which can slightly modify the nanostructures by rounding corners and edges. Electrodynamics simulations show that additional factors include increasing thickness and decreasing aspect ratio, which also tend to blue-shift the resonances. The data show that beyond 50 cycles, the resonance red-shifts due to the dominant effect of narrowing the nanogaps, which is supported by simulations. In this way, the study shows considerable spectral "tunability" by tailoring the optical responses of plasmonic nanoantenna arrays, while creating nanogaps that concentrate electric fields for various applications.

AA14-4 Lithium Aluminum Fluoride as an Ultraviolet Coating Material, ***John Hennessy***, Jet Propulsion Laboratory

Optical systems operating in the far ultraviolet (90–200 nm) often employ protected aluminum mirror coatings. These mirror systems utilize protective thin films of metal fluoride materials to maintain optical transparency in the wavelength range of interest. The most common protective coating material for this application is MgF_2 which limits the short wavelength performance of the mirror to the band edge cutoff of MgF_2 at approximately 120 nm. There is growing interest for astrophysics applications in the use of LiF protective coatings which can extend the short-wavelength performance due to its larger bandgap, however the hygroscopic properties of LiF can present challenges for the stability and longevity of the final optical system. In this work, we investigate the use of atomic layer deposition to create thin films of lithium aluminum fluoride as an ultraviolet coating material. We have employed a supercycle approach utilizing LiHMDS, tris(dimethylamino)aluminum, and anhydrous HF as co-reactants at substrate temperatures between 100 and 200 °C. This chemical pathway avoids possible deleterious interactions that can occur between simple alkylaluminum precursors and alkali materials, and ultimately allows for arbitrary mixed thin film compositions ranging from purely crystalline LiF, to purely amorphous AlF_3. At intermediate supercyle ratios we also show that crystalline films of Li_3AlF_6 can be deposited with this process as confirmed by x-ray diffraction analysis. We present recent results on protected aluminum mirror coatings fabricated with this approach, along with environmental exposure testing comparing the performance of Li_3AlF_6 to LiF and AlF_3. The prospects for utilizing this approach in future NASA instrumentation will be discussed along with the possibility of using these films as battery coating materials. Crystalline films of Li_3AlF_6 are also known to possess moderate Li-ion conductivity and the low deposition temperature investigated in this work may have benefits over other ALD approaches in this material system.

AA14-7 Stress Compensated HfO_2/SiO_2 High-reflective Coatings at 355 nm and 532 nm by Plasma Enhanced Atomic Layer Deposition using Substrate Biasing, ***Vivek Beladiya***, Friedrich-Schiller-University Jena, Germany*; D. Kästner,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany*; S. Riese, P. Hanke,* LAYERTEC GmbH, Germany*; A. Szeghalmi,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany

Atomic layer deposition is a promising thin film deposition technology due to its ability to coat complex formed substrates with precise thickness control and excellent uniformity. The substrate biasing technique in plasma enhanced atomic layer deposition has recently gained attention due to its ability to manipulate material properties such as refractive index, density, residual OH impurity, residual mechanical stress, crystallinity, and surface roughness. The kinetic energy of the plasma species can be varied by applying a substrate bias potential across the plasma sheath at the substrate surface. In this work, we have deposited high-reflective (HR) coatings at 355 nm and 532 nm at 100°C deposition temperature using substrate biasing.

The multilayer system consists of HfO_2 and SiO_2 as a high and low refractive index layer, respectively, which were grown using a substrate biasing. The total film thickness of HR@355nm and HR@532nm were 1.6 µm and 2.3 µm, respectively. The total residual stress measured on double-side polished Si wafers was 76 MPa (tensile) and 112 MPa (tensile) for HR@355nm and HR@532 nm, respectively. The reflectance of 99.9 was measured using a spectrophotometer at 355 nm and 532 nm wavelengths for HR@355nm and HR532nm, respectively.Additionally, a reflectance of above 99.9 was determined at 355 nm wavelength for HR@355nm multilayer coating by means of cavity ring-down measurements. The coatings were free of delamination and visible cracks. The laser-induced damage threshold (LIDT) was performed at 355 nm using the R-on-1 method on HR@355nm multilayer coating. The LIDT of 19 J/cm³ was observed. Hence, we have successfully demonstrated stress compensated high-reflective (HR) coatings for the designed wavelengths of 355 nm and 532 nm with excellent uniformity and mechanical stability.

ALD Applications
Room On Demand - Session AA15
Emerging: Medical/Healthcare/Pharmaceuticals

AA15-1 Atomic Layer Deposition of Nanocomposite Antimicrobial and Antiviral Coatings*, **Anil Mane**, M. Gros, R. Wilton, S. Forrester, Y. Zhang, . Zaluzec, D. Schabacker, S. Darling , J. Elam,* Argonne National Laboratory, USA

Antimicrobial (AB) and antiviral (AV) coatings can play a crucial role in health and safety by preventing the growth and spread of pathogens. Based on the chemical composition of these coatings can drastically reduce or even kill the bacterial and viruses via surface chemical reaction, catalytic reaction activated by light, thermal treatment, in presence of reactive gases or surface functional groups.Antimicrobial and antiviral-coated surfaces are becoming more broadly examined for possible use in areas such as medical clothing and equipment, surfaces encountered in public and private transportation and household use. The most common and most significant use of antimicrobial/antiviral coatings has been used in healthcare in the manufacture of masks and equipment to prevent hospital related infections, which have accounted for more than a million deaths worldwide. In addition, the current pandemic caused by the SARS-CoV-2 virus has infected more than 100 millon people resulting in over 2.2 million deaths from COVID-19. Therefore, it is essential to develop effective antimicrobial and antiviral coatings to address a wide range of needs.

Antimicrobial/viral coatings can be prepared using a variety of thin film coating processes. A thin coating can be applied to a surface that has a chemical composition which is toxic to microorganisms but not to humans. Among the various coatings, layers containing Cu and Ag have been shown particularly effective against microorganisms and viruses. In addition, other coatings such as TiO_2, ZnO and MoO_3 have also shown antimicrobial/antiviral properties. Due to outstanding processing advantages, we have evaluated atomic layer deposition (ALD) as a viable approach for the commercial production of AB/AV coatings.In this study, we prepared a wide variety of ALD materials including binary, ternary, and quaternary oxides and composites on N95 mask filter materials (polypropylene) and polyester fabrics at temperatures as low as 50ºC. All of these ALD materials showed uniform and conformal coatings that infiltrated the porous fabrics. We tested the antibacterial and antiviral properties of these ALD coated materials and identified coating formulations that were highly effective against bacteria and viruses. Moreover, the coatings did not diminish the filtration properties of the N95 mask filters.In this presentation we will discuss the coating materials, the AB/AV testing results and future directions. We think that the technology present here can be used for other air filter applications.

ALD Applications
Room On Demand - Session AA16
Emerging: Others (Protective Coatings, Hardness, MEMs...)

AA16-1 Capacitance Modulation by Light and Mechanical Stimuli in ALD-deposited ZnO Thin Films Integrated in Piezotronic MEMS Strain Microsensors*, **Raoul Joly**, S. Girod, N. Adjeroud, P. Grysan, J. Polesel,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

By the means of Atomic Layer Deposition (ALD), we developed piezotronic strain sensitive sensors integrated in polyimide cantilevers, where a zinc oxide (ZnO) thin film is deposited on top of patterned interdigitated platinum electrodes (Figure 1(a)). The rapidly spreading Internet-of-Things is accelerating MEMS (Micro-ElectroMechanical Systems) industry to deliver highly sensitive and miniaturized self-sensors with low consumption and cost-effective production process. Due to its high film conformality, low temperature processing, self-limiting nature and thickness control at the nanoscale level, ALD technique has emerged as an ideal technique to add new functionalities in MEMS.

We propose to rationalize the ALD processing deposition parameters on the sensor's electrical properties and the sensitivity of detection for mechanical strain and light. We report on the evidence of negative capacitance phenomena occurring at the interface of Schottky junctions over a wide frequency range (between 20 Hz and 100 kHz). We demonstrate an original way to modulate the sensors capacitance characteristics in the presence of a light source as well as by applying a mechanical strain to the devices (Figures 1(b), (c) and (d)). The rationale behind these observations will be discussed. The ALD thin film is made of wurtzite polycrystalline zinc oxide with a privileged (002) orientation. We optimized the deposition temperature to be compatible with microfabrication processing on polymer and photoresists by thin film growth below 100 °C. Hence, Schottky junctions are realized by microstructuring interdigitated micro-combs at the interface of high work function platinum metal electrodes and a semiconducting piezoelectric ZnO thin film. The obtained piezotronic junction has the particularity of an exponential dependence of the flowing diode current as a function of the applied mechanical strain. The sensitivity is thus greatly improved with gauge factor higher than 100.

In the last stage of this work, we will present the strain sensors size miniaturization for integration in microcantilevers in a full polymer body, compatible with AFM (Atomic Force Microscopy) scanning probe operations to highlight the very high sensitivity of detection. These results open up new perspectives and applications towards the miniaturization of highly sensitive and low power consumption environmental sensors, as well as for broadband impedance matching in radio frequency applications by the means of negative capacitance devices.

AA16-2 Applications of Atomic-Scale Processing for the Next Decade of MEMS Technology*, **Daniel Potrepka**, N. Strnad, R. Rudy,* U.S. Army Research Laboratory

Atomic-scale processing has had a major impact in the fields of microelectronics and CMOS fabrication technology, building upon the significant advances in academia. Now the field of micro-electomechanical systems (MEMS) is poised to reap the benefits of atomic-scale fabrication, as gains achieved with standard process technologies remain limited to low-cost devices. To achieve this breakthrough, ALD atomic-scale techniques will play a vital role, driving MEMS deep into the nanoscale regime by engineering innovative designs to take advantage of the scaled piezo- and ferroelectric properties encountered therein. Using a combination of ALD, ALE, and pre- and post- treatments for area-selective growth of function-enhancing features and layers, ALD can hermetically seal off devices from harsh in-process or working environments, eliminate stiction, tailor conformal multilayer geometries to provide new functionalities such as phonon crystals and metamaterials, control stress, enhance polarization and structural integrity, lower operating voltage, increase chip work density by an order of magnitude, and meet thermal, mechanical, geometrical, barrier, interface, and ferroic materials design requirements for competitive commercial MEMS technologies and devices. These breakthroughs will be enabled by a wide array of viable precursors, providing new metal oxides and metals of increasing diversity and complexity from throughout the periodic table, including the recently developed nitrides, sulfides, and tellurides [1-3]. The resulting new materials, along with rapidly occurring growth and integration of computer modeling for precursor-surface chemical reactions [4] and hardware improvements [3] will enhance the scale and pace of MEMS modernization.

ALD commercial infrastructure and equipment sales, currently predicted to increase to about USD $2 billion in 2026 at a compound annual growth rate from 2020 of 26.3% can leverage off the larger MEMS global market. Impacts of the key atomic-scale processes that can fuel this exciting expansion of the MEMS technology arena will be reviewed, emphasizing the benefits for the future of prototyping and scaled fabrication in commercial, industrial, and defense applications.

1. V. Pore *et al.*, J. Am. Chem. Soc. 2009, 131, 10, 3478-3480. DOI 10.1021/ja8090388

2. N. P. Dasgupta *et al.*, Acc. Chem. Res. 2015, 48, 2, 341-348. DOI 10.1021/ar500360d

3. G. B. Rayner Jr. *et al.*, J. Vac. Sci. & Technol. A 38, 062408 (2020). DOI 10.1116/6.0000454

4. S. D. Elliott *et al.*, J. Chem. Phys., vol. 146, 052822 (2017). DOI 10.1063/1.4975085

AA16-3 Texture Control of Piezoelectric Aluminum Nitride Grown by Atomic Layer Deposition for 3D Microelectromechanical Systems*, **Nicholas Strnad**, W. Sarney,* CCDC Army Research Laboratory*; G. Rayner,* Kurt J. Lesker Company, Inc.*; G. Fox,* Fox Materials Consulting, LLC*; R. Rudy, J. Pulskamp,* CCDC Army Research Laboratory

3D microelectromechanical systems (3D-MEMS) are an emerging application space for piezoelectric films grown using ALD. ALD provides an ideal solution for the deposition of piezoelectric materials on trench sidewall or 3D fin structures which may be used to improve the size, weight, power and frequency tunability of MEMS devices. Aluminum nitride is a technologically relevant material for piezoelectric MEMS due to its significant piezoelectric response, high breakdown voltage and large mechanical quality factor. AlN is amenable to film growth by ALD, although there are relatively few reports of ALD AlN used for MEMS due to the need for additional process development to meet stringent crystal structure, film purity and grain orientation requirements for device performance. We explore several strategies for controlling the grain orientation of ALD-grown AlN on planar substrates, which includes the use of {111}-textured Pt as a growth template, precursor chemistry and dose variation, stress-engineered substrates, inductively-coupled plasma conditions for film bombardment during growth, and ALD equipment modifications. For select cases, we report the mechanical Q, determined from measurements of MEMS resonator structures, and piezoelectric coefficients, determined from measurements on MEMS cantilevers, of ALD deposited AlN . We analyze the Pt-AlN interface properties primarily by using TEM with EDS. The baseline ALD AlN process yielded completely c-axis oriented aluminum nitride as determined by x-ray diffraction, and a rocking curve full-width half max of 2.9° was achieved. The relative dielectric constant was measured to be 8.1 < K < 8.6 and an average dielectric loss of < 1% was observed within the an applied electric field range of +/- 3350 kV/cm (+/- 35 V across 104 nm thick AlN) at 10 kHz. The leakage current of the textured AlN was quite low at 1.5 x 10^{-6} A/cm^2 over the applied field range of +/- 1820 kV/cm (+/- 19 V across 104 nm thick AlN).

