ALD Applications
Room Grand Ballroom H-K - Session AA1-TuM

ALD for Batteries

Moderators: Prof. Dr. Hyeontag Jeon, Hanyang University, Prof. Markku Leskela, University of Helsinki, Finland

8:00am **AA1-TuM-1 Nanoscale Surface Engineering for Battery Electrode and Solid Ionic Electrolytes*, Chunmei Ban,*** CU Boulder **INVITED**

This presentation will discuss the effects of using atomic/molecular layer deposition (ALD/MLD) in stabilizing surface/interface of battery electrode materials and facilitating ion diffusion at the surface of ionic conducting materials. ALD and MLD have proven themselves to be the best methods to grow continues, conformal and pinhole-free ultrathin films for high-aspect-ratio microstructures and nanomaterials. Thus, ultrathin oxides layers (<5nm) have been used to protect surface of electrode materials from liquid electrolytes, leading to the greatly improved battery cycling performance of lithium-ion electrodes. In addition, surface coatings via ALD/MLD have been recently applied to ionic conducting materials to increase wettability and electrochemical stability. This talk will summarize recent studies on surface modification using ALD/MLD for electrodes and solid-state electrolytes, to correlate the electrochemical properties of the coated electrochemical materials with chemistry of coating materials. Electrochemical analysis will be used to study how the modified surfaces alter charge transfer and electrochemical reactions at the electrode surface or at the electrode-electrolyte interface. Furthermore, we will combine electrochemical diagnosis with spectroscopic studies to investigate the structural and morphology evolution of the coating materials during electrochemical processes, present insights in design of surface coatings and their applications in solid-state batteries.

8:30am **AA1-TuM-3 Enabling Fast Charging of Lithium-ion Batteries by Coating of Graphite with ALD**, *E. Kazyak, K. Chen, Y. Chen, T. Cho,* ***Neil P. Dasgupta,*** University of Michigan, Ann Arbor

Increasing the achievable charging rate of lithium-ion batteries (LIBs) is critical to the widespread commercialization of electric vehicles (EVs). The primary factor limiting the fast-charge ability of state-of-the-art LIBs is the propensity for Li metal to plate out on the graphite surface during charging.[1] The poor reversibility of Li metal in LIB electrolytes leads to rapid capacity fade, consumption of the electrolyte (cell drying), and possibly even short-circuit from dendrites penetrating the separator. This problem is exacerbated in high-energy density cells with thicker electrodes, leading to energy-power tradeoffs.

To prevent/mitigate these effects, in this study[2] we implement an atomic layer deposition (ALD) surface coating on calendered graphite anodes. We demonstrate that this artificial solid electrolyte interphase (a-SEI) that outperforms the natural SEI in fast-charging ability. The large majority of the previous ALD coatings that have been investigated as electrode coatings for LIBs have been binary metal oxides that have very low ionic conductivity. In contrast, the ALD coating used here is a lithium borate-carbonate (LBCO) solid electrolyte. This ALD single-ion conductor has previously been shown to exhibit ionic conductivities above 2*10^{-6} S/cm and excellent electrochemical stability, including with Li metal.[3]

Here we demonstrate that in comparison to uncoated control electrodes, the LBCO a-SEI coating: 1) eliminates natural SEI formation during formation cycles, 2) decreases interphase resistance by >75% compared to that of the natural SEI, and 3) extends cycle life under 4C-charging conditions, enabling retention of 80% capacity after 500 cycles (compared to 12 cycles in the uncoated control) in pouch cells with >3 mAh-cm^{-2} loading. Not only is this a promising approach to enable fast-charging of LIBs, but it also challenges the prevailing thinking that mass-transport limitations in the liquid electrolyte must be addressed to enable fast charging. In the future, this opens up new possibilities for engineering of LIB interfaces for performance enhancements beyond improved stability and cycle life.

References

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2. E. Kazyak, K.-H. Chen, Y. Chen, T. H. Cho, N. P. Dasgupta*, Adv. Energy Mater.* **12**, 2102618 (2022)

3. E. Kazyak, K.-H. Chen, A. L. Davis, S. Yu, A. J. Sanchez, J. Lasso, A. R. Bielinski, T. Thompson, J. Sakamoto, D. J. Siegel, and N. P. Dasgupta, *J. Mater. Chem. A* **6**, 19425 (2018)

8:45am **AA1-TuM-4 Aluminum Doping of Lithium Phosphate using Atomic Layer Deposition***, **Daniela Fontecha**, K. Gregorczyk, A. Kozen, G. Rubloff,* University of Maryland, College Park

Metal phosphate glasses developed by ALD have been used for a variety of applications in microelectronics. Lithium phosphate deposited by ALD is relevant in solid-state battery (SSB) applications as a Li-ion conducting thin film that is compatible with many Li-ion battery chemistries, enabling the passivation of reactive interfaces between solid-state cathode and electrolyte films. It has also been shown that lithium aluminum phosphate (LAP) is a promising protection layer for cathode materials in SSBs. This work explores the impact of Al-doping of lithium phosphate in terms of its structural, chemical, and Li$^+$ ion conducting properties with a new ALD synthesis method for thin film applications.