AA16-4 Electrically-Conductive Kevlar Fabrics for Multi-Functional Fiber Reinforced Composites Enabled by Atomic Layer Deposition*, **Robin E. Rodríguez**, T. Lee, Y. Chen, T. Cho, C. Huang, E. Kazyak, A. Poli,* University of Michigan, Ann Arbor*; W. LePage,* University of Michigan - Ann Arbor*; M. Thouless, M. Banu, N. Dasgupta,* University of Michigan, Ann Arbor

Multi-functional composites have wide-ranging applications from structural batteries to electronic devices, which are of increasing interest in the aerospace community. To operate as a device, at least one constituent of the composite needs to be electrically conductive. Polymer-matrix composites (PMCs) are generally electrically insulating and often necessitate the inclusion of electrically-conductive additives, but such additives tend to affect the bulk mechanical properties of the final product. A method to impart electrical conductivity without affecting the bulk mechanical properties of the composite is to modify the surface of the reinforcement by adding a thin, conductive coating. Among the coating techniques that can be utilized, atomic layer deposition (ALD) provides unparalleled conformality in coating of the 3-D fiber template, as well as sub-nanometer resolution in film thickness and composition.

In this work we demonstrate the fabrication of electrically-conductive Kevlar-reinforced PMCs without measurably affecting the bulk material properties, by coating Kevlar fabrics with aluminum-doped zinc oxide (AZO) via ALD. The core-shell fabric morphology and structure were characterized by SEM, XPS, and XRD. The conductive properties of the AZO-coated Kevlar fabric were measured using the four-point probe method, which were taken at the single-fiber, single-tow, and fabric level, after varying the thickness of AZO from 80-200 nm. For all the cases, the electrical resistivity decreases as the film thickness increases. The thickness-dependence of the electrical resistivity is well described by an analytical model, which allows for predictive design. These fabrics are sufficiently conductive to serve as an electrode material in textile-based devices ranging from thin-film electronics to energy storage devices.

Additionally, we studied the relationships between electrical conductivity and mechanical deformation of AZO-coated Kevlar fabrics as used in a PMC. The electrical resistance of the composite was continually monitored *in situ,* while loading the sample to failure in a tensile load frame. The ultimate tensile strength and Young’s modulus of the Kevlar-reinforced PMC was not significantly affected by AZO interface coatings, illustrating the advantage of this approach over bulk conductive additives. Furthermore, changes in the electrical resistance at higher strains were observed, which is attributed to the cracking of the AZO coating. These results demonstrate the potential of AZO-coated Kevlar to make electrically conductive composites with applications such as monitoring the state-of-health of the composite within the linear elastic regime.

AA16-5 COO Reduction for Semiconductor Parts via ALD Coatings and Recycling of Parts*, **Russell Parise**, I. Iordanov,* QuantumClean, A Business Unit of UCT*; G. Osoro,* Inficon

The semiconductor industry has considerable experience with thermal spray protective coatings of parts in the etch and deposition areas to modify surface chemistry, provide corrosion resistance, or provide a barrier layer.These coatings are effective but are generally thick (150 - 200 µm) and may not provide sufficiently low porosity for parts exposed to reactive gases or plasmas.The ALD process creates high purity thin-films that are dense, highly conformal and defect free. Materials such as Al_2O_3 and other metal oxides are resistant to the reactive halogens that part surfaces see during semiconductor processing.

To address these challenges, ALD coatings have been developed to uniformly coat showerheads, pedestals, and other parts with high aspect ratios with 100 – 500 nm thin-films such as Al_2O_3, SiO_2, or other metal oxides.These films protect the part from the reactive halogen radicals and extend green to green time. Besides protecting the parts from reactive gases, the high aspect ratio ALD coatings on chamber components can serve as a diffusion barrier to avoid metal migration from the part itself and reduce conditioning times.

Additionally, parts with these ALD coatings can be recycled. Using Selective Coating Removal, the ALD protective coating is removed with minimum damage to the substrate, including the high aspect ratio features, before the part is prepared for ALD recoating. The loop essentially extends part life almost indefinitely which decreases cost of ownership.

This paper addresses the recent advances in the use of ALD thin films as a functional, protective coating that enhances part performance and reduces process costs.It will also cover the technology to selectively remove the deposition layer and ALD coating without damage to the part.Surface preparation, final cleaning, metrology and analytical testing for validation will also be discussed.

Keywords: ALD, Al_2O_3, corrosion, diffusion barrier, SiO_2, aspect ratio, etch, CVD

AA16-8 Aqueous Degradation and Nanoscale Coatings of Al_2O_3 via Atomic Layer Deposition (ALD) of $BaAl_2O_4$: Eu^{2+}, Dy^{3+} Long Afterglow Phosphors*, **Erkul Karacaoglu,* Georgia Institute of Technology, USA and Karamanoglu Mehmetbey University, Turkey*; E. Öztürk,* Karamanoglu Mehmetbey University, Turkey*; M. Uyaner,* Necmettin Erbakan University, Turkey*; A. Okyay,* OkyayTechALD Okyay Technnologies, Turkey and Stanford University*; M. Losego,* Georgia Institute of Technology, USA

In this presentation aqueous degradation studies of $BaAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors synthesized from solid-state reaction methods and coated with nanoscale Al_2O_3 protective layers via atomic layer deposition (ALD) will be presented. The uncoated phosphor powders degrade in water within just 30 minutes of immersion. This degradation directly affects the bluish-green phosphorescence (497 nm), creating both blue- and red-shift which are maximized at 429 nm and 687 nm, respectively. Hydration and decomposition of the $BaAl_2O_4$ phase reveals a continuous change in the phase assemblage over 30 days. ALD coatings of ~10 nm Al_2O_3 protects the phosphor from aqueous degradation upon long-term immersion in water. ALD Al_2O_3 coated $BaAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors retain their phosphorescence for at least 7 days of water immersion. Successful encapsulation of $BaAl_2O_4$-based phosphors will make them possible to store in humid environments or use in applications directly requiring aqueous solution.

ALD Applications
Room On Demand - Session AA17
ALD Applications Poster Session

AA17-1 Atomic Layer Deposition of AlN Films With and Without Plasma. Piezoelectric Effect and Magnetoelectric Coupling With Nickel*, **Noureddine Adjeroud**,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Aluminum nitride (AlN) thin films have attracted significant attention for optoelectronics, piezoelectrics-based devices as surface-acoustic-wave resonators thanks to its excellent properties such as wide band gap of 6.2 eV, piezoelectricity along c-axis and high phase velocities of acoustic waves. Those applications, however, require the control of the c-axis (002) crystalline orientation of AlN in order to achieve the highest piezoelectric effect and surface acoustic velocity. Many efforts have been devoted to grow (002)-oriented AlN films. For instance, (002) oriented AlN film can be synthesized by pulse laser deposition, chemical vapor deposition, plasma assisted physical vapor deposition and plasma enhanced atomic layer deposition (PEALD). Nevertheless, those techniques require either elevated temperatures of substrate from 300 to 1000 oC and/or long period of plasma treatment during each cycle. In this study by carefully adjusting parameters of PEALD we were able to tailor preferred orientations of AlN thin films from a preferred (100) orientation to the (002) orientation at low substrate temperature from 180°C to 250 oC. In addition, X-ray photoelectric spectrometry surveys confirmed high quality AlN films with low impurities level of 1% of carbon and 6-7% of oxygen, which are comparable to the literatures. The direct piezoelectric coefficient e31,f measurements (4-point bending method, aixACCT), which were rarely reported on AlN films grown by PEALD, revealed a strong correlation between crystallographic orientations and e31,f value of AlN films; i.e. e31,f coefficient of (100) AlN film was almost “zero”, whereas that of (002) preferred orientation film was measured to 0.38 C.m-2. In addition, we synthesized 2-2 magnetoelectric composites by depositing (002) oriented AlN film of 500 nm thickness on nickel foil with an excellent interface coupling by the highly conformal coating of ALD technique. The low temperature growth of AlN films allowed to unconcern in degradation of magnetic properties of the nickel magnetostrictive film.. The resulting magnetoelectric coefficient was about 3.5 V.cm-1.Oe-1 at 46 Hz. Though, AlN film is grown at temperature as low as 250 °C, the properties of the AlN film and its magnetoelastic coupling are utmost promising for energy harvesting and sensing applications on silicon-based as well as flexible-organic-substrate-based micro-electro-mechanic-system (MEMS) devices.

AA17-2 ALD SnO P-Type Thin Film Transistors and the Influence of Post Fabrication Annealing Conditions on Device Performance*, **Benjamin Peek**,* Pegasus Chemicals, UK*; P. Chalker, M. Werner,* The University of Liverpool, UK*; P. Williams,* Pegasus Chemicals, UK*; F. Alkhalil, S. Das,* PragmatIC Semiconductor, UK

Flexible oxide electronics are integral to the proliferation of the Internet-of-Things (IoT). Currently, the state-of-the-art is predominantly based on unipolar n-type devices (NMOS). A complementary (CMOS) logic capability would greatly expand the range of low-cost flexible electronics, because the static power consumption is much lower than in unipolar based technology. Tin monoxide (SnO) is a candidate for p-type thin film transistors (TFTs) that could be matched to existing NMOS technology.Previously, p-type SnO films and TFTs have been fabricated by ALD (Atomic Layer Deposition) using bis(1-dimethylamino-2-methyl-2-propoxy) tin(II) (Sn(dmamp)2) and H2O vapour [1]. This precursor is synthesised, via an intermediate, namely bis(bis(trimethylsilyl)amide) Sn(II), which has also been used to deposit SnO with water [2]. Here we report the use of a precursor from Pegasus Chemicals, to deposit the channel of SnO-based p-type TFTs via ALD. The liquid precursor has been used to conformally deposit SnO thin films at 150°C with water vapour, onto 200mm wafers as shown in Fig. 1. An X-ray diffraction pattern of an SnO film deposited using 4000 ALD cycles is shown in Fig. 2. The dominant diffraction peaks are from the <001> and <002> planes of α-SnO, indicating the growth has a <001> preferred texture.P-type TFTs were fabricated at PragmatIC Semiconductor based on silicon (p++) back-gated structure, as illustrated in Fig. 3, which shows the TFT characteristics of this device. The α-SnO channel of which was deposited in 500 ALD cycles. Before the patterning of SnO, the wafer exhibited a sheet resistance of Rsh 1.6 MΩ/sq . The TFT characteristics were measured: as-fabricated and after annealing in air (200° C, 1 hr), vacuum (190° C, 1 hr), nitrogen (200° C, 1 hr) and forming gas (350° C, 30 mins). Air annealing (blue) has little effect on the as-fabricated TFTs (black). The vacuum anneal (red) and nitrogen anneal (green) show a similar effect on the device performance, resulting in a marginal decrease in the on and off-current. Forming gas (H2/N2) annealing (FGA) leads to an enhanced on/off ratio, in addition to a negative shift in Von towards 0 V. Potential mechanisms responsible for the effect of different annealing processes on the TFT characteristics will be discussed .The work demonstrates the feasibility of using ALD-deposited tin monoxide to fabricate p-type TFTs at temperatures compatible with flexible oxide electronics manufacturing processes.[1] Jeong Hwan Han et. al, Chem. Mater. 2014, 26, 6088−6091. [2] Jere Tupalaa et. al. Journal of Vacuum Science & Technology 2017, A35, 041506.