The constituent ALD process for crystalline Li$_3$PO$_4$ (LPO) utilizes lithium tert-butoxide (LiO^{t}Bu), water, and trimethyl phosphate (TMP) at 300 ^{o}C with a growth rate of 0.8 Å/cycle and ionic conductivity of 1.3x10^{-9} S/cm. Trimethyl aluminum (TMA) and water are then used to insert aluminum into the LPOfilm by cycling between 1 cycle of TMA + water and **[n]** cycles of LPO (n = 30-120) to produce a film with Al content between 1-4 %. This work shows that the ionic conductivity of LAPincreases to 4.0x10^{-8} S/cm – one order of magnitude higher than that of LPO– due to the role aluminum plays in cross-linking phosphate groups even at these low Al concentrations. Deposition temperatures ranging from 250 – 300 ^{o}C show growth rates from 0.8 to 0.9 Å/cycle, respectively. The TMA + water pulse appears to have a minimal effect on the overall growth rate, which indicates compatible precursor chemistry between hydroxylated TMA and LiO^{t}Bu.XPS O 1s high resolution spectra of LAP films show an increase in bridging oxygen content with a shift in the bridging oxygen peak to lower binding energies suggesting the increase of Al-O-P bonding. The presence of P-O-P and Al-O-P binding states as well as GIXRD results showing some loss of crystallinity in as-deposited LAP compared to LPO suggest that there is cross-linking between phosphate groups at low Al-doping levels. We find that deposition temperature is a critical factor in controlling resultant film morphology with films deposited at 300 ^{o}C exhibiting an additional peak at 28.3^o 2θ. This peak lies between crystalline Li$_3$PO$_4$ and AlPO$_4$ peaks seen in literature, suggesting that at higher deposition temperatures, a mixture of crystalline LPO and AlPO$_4$ phases develops. In this talk, thin film processing of LAP is discussed along with materials characterization of a new Li-ion conducting thin film by ALD.

9:00am **AA1-TuM-5 Developing High-Performance Nickel-Rich Cathodes of Lithium-ion Batteries via Atomic Layer Deposition***, **Xiangbo Meng**, X. Wang, K. Velasquez Carballo, A. Shao,* University of Arkansas*; Y. Liu, H. Zhou,* Argonne National Laboratory*; X. Xiao,* Brookhaven National Laboratory

LiNi$_x$Mn$_y$Co$_z$O (NMCs, x + y + z =1) are promising for next-generation lithium-ion batteries (LIBs) and emerging lithium metal batteries (LMBs), featuring their higher capacity and lower cost than those of LiCoO$_2$. In particular, the advantages of NMCs in capacity and cost become more evident with increased Ni content. In other words, the higher the Ni content is, the higher the capacity is and the lower the cost is. With the increasing Ni content, however, the issues of NMCs become more challenging, exhibited as performance fading and safety risk. The issues include residual lithium compounds, irreversible phase transition, oxygen release, transition metal dissolution, and microcracking. They can further cause interface problems and electrolyte degradation and eventually lead to cell failure. This is particularly evident for Ni-rich NMCs ($x \geq 0.6$).

In searching for solutions to these issues, surface coating remains as an important technical strategy and has proven effectiveness. In the past decade, atomic layer deposition (ALD) has emerged as a new surface coating process and has been attracting an ever-increasing attention for addressing issues of various battery systems.[1-4] Its advantages lie in multiple aspects: (1) uniform and conformal coating, (2) moderate process temperature, and (3) the only capable technique enabling coatings over either prefabricated electrodes or battery powders. In addressing the issues of Ni-rich NMCs, we have been intensively investigating various surface coatings via ALD, including binary oxides, ternary Li-containing oxides, binary sulfides, and ternary Li-containing sulfides.[5-8] Our efforts revealed that these coatings commonly could inhibit interface reactions, mitigate microcracking, and suppress irreversible phase transition. Among them, Li-containing compounds could enable better ionic conductivity while sulfide coatings could offer some unique protective effects through scavenging oxygen released from NMC lattices. Our original discovery on sulfide coatings is particularly significant, for it opens a new research direction on surface coatings of rechargeable batteries and paves a novel technical avenue for achieving high performance of NMCs and the like in LIBs and LMBs.

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2. Meng, X., *J. Mater. Res.* (2021) **36**, 2
3. Meng, X., *J. Mater. Chem. A* (2017) **5**, 10127
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5. Wang, X., *et al.*, *Nanotechnology* (2021) **32** (11), 115401
6. Liu, Y., *et al.*, *Journal of Materials Science & Technology* (2020) **54**, 77
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9:15am **AA1-TuM-6 Molecular-Layer-Deposited Zincone Films Induce the Formation of LiF-Rich Interphase for Lithium Metal Anodes*, Wei-Min Li,*** Jiangsu Leadmicro Nano-Technology Co., Ltd., China*; S. Chang, A. Li,* Nanjing University, China

Lithium (Li) metal has been recognized as the promising anode material for rechargeable batteries because of its high theoretical capacity of 3,860 mAh g^{-1} and the lowest electrode potential (−3.04 V v.s. the standard hydrogen electrode (SHE)). However, Li metal usually forms a fragile solid electrolyte interphase (SEI), which is not sufficiently dense to passivate the surface of Li metal. During stripping and plating, the SEI cannot suppress the side reaction between Li metal and electrolyte. The poor SEI may also induce the heterogeneous deposition of Li, leading to the formation of notorious dendrites. The uncontrolled Li dendrites not only consume cyclable Li but also accumulate irreversible “dead lithium” owing to the loss of electric connection. Coulombic efficiency (CE) is then dramatically reduced. At a fixed loading, the deliverable capacity decays rapidly. In addition, Li dendrites may cause safety issues such as short circuits and catastrophic cell failures, which hinders the practical application of Li metal batteries.

In this work, we report a zincone (ZnHQ) MLD technology and its application for induced LiF-rich SEI on a copper nanowire (CuNW) anode. Zincone is a zinc-based hydroquinone (HQ) where Zn replaces hydrogen of HQ. As shown in **Figure 1a**, the hydroxyl (-OH) modified Cu is grafted with HQ during the MLD. Diethylzinc further reacts with the hydroxyl groups of grafted HQ to yield ZnHQ. HQ is selected as the backbone molecule because it is relatively stable upon lithiation and a single chain of ZnHQ has a terminal oxygen, which can serve as the nucleophilic group to attack Li bistrifluoromethanesulfonimide (LiTFSI) upon negative polarization. The resultant LiF-rich SEI (**Figure 1b, c**) can facilitate Li ion diffusion and suppress the dendritic Li growth that is usually induced on a pristine Cu (**Figure 1d, e**). More importantly, zinc atoms can facilitate the deposition of Li metal owing to the lithiophilicity.

Furthermore, the high surface area of porous scaffold and CuNWs reduces the local current density and prolongs the Sand’s time. As a result, the CuNW@ZnHQ electrode demonstrates superior cyclability for over 7000 h at a capacity of 1 mAh cm^{-2} and can maintain more than 300 h at a high loading capacity (15 mAh cm^{-2}). In addition, CuNW@ZnHQ is paired with NCM523 at a capacity of 3.2 mAh cm^{-2} with excellent cyclability of 90% capacity retention for 1000 cycles. This work provides an alternative approach to developing nanoscale interfacial coatings for Li metal and demonstrates that the zincone MLD strategy may serve as a potential technology for next-generation high-energy Li metal anodes.

9:30am **AA1-TuM-7 Deconvoluting the Impacts of Lithium Morphology and SEI Stability on Battery Cyclability Using ALD-Grown Thin Films*, Sanzeeda Baig Shuchi,*** *S. Oyakhire, Y. Cui, S. Bent,* Stanford University

The establishment of a fossil-fuel-free world strongly depends on electrification. The Li-ion battery, a universal mode of electrochemical energy storage, is reaching the theoretical limit, creating an urgency to produce more efficient batteries for next-generation applications. A more energy-dense battery configuration is the anode-free Li metal battery (LMB), in which Li is directly plated on and stripped from the Cu current collector (CC).

Electrodeposited Li morphology and solid electrolyte interphase (SEI) are the two most crucial performance modulators in LMBs. The literature has shown that low surface area morphology and anion-derived SEIs are desired for improved performance. However, it is difficult to deconvolute the individual impact of low surface area morphology and anionic SEI species on performance as they coexist and are correlated. We demonstrate a novel interface engineering approach to deconvolve the effects of Li morphology and SEI stability using atomic layer deposition (ALD). First, we modify the Cu CC surface using two thin films with distinct characteristics: resistive, acidic HfO_2; and conductive, acidic ZnO, using TDMAHf-H_2O and DEZ-H_2O precursors.

We leverage ALD to precisely vary the thickness of the nanofilms and establish that increasing the film resistance results in improved performance due to resistance-derived Li morphology. In addition, the HfO_2-modified CCs performed better than the ZnO-modified CCs, consistent with their relative resistivities. To decouple the impact of SEI species from morphology, we preform the SEI before cycling using a simple potential hold step for these two acidic metal oxide films, each of which has different electric properties. We find that with increasing film thickness, the preformed SEI has more anionic species due to the surface acidity of the thin films. Despite being anion-rich, the preformed SEI does not improve performance, which we attribute to its evolution into an organic-rich SEI during plating. Moreover, the impact of the preformed SEI was statistically insignificant during long-term cycling while the role of resistance became more evident.

In conclusion, the results indicate that morphological control is more successful for improved battery cyclability due to the inherent challenges with preformed SEI preservation. Correspondingly, the results suggest that resistance of the ALD-grown thin films is more important than surface acidity for CC modification. We show this resistance-derived Li morphology and performance enhancement in three different electrolytes with at least a twofold increase in cycle life along with improved capacity retention in practical anode-free pouch cells.