AA17-3 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Indium Oxide*, **Ali Mahmoodinezhad**, C. Morales,* Brandenburg University of Technology Cottbus–Senftenberg, Germany*; F. Naumann, P. Plate, R. Meyer,* SENTECH Instruments GmbH, Germany*; C. Janowitz, K. Henkel, M. Kot, J. Flege,* Brandenburg University of Technology Cottbus–Senftenberg, Germany

Indium oxide (In_xO_y) thin films were successfully grown by plasma-enhanced atomic layer deposition (PEALD) using trimethylindium (TMIn) and oxygen plasma (O_2) at low temperatures of 80 to 200 °C. The films were investigated by spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), and electrical measurements. The in-situ SE data confirmed a self-saturated growth mechanism with a growth rate of 0.56 Å per cycle within the ALD window (100 to 150 °C) resulting in a well-defined film thickness with an excellent homogeneity of ≥ 98.8% across 4 inch substrates. We found that the refractive index of the layers increases from 2.04 at 80 °C to 2.07 at 150 °C, and it abruptly decreased to 2.02 at 200 °C. Besides, the In_xO_y layers show indirect and direct transitions in the optical band gap with values of 2.8 ± 0.1 eV and 3.3 ± 0.2 eV, respectively. According to XPS, the PEALD-In_xO_y thin films are free of carbon below the surface; also, they exhibit a temperature-dependent indium-rich off-stoichiometry that increases with temperature. Correspondingly, at temperatures ≥ 150 °C, the electrical conductivity of the layers is higher. In addition, a detailed XPS analysis revealed the presence of hydroxyl groups and defect states whose concentrations decrease with rising deposition temperature. Based on the obtained results, we deem our indium oxide thin films to be suitable for high-performance optoelectronic and photovoltaic devices.

AA17-4 High-Reliable Atomic Layer Deposited N-doped GeSe and Its Leaky-Integrate-and-Fire Neuron Application*, **Woohyun Kim**, M. Ha, C. Yoo, J. Jeon, W. Choi, B. Park, G. Kim, K. Woo, J. Kim, Y. Jang, E. Park,* Seoul National University, Korea (Republic of)*; Y. Lee,* Jeonbuk National University, Korea (Republic of)*; C. Hwang,* Seoul National University, Korea (Republic of)

This study presents the atomic layer deposition (ALD) of N-doped GeSe and its neuromorphic application for leaky-integrate-and-fire (LIF) neuron. The ALD process utilized $Ge^{II}N(CH_3)_2[(N^iPr)_2CN(CH_3)_2]$ and $[(CH_3)_3Si]_2Se$ with an NH_3 co-reagent as Ge- and Se-precursors, respectively. The N-doped GeSe was not deposited by the conventional ALD sequence (Ge-precursor pulse – purge – Se-precursor pulse – purge) without the NH_3 gas. The NH_3 gas changes the surface terminated with $[(N^iPr)_2CN(CH_3)_2]$ to NH_2 group for facilitating ligand exchange reaction with $[(CH_3)_3Si]_2Se$.

The $Ge^{II}N(CH_3)_2[(N^iPr)_2CN(CH_3)_2]$ is stable even at high temperatures (~ 190 ℃) due to the chelating of the ligand, and thus, the ALD window can be extended to high temperatures (Fig. 1(a)). Therefore, this ALD method could be performed at the substrate temperature of 150 ℃, which is significantly higher compared with the previous experiment using $HGeCl_3$ precursor (70 ℃). The ALD process resulted in high-density GeSe thin film deposition with N-incorporation (Fig. 1(b), (c)). In the case of GeSe, the doping of light elements like nitrogen improves amorphous stability, leading to better reliability of Ovonic threshold switching devices. As a result, high crystallization temperature and excellent cycling endurance of GeSe were achieved due to the N-doping effect and high-density thin films by adopting the high deposition temperature (Fig. 1(d)).

Furthermore, the GeSe-based LIF neuron's behavior is verified by the measurement of the electrical waveform using a pulse generator (Fig. 2), and the detailed analysis will be discussed in the presentation.

AA17-5 Zero Temperature Coefficient of Resistance in Back-End-of-the-Line - Compatible Titanium-Aluminum Nitride Nanolaminates Grown by Plasma Enhanced Atomic Layer Deposition

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Thin film resistors with near-zero temperature coefficient of resistance (TCR) are key passive elements in analog integrated circuits. We report here that near-zero TCR resistors can be obtained by atomic layer deposition (ALD) of TiN-AlN nano-laminates at back-end-of-the-line (BEOL)-compatible deposition temperatures.The ALD method provides an ultimate control of the thickness, composition ratio, coverage and uniformity. The nitride films were deposited using plasma enhanced ALD (PEALD) at 300°C. TDMAT and TDMAA were the metalorganic precursors for deposition of TiN and AlN components, respectively. The properties of the binary TiN and AlN compounds were investigated separately as well to find the temperature window for the ternary PEALD process (FIG. 1). A mixture of ammonia and argon gases was used for reactive plasma. The films were deposited on SiO_2/Si substrates with thermal oxide thicknesses of 3nm and 100nm. The electrical resistivity of the deposited films was measured by the transfer length method (TLM). We patterned and etched the nitride films into resistor channels with a fixed width (120µm) and varying lengths (between 440 and 1310µm) in a TLM structure. The TCR was obtained by measuring the resistivity with varying stage temperatures in the range of -40°– 100°C. The electrical resistivity of the nanolaminate increases and the TCR changes from positive to negative as the AlN content is increased from 0 to 44%, with zero TCR (and resistivity ~450 µΩ·cm) around ~20% (FIG. 2). Microstructure analysis shows that the $Ti_xAl_{1-x}N$ films most likely consist of metallic TiN crystallites embedded in the semiconducting $Ti_yAl_{1-y}N$ amorphous matrix (Fig. 3). Near-zero TCR value of these films is achieved by a superposition of the conduction mechanism inside the conductive TiN crystallites and charge transfer between them through the insulating/semiconducting $Ti_yAl_{1-y}N$ matrix. Both resistivity and TCR in our laminate nitride films were found to be stable for thermal treatment of 500°C/1 h. An insignificant increase in these properties after the post-deposition annealing can be attributed to surface oxidation of the uncapped films. The zero TCR behavior of our nitride films can be achieved in as-deposited films, making them compatible with BEOL process of microelectronic fabrication (350°C – 450°C/1 h), unlike present zero-TCR technology (SiCr-based), which requires annealing at temperature ~550°C. These results pave the way toward BEOL-compatible near-zero TCR thin film resistors, which can significantly reduce capacitance and minimize design complexity of passive analog IC components.

AA17-6 Influence of H_2S Dosage on Surface Roughness of Zn(O,S) Films by Atomic Layer Deposition (ALD)

Narmatha Koothan*, T. Chou, Y. Yu, W. Cho, J. Su, C. Kei,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Zn(O,S) is a material commonly used as n-type buffer layer in solar cells such as CIGS, CZTS to replace toxic CdS. The optical bandgap of Zn(O,S) can be varied by adjusting the ratio of oxygen to sulfur ratio. The optical and electrical properties of the buffer layer is a crucial factor in photovoltaic devices. Optimization of the optical properties leads to the increase of light absorption in low wavelength region. Beside the optical bandgap, surface roughness, another important property, is essential in solar cell applications. The high surface roughness of the film influences the absorber/buffer layer interface and also increases the reflectance of device. Therefore, we analyzed the influence of H_2S dosage on the surface roughness of Zn(O,S) films. ALD is adapted to deposit the ZnOS films because of its precise control of thickness and composition. In this study, Zn(O,S) film with the ratio of m: n (ZnO: ZnS) 11:1 were grown by ALD. ZnO was deposited with the ALD sequence of 0.2 s of Diethyl Zinc (DEZ), 0.1 s of H_2O separated by 30 s of N_2 purge. ZnS was deposited with the ALD sequence of 0.2 s of Diethyl Zinc (DEZ), 0.1 s of H_2S separated by 30 s of N_2 purge. The schematic diagram of Zn(O,S) deposition is shown in Fig.1. To study the influence of H_2S dosage on the surface roughness, ZnOS 11:1 ratio films with the H_2S dosage of 0.1, 0.3, 0.5 & 1 s were prepared by ALD. The elemental composition of these materials were analyzed by X-ray electron spectroscopy (XPS), shown in Table 1. Fig.2 shows the increased Surface roughness of Zn(O,S) with the increase in H_2S dosage, measured by Atomic force microscope (AFM) . The changes in transmittance and reflectance with the changes in surface roughness, were studied by UV-vis spectrophotometer.

AA17-7 Bias-Enhanced Atomic Layer Annealing for the Deposition of High-Quality Aluminum Nitride Films on Silicon

Aaron McLeod*, S. Ueda,* University of California at San Diego*; D. Alvarez,* RASIRC*; A. Kummel,* University of California at San Diego

High-quality AlN films are promising for use as buffer layers for the growth of GaN and InGaN on Si and SiC for use in RF and micro-LED devices. Known deposition methods include metal organic chemical vapor deposition (MOCVD) and sputtering, which both present integration concerns: MOCVD requires high (>700°C) temperature while reactive sputtering yields strained, randomly oriented films.[1-2]

Bias-enhanced atomic layer annealing (ALA) allows for lower temperature deposition of crystalline materials by adding ion bombardment to the end of each atomic layer deposition (ALD) cycle. The substrate is mounted on a negatively biased stage heater and ions are accelerated from the plasma source towards the growth surface.[3] This bombardment enhances surface adatom mobility, leading to the deposition of crystalline films.

Tris(dimethylamido)aluminum (III) and anhydrous hydrazine (N_2H_4) (Rasirc) are used as precursors, while Ne, Ar, or Kr plasma was used for the 20s ion bombardment. For all samples, 500 cycles of ALA AlN (~40 nm) was deposited on HF-cleaned Si (111) substrates at 400 ˚C using -10V, -25V, and -40V bias for each plasma gas. In-vacuo x-ray photoelectron spectroscopy (XPS) and ex-situ grazing-incidence x-ray diffraction (GIXRD) and x-ray reflectivity (XRR) were used to determine chemical and structural composition of the films.

As seen in the GIXRD and XRR data in Fig. 1, all conditions yielded preferential AlN (002) orientation and density within 3% of bulk AlN. The full width at half max of the AlN (002) diffraction peak decreases with increasing ion momentum, indicating the growth of larger crystallites. Chemical composition data from XPS (not shown) indicate stoichiometric AlN with low impurity content of 1.2-4.9 At. % and 1.3-2.5 At. % for C and O, respectively.

Using the Ar -25V ALA condition, 20nm films were deposited to template further AlN growth by reactive sputtering. The GIXRD results of this study, as well as reference films of only sputtered material are shown in Fig. 2. It is observed that the ALA layer successfully suppresses the growth of AlN (103) and promotes (002) oriented growth. In summary, it was found that the crystallinity of the ALA AlN films could be tuned by controlling ion momentum and that these films successfully template sputtered AlN. The strong preferential orientation seen in these studies will allow these films to more effectively be used as templating layers for further GaN or InGaN growth.

[1] Liaw, H. M. *et al.* Solid-State Elec. **44**, 4 (2000)

[2] Meng, W. J. *et al.* J. App. Phys. **74**, 4 (1993)

[3] Shih, H. Y. *et al.* Sci. Rep.**7**, 39717 (2017)

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AA17-8 Atomic Layer Deposition of Nio for the Modification of Electro-Catalysts for Alkaline Water Splitting

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Different catalytically active oxides are being used as electrode materials for electro-chemical water splitting under alkaline conditions. The catalytic performance of those materials strongly depends on surface composition and morphology. Modifying the surface of such electrodes to increase the number of potentially active sites offers the opportunity to increase the electrode's catalytic efficiency.

We report the synthesis of NiO modified oxides via ALD directly onto the high-surface area electrodes. The developed ALD process for NiO relies on the use of Bis(cyclopentadienyl)nickel(II) and ozone in a thermal ALD process. The composition, morphology, and crystallinity of the deposited film were controlled by varying different deposition parameters. The varying amount, size, and morphologyof the metal oxide catalysts were homogeneously deposited onto a series of metal oxides. The structural and morphological properties as well as the performance and stability in the electrocatalytic oxygen evolution reaction in alkaline media were investigated in a 3-electrode rotating disc setup in order to elucidate performance-controlling parameters.

AA17-11 Plasma-Resistant Mixed Metal Oxide Films*, **Vasil Vorsa**, A. Pavel,* Greene Tweed & Co.

To prevent contamination of microelectronic devices during semiconductor processing, chamber components of semiconductor tools are often coated with high purity ceramic coatings such as alumina or yttria that exhibit high resistance to plasma erosion in halogen environments.However, even these materials exhibit erosion over time leading to lower yield and costly down time, especially as the industry moves to smaller node sizes.

To overcome these limitations, there has recently been a major effort (Refs) to find new coating materials and processes leading to improved plasma erosion resistance. There are now emerging plasma-resistant coatings deposited by atomic layer deposition (ALD). Advantages of ALD include conformal, dense, and pinhole-free film that can coat complex 3D shapes and high-aspect ratio holes.

In this work, a number of single component and multi-component metal oxide films (homogeneous and nanolaminate) were evaluated for plasma etch resistance.While normal ALD pulsing schemes were employed to deposit single component Al2O3, SiO2, Y2O3, ZrO2 films, YAlO, YSiO, and YZrO films were deposited by various pulsing schemes including sub and super cycles normally used to deposit nanolaminate films and pulsing schemes to simulate codeposition.The films were then subjected to plasma etching in a fluorine-argon environment utilizing a capacitively-coupled parallel plate plasma reactor.Plasma resistance of each film was assessed through calculating etch rates as measured by thickness changes using ellipsometry and fluorine penetration by XPS depth profiling.

AA17-14 Super-Cycle Atomic Layer Deposition of Indium Gallium Zinc Oxide*, **Paul Plate**, L. Marth, F. Naumann,* SENTECH Instruments GmbH, Germany*; A. Mahmoodinezhad, C. Janowitz, K. Henkel, J. Flege,* BTU Cottbus, Germany

Indium gallium zinc oxide (IGZO) is a promising candidate as a transparent conductive oxide (TCO). The amorphous phase of this compound shows a band gap of 3.0 eV and exhibits a high charge carrier mobility and concentration with reported values of 50-80 cm^2/Vs and 10^{17}-10^{20} cm^{-3}, respectively. [1,2] Therefore, it is well suited for photovoltaic applications, light emitting diodes, and thin film transistors. In contrast to single crystalline TCO's, it is much easier and cheaper to realize IGZO films. To date, the established deposition methods for IGZO layers such as DC/magnetron sputtering and pulsed laser deposition fail when the deposition of uniform films over a large substrate area is required. Also, controlling the elemental composition of the quaternary system is crucial for achieving the desired electrical properties. Atomic layer deposition (ALD) can meet both challenges by combining the ALD cycles of their respective binary compounds in a distinct sequence and ratio. This so-called super-cycle process allows controlling the composition of the target film by adjusting the individual cycle ratio.

In this work, we present a approach to deposit IGZO films by ALD. The depositions have been carried out in a SENTECH plasma-enhanced ALD (PEALD) reactor, in which we applied a thermal process for zinc oxide (ZnO) as well as plasma-enhanced processes for gallium and indium oxide (Ga_2O_3, In_2O_3). The growth mechanism of each individual process within the super-cycle has been investigated and monitored by *in-situ* ellipsometry (i-SE, SENTECH ALD Real-Time-Monitor). An *ex-situ* analysis of the compound has been performed by X-ray photoelectron spectroscopy (XPS) to determine the film composition and correlate it to the expected values based on the super-cycle sequence.

The i-SE revealed a nucleation delay for the thermal ZnO process, making it challenging to properly adjust the cycle ratio. Thus, the thermal ZnO cycle has been replaced by a plasma-enhanced ZnO process, which shows no nucleation delay. In further *in-situ* investigations a higher growth rate for the PEALD-ZnO deposition on a Ga_2O_3 surface than on an In_2O_3 surface was observed. Based on this knowledge, we were able to set-up the ideal cycle sequence for the IGZO process. Accordingly, XPS revealed a direct correlation between the applied cycle ratio and the elemental composition of the film. Together, these findings confirm that a full PEALD super-cycle process is an effective approach to deposit well-defined IGZO films.

[1] P. Barquinha, L. Pereira, G. Gonçalves, R. Martins, E. Fortunato, J. Electrochem. Soc. 156 (2009) H161

[2] H. Hosono, J. Non-Cryst. Solids 352 (2006) 851.

AA17-17 Effect of Precursor on Deposition Behavior of ZrO_2 Atomic Layer Deposition*, **Younsoo Kim**, Y. Cho,* Samsung Electronics, Korea (Republic of)*; T. Shiratori, N. Yamada,* ADEKA, Japan*; S. Ryu, S. Kang, S. Chung, H. Kim, J. Seo, M. Park, J. Lim, J. Choi, H. Jung, H. Lim,* Samsung Electronics, Korea (Republic of)

Abstract

As design rule of semiconductor device decrease continuously, a wide variety of high-k materials have been evaluated including ZrO_2, HfO_2, TiO_2, and $SrTiO_3$. Among of them, ZrO_2 is the most commonly used dielectric material in Dynamic Random Access Memory (DRAM) capacitor [1-3]. However, Atomic Layer Deposition (ALD) of transition metal materials such as ZrO_2 doesn't show an ideal behavior and the fundamental understanding about correlation of precursor and deposition is needed to develop ZrO_2 ALD process having high quality [4].

In this study, we have investigated deposition behavior of ZrO_2 ALD using [Tetrakis(EthylMethylAmino)Zirconium] (TEMAZ) and [Cyclopentadienyl(Tris(DiMethylAmino))Zirconium] (CTDMAZ) precursors. TEMAZ and CTDMAZ showed different deposition rates and maximum deposition temperature within ALD window, which were related to the thermal stability of Zr precursors. The thermal stability of precursors was related to the effective atomic number (EAN) around the central metal and showed higher value in case of higher electron configuration. Zr atoms of TEMAZ and CTDMAZ have 8e and 12e configuration, respectively. Consequently, CTDMAZ showed 30°C higher thermal stability and 20°C higher ALD maximum temperature than those of TEMAZ.

In the electrical characteristics of the $TiN/ZrO_2/TiN$ capacitor, the dielectric constant and leakage current density were improved when the ZrO_2 film using CTDMAZ was deposited at a high temperature. Analysis of physical properties showed that impurities were reduced and bandgap increased in the ZrO_2 film using CTDMAZ at high temperature.

References

1. J.-M. Lee et al., IEEE Electron Device Lett. 38(11), 1524, (2017).
2. S. K. Kim et al., Adv. Mater. 20, 1429, (2008).
3. M. Popovici et al., Phys. Status Solidi RRL 10(5), 420 (2016).
4. V. Miikkulainen et al., J. Appl. Phys. 113, 021301 (2013).

AA17-20 Gas-Sensing Properties of Hierarchical Core-Shell Nanofibers: Radial Modulation of Hole-Accumulation Layer*, M. Raza,* Humboldt University Berlin, Germany*; K. Movlaee,* University of Messina, Italy*; S. Santangelo,* University of Raggio Calabria, Italy*; G. Neri,* University of Messina, Italy*; **Nicola Pinna**,* Humboldt University Berlin, Germany

Semiconducting metal oxide (SMOX) based heterostructured gas sensors have been applied in a wide range of environmental and safety applications. However, structurally well-defined hierarchical core-shell heterostructures are needed in order to illustrate their charge transfer and gas sensing properties. Herein, one-dimensional hematite nanofibers (NFs) were selected as a robust substrate in order to provide a high surface area to the sensing films. Firstly, hematite NFs were synthesized by electrospinning method. Secondly, in order to produce hierarchical p-MOX/hematite core-shell nanofibers (CSNFs), these NFs were coated with well-controlled p-type SMOX shell layers with varying thicknesses by atomic layer deposition (ALD).

The morphological and structural analysis confirmed a conformal coating of the hematite NFs with SMOX shell layer depicting a hierarchical core-shell like architecture, where the thickness of the shell layer was precisely controlled by varying the number of ALD cycles. The DC electrical resistance analysis showed a significant effect of the shell thickness to the baseline conductance and ultimately the gas-sensing properties of the core-shell heterostructures. In addition, the sensing-response of the proposed sensors were studied towards different concentration of the target analytes such as VOCs, hydrogen, CO, NO2 and NO. The gas-sensing response along with the other properties of the CSNFs were optimised in terms of the thickness of the p-type shell thickness and a plausible sensing and transduction mechanism is proposed.

AA17-23 Developing a Model for Describing the Effect of Dispersion of P-Type Co-Catalyst on Photocatalytic Activity Using ALD Prepared CuO_X/TiO_2 Photocatalyst, ***Saeed Saedy**, N. Hiemstra, D. Benz,* Delft University of Technology, Netherlands*; H. van Bui,* Phenikaa University, Viet Nam*; J. van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) offers promising solutions for synthesizing well-defined advanced functional nanomaterials such as photocatalysts. Among different photocatalytically active materials, TiO_2 shows an excellent potential for large-scale application; however, it suffers from limited activity to UV light. The decoration of TiO_2 with ultra-fine semiconductor particles with a small band-gap can expand its activity by providing excited electrons/holes from the clusters. However, obtaining the optimum amount/size of co-catalyst is a big challenge for maximizing the photo-activity of TiO_2 in a cost-effective way.

The possibility of depositing uniform nanoparticles (NPs) on the support with controlled size, shape, and morphology using ALD provides an excellent opportunity to obtain high activity photocatalysts with well-controlled structure. We deposited copper oxide (CuO_x) NPs on AEROXIDE® P25 titanium dioxide NPs using a fluidized bed ALD reactor at 250°C using Cu(I)(hfac)(TMVS) and water. The ALD synthesized CuO_x/TiO_2 samples were examined using ICP-OES, TEM, and XPS methods, and were employed as photocatalysts for the solar production of H_2.

A combination of different precursor/co-reactant pulse times and the number of ALD cycles resulted in CuO_x/TiO_2 samples with Cu loading in the range of 0.7-4.8 wt.%. The XPS analysis indicated a mixture of Cu^{1+} and Cu^{2+} in samples that the Cu^{2+} content increases by the increase of Cu content. The averageCuO_x size of samples with Cu content up to 3.8 wt% was about 1.6 nm; the higher Cu concentration resulted in larger clusters. The CuO_x/TiO_2 samples showed significant H_2 productivity improvement compared to pure P25, with about ten times higher produced H_2 for the optimum sample (2.3 wt.% Cu). The higher Cu loading resulted in activity loss.

The evaluation of the H_2 productivity of these samples allowed us to develop a model to describe the activity of CuO_x/TiO_2 photocatalyst as a function of CuO_x loading via predicting the increased photocatalytically active perimeter of Cu_xO clusters; this perimeter is characterized by a higher activity compared to a bare photocatalyst as a result of the injection of photo-excited electrons to the support from co-catalyst. The model results fit well with the experimental data. The XPS spectra of samples showed Ti^{4+} reduction to Ti^{3+} after Cu ALD, with linear increase and plateauing of Ti^{3+} at Cu content of about 2.3 wt.%. Such behavior is predicted precisely by the developed model. This model enables us to predict the optimum CuO_x loading of the CuO_x/TiO_2 system for different particle sizes. This model can be employed for other p-type semiconductor materials as well.

AA17-26 Low-Temperature Deposition of Highly Conformal TiN Films on Pt/C Nanoparticles via Plasma-Enhanced Ald for Fuel Cell Applications*, S. Ilhom, R. Godoy, A. Mohammad, D. Shukla,* University of Connecticut*; M. Kattan, N. Solomatin, Y. Ein-Eli,* Technion, Israel*; J. Jankovic,* ***Necmi Biyikli,*** University of Connecticut

In this work, we present our efforts on the growth of highly conformal titanium nitride (TiN) films on nano-powders via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD). The goal is to deposit a thin protective TiN layer on a Pt/C catalyst for proton exchange fuel cell application in order to prevent carbon corrosion during operation. TiN films were deposited on Pt/C nano-particles (bare and Oleylamine coated) using tetrakis(dimethylamino)titanim(IV) (TDMAT) and Ar/N_2 plasma as the metal precursor and nitrogen co-reactant, respectively. Oleylamine is used to selectively coat Pt catalyst particles and prevent TiN film from formation on them, while carbon is being coated. ALD growth experiments have been performed at 150 °C process temperature. Nano-powders were placed inside a custom-made agitator mechanism to ensure conformal film growth around the particles. Additionally, Si(100) substrate was included in the reactor to serve as a reference sample. Each unit ALD-cycle consisted of 100 msec TDMAT pulse, 10/10 sec purge, and 10 sec plasma exposure at 50 W using Ar/N_2 (50/50 sccm) plasma chemistry. *Ex-situ* multi-wavelength ellipsometry measurements revealed the TiN film growth-per-cycle (GPC) on Si(100) sample at ~0.94 Å/cycle. Bright field Transmission Electron Microscopy (TEM) and High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) were employed to confirm conformal growth of the TiN film on the nanoparticles at the atomic-scale resolution. Additionally, Energy Dispersive Spectroscopy (EDS) mapping was performed to understand the elemental composition of the TiN coated Pt/C nano-powders. The TEM micrographs combined with the elemental EDS analysis demonstrated that homogenous TiN film is formed on Pt/C nanoparticles, having an average thickness of ~5 nm.