ALD Applications
Room Grand Ballroom H-K - Session AA2-TuM

MEMS, Actuators, Hard Films

Moderators: Prof. Anjana Devi, Ruhr University Bochum, Viljami Pore, ASM

10:45am **AA2-TuM-12 ALD for MEMS Sensors and Actuators*, Luca Lamagna,*** STMicroelectronics, Italy **INVITED**

Atomic layer deposition (ALD) has undoubtfully become one of the leading technologies employed for the deposition of nanometer-scale films at an industrial level. ALD allows for the deposition of conformal ultra-thin layers with an extremely precise thickness control. Moreover, ALD processes have been scaled on large area substrates, making this technique very promising for the industrial high throughput need. With ALD it is possible to develop and optimize the growth of novel ultra-thin dielectric, metal, and complex ternary compounds films.

Microelectromechanical systems (MEMS) have been attracted since the very beginning by ALD as a deposition technology that can address with its outstanding conformality the deposition on 3D complex structures. ALD turned out to be also a powerful approach to significantly increase the material selection available for MEMS processing. Simultaneously, ALD came up with the potentiality to offer layers with functional and tunable properties for the more disparate applications. Indeed, ALD is also able to realize thin functional layers that can be employed for specific surface engineering.

We will review the relationship between ALD processes and MEMS technology in terms of equipment and processes and we will provide an outlook for the future applications of ALD on advanced MEMS sensors and actuators.

11:15am **AA2-TuM-14 Applications of Piezoelectric, Ferroelectric, and Antiferroelectric Thin Films Grown by Atomic Layer Deposition*, Nicholas Strnad,*** DEVCOM Army Research Laboratory*; G. Fox,* Fox Materials Consulting, LLC*; T. Tharpe,* Oak Ridge Associated Universities*; R. Knight, R. Rudy, J. Pulskamp,* DEVCOM Army Research Laboratory

Piezoelectric materials offer efficient transduction of electrical and mechanical forces and have been implemented in many commercial products including medical ultrasound transducers, ink-jet print heads, atomic force microscope cantilever drives, and radio-frequency filters (thin-film bulk acoustic resonators, or FBARs). Actuators for microelectromechanical systems (MEMS) that utilize piezoelectric thin films offer larger forces and displacements compared to electrostatic actuators, and higher operating frequencies compared to thermal actuators. Despite the performance advantages offered by piezoelectric thin films, there are few reported ALD processes that have yielded viable piezoelectric properties. This presentation addresses several knowledge gaps in the field of ALD piezoelectric thin films. First, we present ALD processes for some of the most commercially relevant piezoelectric and ferroelectric thin films, including aluminum nitride (AlN), lead zirconate-titanate (PZT), additional Pb-containing perovskites (lead hafnate-titanate or PHT, lead hafnate or PHO), and $Hf_{1-x}Zr_xO_2$ (HZO). Second, we present methods of characterizing the effective transverse piezoelectric coefficient ($e_{31,f}$) which is critical for actuators but is underreported in the literature compared to the effective longitudinal piezoelectric strain constant ($d_{33,f}$). Third, we present new MEMS actuator concepts and initial fabrication results that leverage 3D, conformal ALD piezoelectric thin films that will lead to greater performance (up to 200x larger piezoelectric energy density) compared to traditional planar piezoelectric-enabled MEMS actuators. These new actuator concepts require aggressive aspect ratio scaling, sidewall-selective depositions, and 3D patterning, which presents new challenges and opportunities for atomic layer processing technologies.

11:30am **AA2-TuM-15 Effect of RF Substrate Biasing in Tuning the Tribological Properties of Plasma Enhanced Atomic Layer Deposited Titanium Vanadium Nitride Thin Films***, **Md Istiaque Chowdhury**,* Lehigh University*; M. Sowa,* Veeco Instruments Inc.*; K. Van Meter,* Florida International University*; A. Kozen,* University of Maryland, College Park*; S. Lazarte, B. Krick,* Florida International University*; N. Strandwitz,* Lehigh University

Ultra-low wear rates, approaching those of diamond, have recently been reported for transition metal nitride thin films deposited by plasma enhanced atomic layer deposition (PEALD). Apart from low wear, these films exhibit low electrical resistivities (~100 µΩ cm) comparable to metals (1-100 µΩ cm) and high chemical stability, which opens them up for applications in MEMs, NEMs, as electrodes, etc. Our aim is to understand the synthesis-structure-property relationships of these films by introducing substrate bias during deposition. The substrate bias helps regulate the energy distribution of the incoming plasma ions, which plays a vital role in modifying the resultant structure of the film and ultimately influence the functional properties. Researchers are using substrate biasing to modulate the ion-surface interaction in PEALD films but the correlation between the bias and the resultant structure and properties are not linear.