AA17-29 Low Temperature Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Films Deposited by Thermal Atomic Layer Deposition Using High Purity H_2O_2*,* ***Jin-Hyun Kim****, Y. Jung,* University of Texas at Dallas*; S. Hwang,* university of texas at dallas*; H. Arriaga, J. Mohan, D. Le,* University of Texas at Dallas*; D. Alvarez, J. Spiegelman,* RASIRC*; J. Kim,* University of Texas at Dallas

To implement HZO films to three-dimensional structures and back end of line applications, utilizing atomic layer deposition (ALD) technique, low thermal budget and high conformality are necessary. One of the most well-known ways to reduce the process temperature is to use oxygen plasma as oxygen source [1], However, because of the anisotropic nature of plasma-enhanced ALD with oxygen plasma, using thermal ALD (tALD) is preferable in the aspect of achieving conformal deposition on three-dimensional structures.

In this study, we have demonstrated ALD of HZO films using high purity H_2O_2 in comparison with O_3/O_2 mixture (340 g/m^3) as oxidants. Metal-ferroelectric-metal (MFM) capacitors were fabricated on thermally grown 300 nm SiO_2 layer. 90 nm TiN top and bottom electrode deposited by reactive sputtering and 10 nm HZO with Hf:Zr ratio of 1:1 was deposited between the electrodes using tALD with TDMA-Hf, TDMA-Zr, O_3, and H_2O_2 at 250 °C. The MFM stack then annealed for 60 s under N_2 atmosphere varying 300 °C to 400 °C using rapid thermal annealing (RTA) and patterned to form Au/Pd hard mask to define the area of MFM capacitors. With H_2O_2, higher growth per cycle (GPC) of 0.24 nm/cycle compared to 0.19 nm/cycle for O_3 was observed. Interestingly, even with high GPC HZO films, x-ray reflectometry results showed that with H_2O_2, the HZO film was denser (8.5 g/cm^3) than using O_3 (8.2 g/cm^3). After 400 °C RTA annealing, both HZO samples experienced orthorhombic phase growth with suppressed monoclinic phase growth was observed by X-ray diffraction. Polarization-electric field hysteresis curves and pulse write/read measurement were performed after 10^5 wake-up cycles at 2.5 MV/cm field. HZO samples using H_2O_2 showed higher remnant polarization ($2P_r$) of 62 μC/cm^2 and O_3 showed $2P_r$ of 54 μC/cm^2. Moreover, the HZO samples using H_2O_2 started to exhibit ferroelectric properties from 325 °C, but this was not observable in the case of O_3 at the same temperature, which implies the capability of H_2O_2 for low-temperature applications. Also, HZO using H_2O_2 had lower leakage current and better endurance compared to O_3 samples, and both showed similar breakdown behaviors at 3 MV/cm. Low carbon content (<1 at%) in both samples confirmed by X-ray photoelectron spectroscopy supports this result and shows the capability of carbon removal in both oxidants.

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[1] Takashi Onaya et al., ME 215 (2019) 111013.

AA17-32 Effect of NH_3 Flow on Electrical and Mechanical Properties of ALD TiN Thin Films*,* ***Hyunchol Cho****,* Eugenus, Inc., Korea (Republic of)*; B. Nie,* Eugenus, Inc.*; A. Dhamdhere,* Eugenus, Inc., India*; Y. Meng, M. Neuburger,* Eurofins EAG Materials Science*; J. Mack,* Eugenus, Inc.*; J. Ahn,* Hanyang University, Korea (Republic of)*; S. Jung, H. Kim,* Eugenus, Inc., Korea (Republic of)

In recent nano-scale device applications, especially in DRAM capacitor electrodes, ALD TiN films have been used due to the excellent physical and electrical properties. However, it is necessary to improve mechanical properties such as hardness and modulus, especially under 30 nm film thickness, because ALD TiN films can be easily bent and/or broken during the following integration steps. From the perspective of the intrinsic ALD TiN film property improvement, many studies have been conducted on the ALD TiN thin-film physical and electrical properties, however, there are not many reports focused on mechanical properties such as hardness and modulus. In this paper, we report on the strong relationship between ALD TiN thin-film mechanical and electrical properties and NH_3 flow rate, especially on thinner films from 25 nm to 150 nm.

AA17-35 ALD Al_2O_3 and MoS_2 Coated TiO_2 Nanotube Layers as Anodes for Lithium Ion Batteries*, H. Sopha, R. Zazpe,* Uni Pardubice, Czechia*; T. Djenizian,* Ecole de Mine, France*;* ***Jan Macak****,* Uni Pardubice, Czechia

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

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

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

References

1. B.L. Ellis, P. Knauth, T. Djenizian, Adv. Mater. 26 (2014) 3368
2. G. F. Ortiz et al., Chem. Mater. 21 (2009), 63.
3. T. Djenizian et al., J. Mater. Chem. 21 (2011) 9925
4. Y. S. Jung et al., Adv. Mater. 22 (2010) 2172
5. E. M. Lotfabad et al., Phys.Chem. Chem. Phys., 15 (2013) 13646
6. M. Y. Timmermans et al., J. Electrochem. Soci., 164 (2017) D954.
7. D. K. Nandi et al., Electrochim. Acta 146 (2014) 706.
8. H. Sopha et al., ACS Omega 2 (2017) 2749.
9. H. Sopha et al., FlatChem 17 (2019) 100130

10)A. Teklit Tesfaye et al., Nanomaterials 10 (2020) 953.

AA17-38 Experimental Ru Precursors for Cutting Edge ALD & CVD Processes*, **Ivan Zyulkov**,* Umicore, Belgium*; W. Schorn,* Umicore, Germany*; S. Tymek, J. Bachmann,* University of Erlangen-Nuremberg, Germany*; S. Armini, G. Pourtois,* IMEC, Belgium

Integrated circuits downscaling constantly enforces stringent requirements on various properties of functional and sacrificial materials in a device stack, which leads to multiple challenges in process development. Process engineers are working on solutions to pattern alignment and placement error issues, on improvement of etch processes selectivity and line edge roughness, on selective deposition of functional layers and sacrificial hard-mask materials, on ultra-thin layer closure and many others. In addition to the downscaling trend, a general transition to new 3D device architectures is happening in both logic and memory. To deliver deposition processes in compliance with all the requirements mentioned above, ALD and CVD technologies start to play a much more significant role in the process development toolbox than ever before. And new metal precursors with superior volatility and preferential surface reactivity are needed to make cutting edge ALD and CVD processes possible. These new tailor-made precursors enable wider process parameter space, lower chemical consumption and higher process efficiency in comparison with standard on-shelf precursors.

One of the materials expected to be introduced into HVM within the next couple of years is Ruthenium (Ru). Ru is commonly exploited as a liner for copper electroplating and electroless copper deposition. It has a relatively low bulk resistivity (7.1 μΩ cm), a conductive oxide and a high work function (> 4.7 eV). While the demand of Ru precursors for advanced vapor deposition processes is increasing, concerns arise regarding the stability and sustainability of their supply. Industry demands a robust and undisturbed supply chain while the availability of Ru metal on the market is limited, essentially as Ru appears as side product in platinum metal mining and is required in a few industrial applications only. As a major supplier of platinum group metals, Umicore has access to Ru from recycling and metal refining activities and will be a major contributor to provide availability.

In this work we report the development of a Ru ALD precursor from ideation phase, through material supply chain set up and precursor synthesis all the way to thin film property evaluation. We target several Ru applications in IC manufacturing, such as BEOL bottom-up via prefill, conformal Cu liner deposition and area-selective hard-mask deposition for self-aligned block application. We will present our methodology, precursor chemical characterization data and Ru layer properties, such as chemical composition measured by XPS and substrate-dependent selectivity measured by SE and RBS.

AA17-41 Characterization of Al Doped SnO_2 Thin Films With Various Doping Positions Using Atomic Layer Deposition*, **Hyunwoo Park**, N. Lee, Y. Choi, S. Song, J. Lee, G. Lee, E. Lee, S. Lee, H. Jeon, C. Jung,* Hanyang University, Korea

Oxide semiconductors have begun to be used in thin film transistors (TFTs) as a channel layer. Oxide semiconductors are used for a variety of applications due to their advantages such as wide band gap and low process temperature. However, since indium (In) is a rare element that is not abundant on earth, there are problems associated with mass production. Tin (Sn) is an element adjacent to indium on the periodic table, and both Sn^{4+} and In^{3+} have an electron structure of [Kr] $4d^{10}5s^0$, which has a good influence on the electrical characteristics due to the superposition of states of the large s orbital. Tin oxide (SnO_2) has many advantages for applications to thin film transistors such as high transmittance, wide bandgap, and high conductivity.However, the high conductivity tends to reduce the on/off current ratio of TFTs. Therefore, there is a need for a doping method that can reduce the conductivity. In this respect, it has been reported that aluminum (Al) atoms act as suppressors to decrease the conductivity of SnO_2 films. Among the gas phase depositions, atomic layer deposition (ALD) has benefits such as excellent step coverage, uniformity, and thickness control. Also, ALD involves injecting an appropriate amount of dopant into thin films using a cyclic system while controlling the chemical quantities. Another important advantage of ALD is that the dopant can be inserted into the ALD cycle in any order, which makes it very easy to control the position of the dopant. Therefore, it is possible to study the characteristics of thin film transistor achieved by adjusting the doping position of the thin film channel through the ALD process.

In this work, we investigated characterization of SnO_2 thin films with a single Al_2O_3 cycle at various positions using ALD. SnO_2 thin films were deposited with TDMASn, TMA and ozone as a Sn, Al and oxygen sources, respectively. The Al doping positions are investigated using secondary ion mass spectroscopy (SIMS) in 20 nm thickness of SnO_2 thin films. The crystallinity and thickness were analyzed by transmission electron microscope (TEM). The single Al_2O_3 cycle is not affected to crystallinity of SnO_2. Also, on/off current ratio of thin films transistor are changed according to Al doping position using semiconductor analyzer (Agilent B1500A). We also characterize the bonding states and carrier concentration of SnO_2 thin films by analyzing X-ray photoelectron spectroscopy (XPS), and Hall effect measurement. We will present more results in the meeting and will discuss SnO_2 application areas.

ALD Applications
Room On Demand - Session AA2
Energy: Solar Energy Materials

AA2-1 Synthesis of a Composite Dielectric With Conformal Coating of Aluminium Nitiride Over the Distribution of Titanium Nitride Nanoparticles, for Concentrated Solar Power Applications*, **Nikhar Khanna**, M. El Hachemi,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Solar-thermal energy conversion is a promising technology that enables efficient energy harvesting from concentrated solar power (CSP). Recently, there is a lot of interest in metal -insulator based metamaterial absorbers due to complete hold on the permittivity and permeability of these absorbers. In our case the metamaterial absorber would consist of near homogeneous distribution of nanoparticles (Titanium Nitride) in a matrix of (Aluminium Nitride) to form a composite, and an omega shape resonator to couple the electric and magnetic field component of the incoming electromagnetic wave.

Electromagnetic wave absorbers have been investigated for many years with the aim of achieving high absorbance and tunability of both the absorption wavelength and the operation mode by geometrical control, small and thin absorber volume, and simple fabrication.

The present work involves the synthesis of a composite dielectric of approximately 1 µm thickness where nanostructure control is a very challenging task. In this work, we choose a bottom-up approach by constructing a stack of, TiN nanoparticles distribution over a substrate and then a layer of Aluminium Nitride of (85-90nm) thickness, and so on. Titanium nitride particles laid on Si wafer by wet chemical method are coated with conformal coating of Aluminium Nitride, via Plasma- enhanced

Atomic Layer deposition. These components together form the dielectric, which helps in transporting the generated heat in the solar absorber. The control of the morphology at the nanoscale is primordial to improve the material's optical performance, thus in our case maximise the wave extinction inside the composite for the application as solar absorber. The optical properties of the dielectric are measured by ellipsometry and UV-Visible measurements.