In this study, the magnitude of RF substrate bias, $|V_{bias}|$, was varied from 0 to 40 V during PEALD growth of ternary $Ti_xV_{(1-x)}N$ thin films to observe how $|V_{bias}|$ correlates with structure and tribological properties. Tetrakis (dimethylamido) titanium, tetrakis(dimethylamido) vanadium, and N_2 plasma were used as precursors. The growth rate per metal precursor exposure was 0.5-0.6 Å/cycle. The film densities approached 95% of the theoretical density as estimated by X-ray reflectivity. The electrical resistivity was evaluated to be 130-170 µΩ cm by four-point probe measurements. X-ray diffraction measurements revealed that the films have a cubic rocksalt crystal structure formed by a solid solution of TiN and VN. The crystal quality, indicated by the Bragg peak intensity, changed non-monotonically with $|V_{bias}|$. The (200) peak had the highest intensity for $|V_{bias}|$=20 V which was reflected in the minimum wear rate (10^{-8} mm^3/Nm) observed at this $|V_{bias}|$. The distribution of ion energies of the bombarding plasma was modified by $|V_{bias}|$, which provides an additional boost of energy to the adatoms promoting the crystal growth up to $|V_{bias}|$=20 V. Beyond 20 V, the additional energy from the bias causes continuous re-nucleation resulting in poor crystal quality, thus increasing the wear rate. The impact of $|V_{bias}|$ on tuning tribological properties of PEALD films have not been extensively studied, but it has been demonstrated that the residual stress of PEALD nitride films can be switched from compressive to tensile with $|V_{bias}|$. Substrate biasing can be a very useful tool to tune the tribological properties of PEALD nitride films and potentially create ultra-low wear materials.

11:45am **AA2-TuM-16 Towards ALD of hard AlTiN coatings***, **Pamburayi Mpofu**,* Linköping University, Sweden*; J. Lauridsen, O. Alm, T. Larsson,* Seco Tools AB, Sweden*; H. Högberg, H. Pedersen,* Linköping University, Sweden

AlN has a wide bandgap (6.2 eV), high dielectric constant (k ∼ 9), high electrical resistivity (ρ ∼ 1011–1013 Ω cm), and a very good thermal conductivity (2.85W/K cm)[1] making it interesting for microelectronics and optoelectronics. AlN is also used in microelectromechanical systems (MEMS devices) because of its piezoelectric properties. As AlN has good miscibility with other nitrides, it also has the potential to be used in ternary materials with e.g., Ga, In, Ti, or Hf, increasing the range of its possible applications. One such material is meta-stable $Al_xTi_{1-x}N$ where the cubic rock salt structure of TiN is preserved even with x = 0.9. $Al_xTi_{1-x}N$ primarily finds use as hard material in protective coatings, often on cemented carbide tools. While ALD of AlN has been reported several times, reports on ALD of ternary materials comprising AlN are scarce. $Al_xTi_{1-x}N$ has only three entries in the Atomic Limits database[2], for semiconductor-related applications. Our aim is to explore the possibility of using ALD, for the first time, to deposit hard protective coatings of $Al_xTi_{1-x}N$. We aim to explore both an ABC-type ALD cycle with $AlMe_3$, $Ti(NMe_2)_4$, and NH_3, and an AB-type ALD cycle with co-evaporation of $Al(NMe_2)_3$ and $Ti(NMe_2)_4$.

We will present an ALD comparison study of AlN, from a hard coating perspective. We compare $Al(NMe_2)_3$ and $AlMe_3$ as Al precursors and NH_3 with and without plasma activation as the N precursor. In addition to standard Si (100) substrates, we also deposit on cemented carbide, i.e., tungsten carbide particles sintered in a cobalt matrix, with and without a TiN coating. We studied the AlN ALD process in the temperature range from 100 to 400 °C with the aim to optimize the process for crystalline quality rather than electronic properties. Polycrystalline, stoichiometric, and high-purity AlN films have been obtained when using $AlMe_3$ (both plasma and thermal) but with varying thicknesses, growths per cycle, saturation times, nucleation delays, and temperature windows. Films prepared via the plasma route exhibit improved properties concerning the growth rate per cycle, total cycle duration, and homogeneity. By comparing our experimental results to recent modeling results from density functional theory methods, we can show strong evidence for the surface chemical mechanism of TMA on an NH_2-terminated AlN surface.

We will also describe our initial results from depositions of $Al_xTi_{1-x}N$ using the ALD approaches outlined above.

Refs.:

1. Kot, M. et al. J. Vac. Sci. Technol. A 37, 020913 (2019).

2. https://www.atomiclimits.com/alddatabase/

ALD Applications
Room Grand Ballroom H-K - Session AA1-TuA

Energy: Catalysis and Fuel Cells

Moderator: Dr. Chang-Yong Nam, Brookhaven National Laboratory

1:30pm **AA1-TuA-1 Surface Texture Design of Pt/C Catalyst to Enhance Oxygen Reduction Reaction by FBR-ALD***, J. Baek, M. Jung, S. Lee, S. Kwon, **MinJi Kim**,* Pusan National University, Republic of Korea