In order to choose a composite that is best suited for our requirement, two types of composites were prepared. One with Titanium Nitride powder with particles in the range 20-30 nm with a layer of Aluminium Nitride on top of it, and the other with Titanium Nitride dispersions also with particles in the range 20-30nm with a layer of AlN on top. In both the cases, fewer clusters of 500nm to1um of TiN were present however, enough steps were taken to minimize these clusters into smaller particles.

In conclusion, the work presented here is the comparison of the two kinds of composites with their optical properties (n, k) measured by ellipsometer, and (absorbance, reflectance) measured by UV-Visible Spectroscopy.

AA2-2 *Interface Chemistry in Metal Halide Perovskite/ALD Metal Oxide Systems, Andrea E.A. Bracesco*, *C. Burgess, A. Todinova,* Eindhoven University of Technology, Netherlands*; V. Zardetto,* Solliance Solar Research, Eindhoven, Netherlands*; D. Koushik, W. Kessels,* Eindhoven University of Technology, Netherlands*; I. Dogan,* Solliance Solar Research, Eindhoven, Netherlands*; C. Weijtens,* Eindhoven University of Technology, Netherlands*; S. Veenstra, R. Andriessen,* Solliance Solar Research, Eindhoven, Netherlands*; M. Creatore,* Eindhoven University of Technology, Netherlands

The conversion efficiency of perovskite solar cells, PSCs, has surpassed 25%.[1] The present PSC architecture includes organic charge transport layers, CTLs, which in certain cases limit the long-term stability and device's efficiency. Metal oxide CTLs, such as ALD metal oxides, are deemed valid alternatives. Among them, NiO and $SnO_{2,}$ always processed prior to the synthesis of the absorber, are adopted as hole, HTL, and electron transport layers, ETL, respectively.[2,3] Instead, ALD processing directly on top of the perovskite is a major challenge yet to be solved. A well-known example is SnO_2: processed directly on perovskite leads to poor cell performance.[4,5,6] Instead, with the inclusion of an organic buffer layer, it leads to highly efficient and stable devices.

In this contribution[7], we systematically investigate the chemical changes occurring at a $CsFAPb(I,Br)_3$ perovskite (sub-)surface upon ALD growth of SnO_2 and TiO_2. TiO_2 is less investigated in literature, but it allows the comparison in terms of reactivity of the perovskite to similar ALD metalorganic precursors, namely tetrakis(dimethylamido)-Sn(IV) (TDMA-Sn) and TDMA-Ti(IV), with H_2O as the co-reactant in both cases.

The bulk crystalline structure of the perovskite absorber is not affected by the ALD growth, as inferred by XRD analysis. Instead, XPS analysis reveals that the growth of SnO_2 is accompanied by the formation of molecular halide species at the perovskite/metal oxide interface. In parallel, the initial growth of SnO_2 is characterized by sub-stoichiometry and sub-gap defects present above its valence band maximum, associated to Sn(II) states, as observed by UPS. We speculate that a redox reaction involving Sn(IV) metal centers of the ALD precursor and halide anions in perovskite occurs, leading to the reported defects. These sub-gap states are expected to reduce the charge selectivity of SnO_2, since they can promote hole injection from the perovskite valence band to that of SnO_2, thus inducing non-radiative electron-hole recombination. The chemical changes and the decreased charge selectivity at the perovskite/SnO_2 interface support the poor performance of devices with SnO_2 grown directly on top of the absorber. As for TiO_2, instead, we observe limited chemical modifications. Devices employing TiO_2 directly grown on perovskite, show a promising (unoptimized) efficiency of 11%.

[1] J. Yoo et al., Nature 2021

[2] D. Koushik et al., J. Mat. Chem. C 2019

[3] Y. Kuang et al., ACS Appl. Mater. Interfaces 2018

[4]K.O. Brinkmann et al., Sol. RRL 2020

[5] A. F. Palmstrom et al., Adv. Energy Mater. 2018

[6] A. Hultqvist et al., ACS Appl. Energy Mater. 2021

[7] A.E.A. Bracesco et al., JVSTA 2020

AA2-3 ALD of Lead Halide Perovskites*, Jake Vagott*, *K. Bairley, A. Castro Mendez, C. Perini, J. Correa-Baena,* Georgia Institute of Technology

Perovskite solar cells (PSCs) have quickly risen in efficiency since their initial fabrication in 2009, with the current record power conversion efficiency (PCE) being 25.2% [1]. Quickly approaching the Shockley—Queisser limit of 33% for single-junction solar cells, stability and scalability research has become crucial. While solution deposition of the perovskite absorber layer by spin-coating has resulted in the highest efficiency devices so far, vapor deposition methods have shown promise and may help resolve both the stability and scalability problems that PSCs are currently facing. Atomic layer deposition (ALD), as a vapor deposition process, provides advantages such as fine thickness control, improved conformity, high uniformity, and ability to be incorporated into existing industrial processes such as roll-to-roll manufacturing. The stoichiometry of the perovskite may also be easily tuned through manipulation of the precursor doses. My work focuses on depositing perovskite through a two-step ALD/ molecular layer deposition (MLD) hybrid process, with ALD referring to the inorganic aspects of the process and MLD incorporating organic materials. The first step, which we have recently achieved, is to deposit a conformal lead iodide film which may be converted to methylammonium lead triiodide ($MAPbI_3$) through exposure to methylammonium iodide (MAI). For the lead precursor, $Pb(dmamp)_2$ was chosen as it is more volatile than other common lead precursors such as $Pb(acac)_2$ and has not shown signs of CVD—like growth which has been the case with $Pb(tmhd)_2$ [2]. HI (aq) was chosen as the iodine precursor due to its high vapor pressure and reactivity. The precursors involved are easily accessible through commercial means and do not require any additional processing before use. The second step, which we are currently developing, involves the introduction of a third precursor within every cycle of the previous recipe, which would allow for an effective ALD/MLD process for $MAPbI_3$. Once we are able to deposit highly uniform perovskite thin films by ALD/MLD, this will allow us the ability to deposit 2D perovskite passivation layers which will help improve stability by decreasing defects at the perovskite/charge transport layer interface. This will increase moisture and thermal stability in the PSCs while also being a scalable process.

References

[1] Yoo, Jason J., et al. "Efficient Perovskite Solar Cells via Improved Carrier Management." *Nature News*, Nature Publishing Group, 24 Feb. 2021

[2] Strnad, Nicholas. "ATOMIC LAYER DEPOSITION OF LEAD ZIRCONATE-TITANATE AND OTHER LEAD-BASED PEROVSKITES." *Thesis / Dissertation ETD*, Digital Repository at the University of Maryland, 2019.

AA2-4 Atomic Layer Deposition of $Zn_{1-x}Mg_xO$ as Transparent Conducting Films for Chalcopyrite Solar Cells*, Poorani Gnanasambandan,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; M. Sood,* University of Luxembourg*; N. Adjeroud,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; R. Leturcq,* luxembourg Institute of Science and Technology (LIST), Luxembourg*; S. Siebentritt,* University of Luxembourg

We investigate atomic layer deposited zinc magnesium oxide films with varying Mg content as transparent conducting films and as electron transport layers for chalcopyrite solar cells. Previous studies on the impact of $Zn_{1-x}Mg_xO$:Al as transparent electrodes and Mg doped ZnO thin films for the window layer of CIGS $Cu(In,Ga)(S,Se)_2$ solar cells employed co-sputtering, electrodeposition and ALD respectively [1][2][3][4]; these were limited to fixed composition and deposition temperatures. We examine the effect of $Zn_{1-x}Mg_xO$ films, deposited by atomic layer deposition (ALD) under different growth conditions, on the performance of high-bandgap solar cells based on $Cu(In,Ga)S_2$ absorbers.

Optimizing a ternary process by mixing two binary ALD process has its challenges [5]. We achieve high degree of control on composition by optimizing the growth conditions with varying deposition temperatures and supercycle parameters such as pulse ratios and bilayer period. With the advantage of low temperature and highly conformal thin film growth, we study ALD grown $Zn_{1-x}Mg_xO$ with x varying from 0.1 to 0.4 and elucidate the effect of doping on the band alignment, electrical and optical properties. By varying Mg content we were able to achieve 11% efficient $Cu(In,Ga)S_2$ solar cell with an open-circuit voltage of 941 mV.

[1].Hiroi H, Iwata Y, Adachi S, Sugimoto H, Yamada A. New World-Record Efficiency for Pure-Sulfide Cu(In,Ga)S2; Thin-Film Solar Cell With Cd-Free Buffer Layer via KCN-Free Process. IEEE J Photovolt. 2016;6(3):760-763.

[2].Kuwahata, Yoshihiro, and Takashi Minemoto. "Impact of Zn1-xMgxO: Al transparent electrode for buffer-less Cu (In, Ga) Se2 solar cells." Renewable energy 65 (2014): 113-116.

[3]. Wang, Mang, et al. "Electrodeposition of Mg doped ZnO thin film for the window layer of CIGS solar cell." Applied Surface Science 382 (2016): 217-224.

[4]. Inoue, Yukari and Hala, Matej et al. "Optimization of buffer layer/i-layer band alignment" in 42nd IEEE Photovoltaic Specialist Conference (IEEE, New Orleans, 2015), pp. 1

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

ALD Applications
Room On Demand - Session AA3
Energy: Batteries and Energy Storage

AA3-1 Revealing the Control of Lithium Plating Microstructure Derived from ALD-Grown TiO_2*,* ***Solomon Oyakhire****, W. Huang, Y. Cui, S. Bent,* Stanford University

Lithium (Li) metal batteries are desirable as rechargeable storage devices due to their high energy density; however, their practical implementation is hindered by the difficulty in controlling the Li metal plating microstructure. Artificial solid-electrolyte interphases (SEIs) have shown the potential to curtail the electrochemical instabilities of lithium, and atomic layer deposition (ALD) is commonly employed for the synthesis of thin-film artificial SEIs such as Al_2O_3 and alucone. However, these films quickly become delaminated because of their innate resistance to the cyclic shuttling of Li ions, resulting in marginal improvements in cell performance.

While previous ALD studies have focused on directly coating the top of Li metal with thin-film artificial SEIs, we adopt a different approach, situating the ALD film beneath Li metal and directly on the copper current collector. We show that by depositing TiO_2 directly on the Cu current collector, we can control the deposition morphology of Li in the widely studied ether-based electrolyte - 1M LiTFSI in a 1:1 mixture of 1,3 dioxolane and 1,2 dimethoxyethane, with 1 weight percent $LiNO_3$ as an additive. By optimizing the thickness of TiO_2, we reveal that lithium nucleates into large deposits atop the TiO_2 film under significantly reduced overpotential, resulting in a reduction in contact surface area with the electrolyte and an increase in cell performance. We report substantial improvements in cycling efficiency with an average Coulombic efficiency of 96% after 150 cycles at a current density of 1 mA cm^{-2} in Li/Cu cells. In comparison to the unmodified cells, voltage profiles for the champion TiO_2-modified cell display negligible loss in charge capacity in the mid and late-stage electrochemical cycles, indicating an improvement in the reversibility of lithium stripping and plating.Using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS), we establish that lithium plates atop TiO_2, rather than beneath it, suggesting that the presence of TiO_2 supports the enhanced reversibility of Li stripping and plating. Also, we utilize coulometry and cryogenic transmission electron microscopy (cryo-TEM) measurements to establish that prior to its nucleation, Li reacts with TiO_2 to form an amorphous Li_xTiO_2 complex. We propose that this complex serves as a lithiophilic layer that promotes the coalescence of large lithium particles and improves cell performance.

AA3-2 Li, N co-controlled Lithium Phosphorous Oxy-nitride(LiPON) Coating for Three Dimensional Thin Film Solid-state Batteries (3D TSSBs) using ALD*,* ***Ha Yeon Kwon****, S. Hong, T. Park,* Hanyang University, Korea

Recently, various types of solid electrolytes have been studied due to the stability problem of liquid electrolytes.[1] At the same time,three-dimensional thin film solid-state batteries for microbatteries is in the spotlight due to reduced device size. LiPON is the most commonly used solid material for implementing 3D TSSB. LiPON is chemically stable by having a wide electrochemical window and can be applied on flexible substrates with amorphous phase. [2], [3] Unfortunately, LiPON does not have high ionic conductivity among all solid electrolytes. To compensate this point, existing studies have conducted studies to increase ion conductivity by controlling the composition of LiPON. Existing studies have noted that ion conductivity increases with increasing N content of LiPON. However, there were several problems in the process of adjusting the N content. [4], [5], [6] In this study, Li, N composition of LiPON was co-controlled by adjusting ALD super cycleof the LiPON and LiN. By simultaneously adjusting Li and N content, the ion conductivity of LiPON is improved. In addition, a very uniform 3D TSSB can be produced by depositing LiPON using ALD. Details of experimental methods and results will be presented.

References [1] Renew. Sust. Energ. Rev., 81 (2018): 1427-1452., [2] ACS Appl. Mater. Interfaces 7.42 (2015): 23685-23693. [3] J. Am. Chem. Soc.,140.35 (2018): 11029-11038. [4] ECS Solid State Lett., 5 (1) A14-A17 (2002) [5] Solid State Ionics 186 (2011) 29–36 [6] Chemistry of Materials 27.15 (2015): 5324-5331.

AA3-3 Rational Modification of $LiMn_2O_4$ Surfaces by Controlling the Acid-Base Surface Chemistry of Atomic Layer Deposition*, D. Kang,* Argonne National Laboratory, USA*; R. Warburton,* Purdue University, USA*; A. Mane,* Argonne National Laboratory, USA*; J. Greeley,* Purdue University, USA*;* ***Jeffrey Elam,*** Argonne National Laboratory, USA

Next-generation energy storage devices demand superb control over interfaces. Atomic layer deposition (ALD) coatings can suppress undesirable electrochemical reactions between lithium ion battery (LIB) cathode surfaces and the organic liquid electrolyte. However, our limited understanding of ALD cathode coatings restricts our ability to predict which coating/cathode combinations will succeed. In this study, we performed a combined theoretical-experimental study of a model coating/cathode system aimed at elucidating synthesis-structure-property relationships. We selected five ALD Al precursors exhibiting a range of Lewis acid-base properties to establish trends in the ALD Al_2O_3 chemistry on $LiMn_2O_4$. Density functional theory calculations deduced a correlation between the Lewis acidity of the ligands and the ALD thermochemistry. X-ray photoelectron spectroscopy and *in situ* infrared spectroscopy measurements supported these predictions and further revealed how the Al precursors modify the $LiMn_2O_4$ atomic and electronic surface structure. Finally, coin cell electrochemical measurements established the link between materials properties and device performance. We discovered that while the Mn oxidation state is strongly influenced by the Lewis acidity of the precursor ligand, the surface coverage and thickness of the Al_2O_3 coating are a more representative descriptor of the electrochemical performance measured in coin cell experiments.

AA3-6 ALD of Thin-Film Na_xMn_yO Cathode Materials for Sodium Ion Batteries*,* ***Nikhila Paranamana****, M. Young,* University of Missouri, Columbia

In recent years, sodium ion batteries have been of increasing interest due to the limited availably of lithium resources for the production of lithium-ion batteries. Because of its abundance in the earth's crust and similar chemical properties to lithium, sodium is viewed as an attractive alternative to lithium. Unfortunately, sodium ion batteries suffer from materials instability issues that limit cycling performance. For example, sodium manganese oxide (Na_xMn_yO) is a promising cathode material for sodium ion batteries but suffers from chemical and structural degradation during electrochemical cycling. Unfortunately, it is difficult to understand the origins of Na_xMn_yO degradation because the local behavior at the Na_xMn_yO surface cannot be observed *in situ* within assembled battery cells. In this work aim to enable the study of the degradation processes in Na_xMn_yO by creating model thin film Na_xMn_yO using atomic layer deposition (ALD). We report on the ALD growth Na_xMn_yO using alloys of MnO_x and NaOH ALD chemistries. $Mn(thd)_3$ and O_3 precursor doses are used to form MnO_x, while Na^tOBu and H_2O doses are used to form NaOH. We examine the effect of mixing these ALD chemistries in varying ratios on the growth behavior and final material composition and structure, and characterize the optical and electrochemical properties of the resulting films. In particular we identify that NaOH facilitates nucleation of MnO_x, and identify slow oxidation processes requiring >300 s O-$_3$ exposures for saturation. Correspondingly, the growth rates of MnO_x using 6 s and 300 s O_3doses were measured to be 0.12 Å/cycle and 0.42 Å/cycle, respectively. The Na_xMn_yO alloy growth proceeds with a linear growth rate of 8.88 Å/supercycle. Additionally, our studies suggest that at high MnO_x content, the NaO^tBu exposure yields a bulk sub-surface reaction with MnO_x. This work expands upon previous work and contributes to growing understanding of the ALD-growth of alkali-containing ternary oxides.

ALD Applications
Room On Demand - Session AA4
Applications in ULSI FEOL: High-k

AA4-1 Plasma Impact on the Hfo_2 High-K Dielectric: Continuous-Wave Plasma Etch Versus Quasi-Atomic Layer Etch*,* ***Dunja Radisic****, Q. Smets, T. Schram,* IMEC, Belgium

Etch stop layers (ESL) are commonly used to protect critical films. This is also the case for 300 mm 2D material integration where HfO_2 ESL is used first for the contact trench etch, and again for the damascene high-k first/top gate last process steps. For the latter, the HfO_2 ESL also serves as top gate dielectric and is hence highly sensitive to plasma-induced damage (PID).

In this paper, two main approaches were investigated for the SiO_2 removal stopping on HfO_2. Conventional, Continuous-Wave (CW) plasma experiments (Fluorine-based) were performed in the ICP, and the Quasi-Atomic Layer Etch (Q-ALE) in CCP reactor, both from Lam Research Corporation. The goal was to explore Q-ALE and make a general comparison between the two approaches. The advantage of ALE, as well as Q-ALE over CW plasma etch is its unique capability to remove the material with an angstrom precision, causing minimal or no damage and material removal with high etch selectivity.

Simple metal oxide metal capacitor (MIMCAP) test vehicle was used for the study. First, a 10nm TiN bottom electrode was deposited on Silicon wafers, followed by a 10nm HfO_2 layer and a SiO_2 hard mask. The SiO_2 is etched with a spin-on carbon/spin-on glass/photoresist stack, stopping on the underlying HfO_2. Following the plasma processing, the TiN/W top electrode metal stack is deposited in the trenches, and planarized with chemical mechanical polishing (CMP) to electrically isolate the devices.

Our results show that for the CW approach, longer over-etch (OE) thins the HfO_2, and consequently, increases the leakage current and lowers the breakdown voltage. In the case of Q-ALE, the HfO_2 thickness is intact even with the prolonged OE, implying high process selectivity to HfO_2, with no morphological or electrical evidence of PID. However, in the case of Q-ALE, longer OE causes more spread in the electrical performance. This is likely the result of more residues, formed during the passivation step, and remaining on the HfO_2 surface after processing. (Further process performance improvement can be potentially achieved using the effective post-plasma cleaning, but it was not the goal of this study).

We conclude that Q-ALE is a promising technique for the applications where the HfO_2 ESL also serves as the gate oxide. The high etch selectivity and low PID make it ideal for novel integration flows, like 300 mm 2D material integration.

AA4-2 Self-Aligned Atomic Layer Deposited Gate Stacks for Electronic Applications*, **Amy Brummer**, A. Mohabir, M. Filler, E. Vogel,* Georgia Institute of Technology

The formation of self-aligned MOSFET gate stacks via area-selective atomic layer deposition (AS-ALD) of high-κ dielectric and metal films offers a route to reduce the number of lithography steps, maintain a low thermal budget, and improve performance by eliminating overlap capacitance. In this work, a new method for bottom-up masking of semiconductor surfaces and nano/microstructures is combined with AS-ALD to fabricate a high-performance gate stack that is self-aligned to the underlying doped source-drain regions. We begin with the SCALES process, which involves a poly(methyl methacrylate) (PMMA) brush grown from a silicon surface [1]. The PMMA brush is then patterned via a mild selective etching of the underlying semiconductor based on the Si dopant concentration. KOH etches lightly doped Si much faster than heavily doped Si, allowing for selective removal from only the lightly doped regions. The full gate stack is then deposited via AS-ALD in areas where the brush has been removed, as shown in Figure 1. Figure 2 shows XPS data of an example gate stack sequence deposited via AS-ALD, including a HfO_2 dielectric and a Pt gate electrode. Both spectra show good selectivity of deposition toward the regions where PMMA had been removed. Figure 3 shows the C-V characteristics of a gate stack on both a silicon substrate that did not undergo the PMMA process as well as a silicon substrate in which the PMMA was removed via etching. The C-V characteristics are almost identical for both cases indicating that the PMMA brush growth and removal does not strongly impact the silicon-HfO_2 interface. The maximum capacitance was used to determine a relative dielectric constant of ~24 which is expected for HfO_2. The interface state density was extracted from the C-V characteristics to be on the order of 10^{12} cm^{-2}. Ongoing work aims to reduce defect density in this and other high-κ dielectrics (e.g. TiO_2, Al_2O_3, ZrO_2).

[1] Mohabir, Amar T., et al. "Bottom-Up Masking of Si/Ge Surfaces and Nanowire Heterostructures via Surface-Initiated Polymerization and Selective Etching." ACS nano 14.1 (2020): 282-288.

AA4-3 Film Characteristics of Lanthanide Oxide Thin Film by Using Atomic Layer Deposition Method*, **Se-Won Lee**, M. Kim,* Merck Electronics, Korea (Republic of)*; S. Ivanov,* EMD Electronics

Lanthanide oxide films possess a wide variety of functional properties. In particular, using them as insulators in MIM structures offers a number of advantages over silicon dioxide. Lanthanide oxide based thin films can be used as gas sensors or hard mask. They are potentially attractive materials for the fabrication of multi layer optical coatings, beam splitters, passive components of integrated circuits, and heat based laser recording devices. Among them, terbium oxide (Tb_2O_3) and gadolinium oxide (Gd_2O_3) have proven to be promising materials for conventional silicon dioxide replacement in nano device applications. It has a relatively high dielectric constant (14 ~ 20) and a large band gap. Our research examines the electrical and physical characteristics of TbO_x and GdO_x thin film by atomic layer deposition (ALD) with as-dep and post rapid thermal annealing (RTP) to improve dielectric characteristics and optimize performance for potential application in nano devices.

Here, we report thermal ALD of TbO_x and GdO_x thin films using high purity Tris(i-propylcyclopentadienyl) terbium(III) (Tb(iPrCp)3) and Tris(i-propylcyclopentadienyl)gadolinium(III) (Gd(iPrCp)3). Deposition of both films was investigated by thermal ALD process with ozone reactant at 150-350 °C on Si and TiN substrates. After film deposition, RTP was conducted to observe post annealing effects. Some ALD conditions, including ALD window, and other film properties were very similar to the two films. In both films, amorphous phase with no XRD peak was observed at 200 °C samples, but crystallization peak was observed over 250 °C. The film density of GdO_x film was ~ 15% higher than the TbO_x film. XPS results showed that carbon is detected in 200 °C samples, but it is not detected at temperatures above that. Both samples showed a good step coverage of more than 90% at 200°C, but step coverage was deteriorated rapidly in samples of more than 250°C. Dielectric constant was measured by TiN/TbO_x or GdO_x/TiN (MIM) structure.

As a result, we conducted atomic layer deposition of lanthanide oxide, TbO_x and GdO_x films and analyzed its properties. Both films showed low process temperatures of 200 °C, good step coverage, and high dielectric constant, so these characteristics are expected to be used in applications such as high-k gate insulators or hard mask.

ALD Applications
Room On Demand - Session AA7
Applications in ULSI BEOL: Interconnects, Diffusion Barriers, Low-k

AA7-1 Grain-Resistivity Relationship of Ru ALD Precursors*, **Michael Breeden**, V. Wang,* University of California at San Diego*; R. Kanjolia, M. Moinpour, J. Woodruff,* EMD Performance Materials*; H. Simka,* Samsung*; A. Kummel,* University of California at San Diego

Ru is viewed as an alternative to Cu and Co interconnect layers at M0/M1 due to its lower effective resistivity in confined vias. In addition, Ru's low diffusion into porous low-K dielectrics (SiCOH) removes the need for a barrier layer, further decreasing effective resistivity [1,2]. However, the search for a Ru ALD process that can deposit Ru with near-bulk resistivity (6 μΩ·cm) is ongoing, with an emerging interest in selective ALD without passivants. In this work, the grain structure-resistivity relationship for 300C Ru ALD with precursors Ru-Carish ($Ru(IHD)_2(CO)_2$) and $Ru(CpEt)_2$ using O_2 as co-reactant were investigated by four-point-probe measurements, in-situ X-ray photoelectron spectroscopy (XPS) for chemical composition, and X-ray diffraction/reflectometry (XRD/XRR) for grain size and thickness.