Proton exchange membrane fuel cell (PEMFC) is an efficient electrochemical energy conversion device that directly generates electricity from the chemical energy of fuels without the emission of greenhouse gases. The most reliable catalyst in PEMFC is Platinum (Pt) metal nanoparticles (NPs) that exhibit excellent electrochemical activity and stability compared to other catalysts. However, using of Pt catalyst is limited due to its very high cost and low abundance on Earth. Therefore, it is important to use Pt catalyst efficiently for making the PEMFC economically viable. In this regard, several synthesis techniques have been developed to reduce the loading and uniform distribution of Pt NPs on carbon support with high electrochemically active surface area (ECSA).One of the most efficient techniques to uniformly deposit Pt NPs with a controllable size on carbon support is to use a fluidized bed reactor (FBR) atomic layer deposition (ALD). Our group recently demonstrated that FBR-ALD Pt/C catalysts can exhibit high fuel cell performance and high endurance even with low Pt NPs loading by optimizing the surface of carbon supports combined with proper ALD process parameters [1]. However, it is still challenging to further improve the fuel cell performance by rational designing the Pt NPs surfaces in order to make FBR-ALD into a viable commercial production.

In this study, a unique way to improve the fuel cell performance was suggested to design and optimize atomic scale surface textures of Pt NPs. During the FBR-ALD of Pt NPs, in-situ surface modulation of Pt NPs was applied via a proper protective oxide deposition and etching. A careful surface studies was performed to analyze the surface morphology, distribution and uniformity of Pt NPs. Electrochemical performances were evaluated and optimized by measuring cyclic voltammetry (CV) and oxygen reduction reaction (ORR).

References

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1:45pm **AA1-TuA-2 Stabilization of ALD-grown Iridium Species for the OER Activity***, **Muhammad Hamid Raza**,* Humboldt-Universität zu Berlin, 2-Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), Germany*; M. Frisch, R. Kraehnert,* Department of Chemistry, Technische Universität Berlin, Germany*; N. Pinna,* Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Water-splitting electrocatalysts are vital because of the growing demand for renewable energy and the concurrent depletion of fossil fuels. Different types of catalytically active oxides are used as electrode materials for electrochemical water splitting. The catalytic performance of those materials depends on the surface composition and morphology of the active species. Increasing the number of potentially active sites on electrode surfaces leads to enhancing the catalytic efficiency of such electrodes. Iridium (Ir) / iridium oxides (IrO_x) are currently one of the most promising candidates for competent oxygen evolution reaction (OER) in acidic media. So far, the very high costs for Ir impede the large-scale production of hydrogen (H_2). Atomic layer deposition (ALD) has been researched to maximize the utilization of Ir-based electrocatalysts. However, the stability of the system with an ultra-thin film of electrocatalytically active species is challenging especially in acidic media. We report an electrode coating concept with template-controlled mesoporosity surfaces modified with Ir species. A temperature-controlled ALD process of Ir/IrO_x films grown has been studied and the resulting films have been examined structurally and in terms of their electrocatalytic activities. Ir/ IrO_x films are successfully grown using 1-Ethylcyclopentadienyl-1,3-cyclohexadieneiridium(I) and ozone between 160 and 120 °C. Metallic Iridium can be deposited at higher temperatures. However, a pseudo amorphous Iridium oxide film is deposited at a lower temperature that not only provides a remarkable catalytic performance but also stabilizes the overall system by conformally covering the carrier's surfaces. With our ALD process at low temperatures, we can achieve an outstanding mass-specific OER activity of the order of 3000mA mg_{Ir}^{-1} at 1.60 V vs. RHE at 25°C and 0.5 m H_2SO_4. This shows great promise for the development of highly efficient (electro-)catalysts. The peculiarities of ALD not only make this a technique of choice to synthesize optimized electrocatalysts, but also provide the possibility to verify fundamental theories and develop a clear structure−property relationship will be discussed.

2:00pm **AA1-TuA-3 Atomic Layer Deposited Nickel Sulfide as a (Pre)Catalyst for Oxygen Evolution Reaction***, **Miika Mattinen**, T. Hatanpää, K. Mizohata,* University of Helsinki, Finland*; S. Bent,* Stanford University*; M. Ritala,* University of Helsinki, Finland

Hydrogen gas (H_2) is currently one of the most important feedstocks of the chemical industry. In the future, H_2 is foreseen to play a major role in decarbonizing society, for example by acting as a clean fuel and replacing carbon in steelmaking. These uses require replacement of the current fossil fuel based H_2 production with cleaner alternatives, such as electrochemical water splitting. Of its two simultaneously occurring half-reactions, the oxygen evolution reaction (OER) is limiting the efficiency of water splitting. Thus, development of highly active, stable, and affordable OER catalysts is critical.

Nickel sulfides (NiS_x) have been identified as highly active OER electrocatalysts. It has been shown that at least the surface of NiS_x may transform to oxyhydroxide under the highly oxidizing OER conditions.[1] Therefore, NiS_x electrocatalysts may best be described as precatalysts for the actual catalyst. However, factors such as the extent and rate of the catalyst transformation process and ultimately the catalytically active species remain poorly understood. Well-defined thin films catalysts prepared by ALD are ideal for obtaining such insights.

We began by developing a new ALD process for NiS_x using a low-cost, easily synthesized $NiCl_2$(TMPDA) precursor[2] (TMPDA = *N,N,N′,N′*-tetramethyl-1,3-propanediamine) with H_2S. The process exhibits saturating growth behavior and deposits highly conducting films on a range of different substrates at 165–225 °C. The deposited films are highly pure (<3% total H, C, N, O, and Cl impurities) and consist of a mixture of β-NiS and Ni_9S_8 phases.

For the OER electrocatalysts, we deposited NiS_x films on SnO_2:F coated glass and studied them under alkaline conditions. X-ray photoelectron spectroscopy measurements indicate that the NiS_x films lose the vast majority of S under the OER conditions and transform to (oxy)hydroxide-like material. Electrochemical measurements and electron microscopy show that this transformation is accompanied by an increase in surface area due to the films becoming porous. We propose that the porosity enables the nickel atoms inside the films to participate in OER, thus increasing the electrocatalyst activity. Additional studies examine the transformation process in more detail as well as the long-term stability of catalysts formed from NiS_x. In order to tailor the porosity and surface area of nickel-based electrocatalysts, we are also working on expanding the family of thiolate hybrid materials[3] to nickel.

1 Wygant et al., *ACS Energy Lett.*, 2018, **3**, 2956

2 Väyrynen, Ritala et al., *Adv. Mater. Interfaces*, 2018, **3**, 1801291

3 Shi, Bent et al., *JVSTA*, 2022, **40**, 012402

2:15pm **AA1-TuA-4 Novel Phosphite Doping into ALD SiO_2 to Improve H^+ and H_2 Permeability in Water Electrolyzers***, **Sara Harris**, M. Weimer,* Forge Nano*; K. Yim, L. Cohen, D. Esposito,* Colombia University*; A. Dameron,* Forge Nano

H2 is a carbon-free and versatile energy carrier, anticipated to be an integral part of the clean energy future. Hydrogen fuel has significant relevance today; currently comprising roughly 1.5% of global energy use. Unfortunately, over 95% of H2 production comes from highly polluting, oil and coal, or grey (methane) sources. Currently, the cost of green H2 from electrolysis is not competitive with fossil fuel sources.[i] One pathway to drive down cost is by increasing the efficiency of polymer electrolyte membrane (PEM) electrolyzes by reducing the ohmic overpotential required by the cell. In this work, the path to ohmic overpotential reduction, which is partially dictated by the membrane thickness [ii] and the H^+ conductivity, will be explored by replacing Nafion with an ultra-thin proton-conducting oxide membrane (POM) deposited by ALD. Specifically, an SiO2 ALD film deposited with a unique catalytic process has been explored over a range of temperatures and thickness to measure the H^+ conductivity and gas permeation (H2). To address the inherently low H^+ permeability of baseline SiO2 films, phosphorous-based dopants were explored to increase H^+ permeability without sacrificing other requirements. Phosphate, $PO4^{-3}$ species were doped into an SiO2 ALD film using two novel ALD precursors.[iii] Both precursors were found to incorporate into the growing SiO2 film, as measured by X-ray photoemission spectroscopy (XPS), but not grow a P2O3 or P2O5 monolith with H2O, O2 or O3. The largest PO4^{-3} percent incorporation was observed in an ABC-type ALD sequence, where the PO4^{-3} precursor did not see a separate oxidant, shown in Figure 1 below. All POx:SiO2 films also showed a decrease in refractive index. Critically, H^{+} permeability improved with PO4^{-3} addition. An ABC-type ALD processes showed the largest improvement of ~8.5x in acidic solution with a rotating disk electrode. Unexpectedly, the addition of PO4^{-3} also decreased H2 gas permeability across all samples by up to 12x. Importantly, ALD POM films have the potential to directly coat membranes onto high surface area porous transport or gas diffusion layers for integration into current PEM electrolyzer cells, further improving efficiency. This work is the first step in building full electrolyzers that employ a novel ultra-thin ceramic membrane with the potential to enable a competitive green H2 market.

[i] https://hub.globalccsinstitute.com/ and https://www.mckinsey.com/industries/oil-and-gas/our-insights/global-energy-perspective-2022

[ii] Han, et al., Int. J. Hydrogen Energy, 40, 2015

[iii] Henderick, L., et al., Appl. Phys. Rev. 9, 011310, 2022

2:30pm **AA1-TuA-5 Atomic Layer Deposition of Copper Catalysts for Electrochemical Recycling of Carbon Dioxide***, J. Lenef, S. Lee, K. Fuelling, K. Rivera Cruz,* University of Michigan, Ann Arbor*; A. Prajapati, C. Hahn,* Lawrence Livermore National Laboratory*; C. McCrory,* ***Neil P. Dasgupta,*** University of Michigan, Ann Arbor