Ru ALD precursor dose studies have shown a relationship between the precursor dose and resistivity. To limit pressure through the turbomolecular pump, multiple precursor pulses were dosed to control dosing. For Ru ALD using Ru-Carish on SiO_2, doubling the Ru-carish dose decreased resistivity from 18.5 to 10.2 μΩ·cm at 40 nm thickness. This effect can be attributed to the additional precursor dose consuming oxygen to form volatile RuO_4 resulting in a film with less oxygen content. Furthermore, film thickness can be scaled to 16 nm without increasing resistivity, consistent with studies showing the deposition mechanism involving the presence of adsorbed oxygen, promoting nucleation and reducing resistivity [3].

While the Ru-Carish process requires passivation for selective ALD, inherent selectivity using $Ru(CpEt)_2$ is demonstrated with low resistivity. Substrate selectivity for the $Ru(CpEt)_2$ precursor on SiO2 was demonstrated, with increased oxygen dose increasing the growth rate, but retaining high selectivity after 350 cycles. A resistivity-oxygen relationship can be observed, with a doubling of oxygen dose reducing resistivity from 14 to 9 µΩ·cm for a 30 nm film and XRD showing an increase in grain size from 18 nm to 28 nm for the Ru(002) orientation. Additionally, post deposition forming gas anneal at 450C for 30 min further reduced the resistivity to 8.1 µΩ·cm. These low resistivity Ru ALD processes have potential to allow for low-resistivity Ru films in barrierless via filling for M0/M1 interconnect fill, and the $Ru(CpEt)_2$ precursor shows promise for selective Ru ALD without passivation.

1. D. Gall. J. Appl. Phys, 2020 **119**, pp. 050901.

2. X.P. Qu, et al. Appl. Phys. Lett., 2006, **88**, pp. 151912

3. T. Aaltonen, et. al. Electrochem. & Solid State Lett. 2003, 5 pp. C130-C13

AA7-2 Atomic Layer Deposition of RuO_2 Using a New Metalorganic Precursor as a Diffusion Barrier for Ru Interconnect*, **Youn-Hye Kim,*** Yeungnam University, Korea (Republic of)*; Y. Kotsugi,* Tanaka Precious Metals, Japan*; T. Cheon, R. Ramesh, S. Kim,* Yeungnam University, Korea (Republic of)

The extremely narrow dimensions required for the metal interconnect in the sub-10 nm technology node would lead to very high electrical resistance of Cu due to the significant influence mainly from the surface scattering of electrons. For these reasons, the trend in interconnect technology is changing from Cu to Ru due to its low resistivity at narrow line width. However, there are some reports that Ru starts to diffuse into Si at temperature above 700°C. Therefore, a diffusion barrier layer is required to prevent diffusion of Ru that degrades electrical properties. In this regard, RuO_2 has good properties as a diffusion barrier, such as low resistivity(~46 µΩ・cm), high chemical and thermal stability. In this study, the RuO_2 thin films were grown at the relatively low temperature of 180 °C by ALD using the new liquid Ru precursor, tricarbonyl (trimethylenemethane) ruthenium and O_2 molecules for diffusion barrier application of Ru interconnect. For optimization of deposition parameters, the effects of pulsing time ratio (t_{O2}/t_{Ru}) and deposition pressure on the formation of RuO_2 phase were investigated. The formation of a RuO_2 phase is favorable with increasing the pulsing time ratio (t_{O2}/t_{Ru}) and deposition pressure. It was also demonstrated that Ru single phase, the mixture phase of Ru and RuO_2, and RuO_2 single phase could be controllably grown with deposition condition. The ALD-RuO_2 films deposited with optimized conditions have a resistivity of ~103 µΩ・cm and a growth rate of ~0.056 nm/cycle with short incubation cycles of 15. The non-barrier layer structure [ALD-Ru(50 nm)/Si] began to lose its stability by forming ruthenium silicides at 750 °C, while the structure with a barrier layer [ALD-Ru/ALD-RuO_2 (5 nm)/Si] were stable up to 850 °C. This indicates that the ALD-RuO_2 thin films have superior performance in preventing the diffusion of Ru. Furthermore, it is expected to improve the process throughput by depositing in the same chamber using same precursor and reactant as Ru.

Acknowledgements

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ALD Applications
Room On Demand - Session AA8
Memory Applications: DRAM

AA8-1 Influences of Oxygen Source and Substrate Temperature on Growth Mechanism of Atomic Layer Deposited Magnesium Oxide Using Bis(Cyclopentadienyl)Magnesium Precursor*, **Bowen Wang,** J. Choi, H. Kim, S. Hyun, H. Lee, C. Hwang,* Seoul National University, Korea (Republic of)

This research mainly studied the dissimilarities of MgO thin film's growth mechanisms in the atomic layer deposition (ALD) process depending on the oxygen sources, such as O_2 plasma, O_3, and H_2O (Fig. 1a, b). The bis(cyclopentadienyl)magnesium (Cp_2Mg) was adopted as the Mg-precursor. The effects of the oxidizing power and the temperature from 230℃ to 390℃ on the Cp-ring rupture reactions in the ALD process were analyzed by ex-situ techniques, such as X-ray diffraction/reflectometry, X-ray photoelectron spectroscopy (Fig. 1c and d), time of flight secondary ion mass spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy and transmission electron microscopy (Fig. 2a, b). It was intended to examine the crystallization, impurities and their depth profiles, stoichiometric ratio, surface/interface bonding, relative volumetric density. At relatively low substrate temperature (~ 250℃), albeit the similar crystallization and surface morphology were measured by glanced incidence X-ray diffraction and the field emission scanning electron microscope, O_2 plasma-enhanced ALD MgO showed the least impurity level and highest density. At the same time, the O_3-based thermal ALD-MgO exhibited the lowest density and highest impurity level among those three co-reactants. Unlike the overgrowth and void formation (Fig. 2b) at the growth temperature of 290℃, the O_3 ALD showed a comparably lower impurity level than the plasma-enhanced ALD at 335℃. Figure 1e shows the suggested ALD reaction mechanism. This was corroborated by the electrical characteristics using the planar metal-insulator-metal capacitors (metal layer was TiN). Furthermore, the pre-, post-annealing conditions were optimized for the optimal leakage current and dielectric constant of ALD-MgO.

AA8-2 Atomic Layer Deposition of Y-Doped TiO_2 Thin Films to Decrease the Leakage Current for DRAM Capacitor Applications*, **Tae Kyun Kim**, C. Hwang,* Seoul National University, South Korea

This work reports the electrical behavior of Y-doped TiO_2 (YTO) thin film as a dielectric layer for a capacitor of dynamic random access memory. The electrical performance of YTO thin films is comparable to that of Al-doped TiO_2 (ATO) thin films (Fig. 1(a)), which is well-known for its excellent leakage current property among other series of doped rutile TiO_2 thin films [1]. Nonetheless, YTO thin films appear to suppress the leakage current via a different mechanism from that of the ATO thin films. The large ionic size of Y ion compared with the Ti inhibits the efficient diffusion of them into the lattice of the rutile TiO_2 thin film, which results in a nano-laminate structure (Fig. 1b). In contrast, the small ionic size of Al in ATO fluently diffused into the TiO_2 film and form acceptor states. Therefore, it could be guessed that the leakage current suppression mechanism in YTO film is similar to that in the $ZrO_2/Al_2O_3/ZrO_2$ case, where the interrupted columnar grain structure of the ZrO_2 layer has contributed to the leakage current control.

AA8-3 Improved Properties of the Atomic Layer Deposited Ru Electrode for Dynamic Random-Access Memory Capacitor Using Discrete Feeding Method*, **Dae Seon Kwon,*** Seoul National University, Korea*; W. Jeon,* Kyung Hee University, Korea*; D. Kim, T. Kim, H. Seo, J. Lim, C. Hwang,* Seoul National University, Korea

A ruthenium (Ru) thin film as a bottom electrode of dynamic random-access memory (DRAM) capacitor was grown via atomic layer deposition (ALD) with a discrete feeding method (DFM). The DFM-ALD was conducted by dividing the Ru source feeding and purge steps of the conventional ALD process into four steps (shorter feeding + purge times). The DFM-ALD could efficiently eliminate the adverse effects of the Ru precursors' physisorption and byproducts during the ALD process, resulting in a more fluent ALD reaction. The physicochemical properties of the Ru films deposited via conventional ALD, DFM-ALD, and sputtering were investigated and compared in detail. The Ru films deposited via DFM-ALD showed a higher density, smoother surface morphology (Fig.1), and preferred orientation of a (101) phase compared to the conventional ALD process. Also, the Ru films grown via DFM-ALD showed higher susceptibility of oxygen atoms into the Ru films, resulting in a higher proportion of the RuO_2 layer on the Ru film surface, which is formed during the subsequent ALD process of the high-*k* TiO_2 thin film. Such a higher RuO_2 portion led to more fluent lattice-matched local epitaxial growth of the TiO_2 films with a rutile structure as well as the smoother surface morphology without local protrusions. The possible mechanism of the improved TiO_2 film growth mechanism was suggested (Fig. 2). These improvements in the physical performances also improved the electrical properties of the $Pt/TiO_2/Ru$ capacitors. A decrease in the interfacial component of equivalent oxide thickness by ~ 0.1 nm could be achieved by the DFM-ALD process compared with the cases on the sputtered Ru film. Consequently, minimum EOT values of ~0.76 nm and ~0.48 nm were obtained with enough low leakage current density ($<10^{-7}$ A/cm^2 at 0.8 V) for TiO_2 and Al-doped TiO_2 (ATO) dielectric films, respectively. The minimum EOT of 0.48 nm was comparable to the most remarkable results from the ATO/RuO_2 layers, which would have induced integration issues caused by the reduction of RuO_2. This finding indicated that the electrical performance of the high-*k* dielectric film was determined by not only the surface morphology but also the chemical properties of the underlying Ru substrate.

AA8-6 A Comparative Study on the Crystallization Behavior of Atomic Layer Deposited ZrO_2 / Y_2O_3 / ZrO_2 Dielectric Thin Films for DRAM Capacitors

***Haengha Seo**, D. Kim, D. Kwon, J. Lim, T. Kim, H. Paik, C. Hwang,* Seoul National University, Korea (Republic of)

ZrO_2 / Al_2O_3 / ZrO_2 (ZAZ) thin films have been applied as a representative dielectric for metal-insulator-metal (MIM) capacitors in mass-produced dynamic random-access memory (DRAM) devices. However, the inserted Al_2O_3 layer required for the leakage current suppression degraded the overall crystallinity of the dielectric film, resulting in a much higher equivalent oxide thickness (EOT) compared with the undoped ZrO_2 film as the films became thinner (< 6 nm).

In this work, ZrO_2 / Y_2O_3 / ZrO_2 (ZYZ) thin films were grown on TiN (bottom) electrode by atomic layer deposition (ALD) using $Zr[N(CH_3)C_2H_5]_4$ and $Y(EtCp)_2(^iPr\text{-amd})$ as precursors. ZAZ films were also deposited in the same manner for comparison. The thicknesses of both the Y_2O_3 and Al_2O_3 layers were fixed at ~ 0.3 nm, and they were deposited on top of the ~ 2.1 nm thick ZrO_2 bottom layer. Only the top ZrO_2 layer thickness was varied between 0 and 8 nm. All samples were subjected to post-metallization annealing (PMA) at 600 °C, after TiN/Pt (top) electrode deposition.

As can be seen from **Figure 1**, the EOT of the ZrO_2 and ZYZ films showed a sudden drop at a similar physical oxide thickness (POT) of ~ 3.5 nm, whereas that of the ZAZ curve showed a similar decrease at a much greater POT (~ 6.0 nm). The result evidently indicates that the minimum POT required for the crystallization of the top ZrO_2 layer during the PMA increased significantly on the Al_2O_3 layer, while the impact of the Y_2O_3 layer on the crystallization was almost negligible.

It is noteworthy that there was another transition point in the case of the ZAZ at ~ 7 nm, which might indicate the crystallization of the bottom ZrO_2 layer. This implies that even the bottom ZrO_2 layer had not been crystallized in the thinner ZAZ case due to the presence of the Al-doping, which was not the case in ZYZ. Although the Y_2O_3 insertion layer in ZrO_2 based dielectric did not inhibit the crystallization, the leakage current was still well suppressed (2.9×10^{-8} A cm^{-2} at 0.8 V, POT ~ 6.8 nm). ZYZYZ thin films exhibited the most stable and improved leakage current control among the tested candidates.

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