Electrochemical recycling of carbon dioxide into value-added products is a promising strategy to mitigate climate change as the CO_2 reduction reaction (CO_2RR) can be driven using renewable electricity (i.e. wind, solar). So far, copper metal is the only known single element catalyst to form multi-carbon products, such as ethylene and ethanol, from CO_2RR. Numerous synthesis strategies have been employed to deposit copper-based catalysts including sputtering, evaporation, electrodeposition, and solution processing; however, they do not enable atomically precise control of film thickness and particle size and have limited conformality on 3D substrates such as carbon gas diffusion electrodes. To address this knowledge gap, we fabricate Cu catalysts using plasma-enhanced atomic layer deposition (PE-ALD) with varied PE-ALD cycle numbers on 3D carbon electrodes to achieve precise control of catalyst loading. A polycrystalline Cu metal layer was confirmed by grazing incidence X-ray diffraction. The catalyst surface morphology was probed by scanning electron microscopy and atomic force microscopy, highlighting the island-growth mode of the metal catalyst.

We demonstrate that Cu surfaces prepared by PE-ALD can reduce CO_2, forming value-added products such as carbon monoxide, methane, and ethylene. Parasitic hydrogen evolution was minimized to Faradaic efficiencies of ~10%, as quantified using *in situ* gas chromatography measurements. We further demonstrate a selectivity over 40% Faradaic efficiency for ethylene production, which is among the highest values reported to date in an H-cell geometry. Compared to evaporated Cu catalysts, we show significant methane suppression for the PE-ALD Cu. Finally, we demonstrated stability for up to 15 h for CO_2 reduction products with minimum loss in the ethylene production rate. In summary, we demonstrate CO_2RR using PE-ALD of Cu catalysts with high selectivity and stability, which provides a pathway to conformal deposition on 3D substrates with precise control of particle size and catalyst loading.

2:45pm **AA1-TuA-6 Stability of Molecular Layer Deposited (MLD) Alucone in Acetonitrile for Photoelectrochemical CO_2 Reduction Applications***,* ***Hyuenwoo Yang,*** North Carolina State University, Republic of Korea*; H. Margavio, L. Keller, G. Parsons,* North Carolina State University

In this work, we study an organic-inorganic hybrid metalcone material deposited by molecular layer deposition (MLD) for applications in solar-energy driven CO_2 reduction to liquid fuel.In the field of photoelectrochemical CO_2 reduction reaction (CO_2RR), controlling the selective absorption of CO_2 on silicon-bound molecular catalysts for photo-electron driven reduction ischallenging to avoid the hydrogen evolution reaction (HER) that proceeds during the competitive reduction of available protons.Recently, researchers have shown that for some geometries, organic encapsulation layers can improve the stability of the catalysts and at the same time increase the selectivity of CO_2 conversion.To date, however, organic layers formed by MLD have not been significantly studied for this application. Advantages of metalcones have great potential as an encapsulation layer for inducing selective catalytic reactions. Here, we demonstrate photoelectrochemical compatibility of alucone thin films on Si photoelectrode in acetonitrile electrolyte. Alucone layer was deposited with trimethylaluminum (TMA) and ethylene glycol (EG) in low temperature (< 100°C). Alucone showed outstanding stability in acetonitrile (0.1 M Tetrabutylammonium hexafluorophosphate, $TBAPF_6$) electrolytes under 1 sun illumination and applied potential of -1.8 to 0.7 V versus Ag/$AgNO_3$ reference electrode. In contrast, the thickness of alucone shrank by 94% within an hour in water based electrolyte (0.1 M potassium chloride, KCl) under -1.5 to 0 V versus Ag/AgCl reference electrode. This result matches with the previous research that vapor absorption changes the thickness of metalcone. This results supports the photoelectrochemical stability of alucone to acetonitrile which has high solubility of CO_2.

Our study opened the new possibility of applying MLD metalcone thin films to CO_2RR fields through its excellent transparency, molecular permeability and CO_2 selectivity. MLD alucone layer is expected to be feasible as an encapsulation layer for Si photoelectrodes and surface modification layer to form favorable CO_2 microenvironment with its permeability, transparency and hydrophobicity.

3:00pm **AA1-TuA-7 Enhanced Green Hydrogen Production Using ALD-based Catalysts for Ammonia Decomposition***,* ***Yu-Jin Lee,*** *H. Sohn, H. Jeong, S. Nam,* Korea Institute of Science and Technology (KIST), Republic of Korea*; J. Park,* Seoul National University, Republic of Korea*; Y. Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea

Ammonia-based hydrogen value chains are emerging as one of the most promising ways for achieving a carbon-neutral hydrogen economy. In order to expedite the development, it is essential to develop highly efficient and scalable catalysts for ammonia decomposition. In this study, we demonstrate the use of atomic layer deposition (ALD) to fabricate highly efficient Ru/TiO_2-ALD/γ-Al_2O_3 bead catalysts for ammonia decomposition. By utilizing the ALD technique to introduce an ultrathin TiO_2 layer between Ru nanoparticles and the γ-Al_2O_3, followed by high-temperature alloying, we were able tochange the electronic structure of the Ru and shift the nitrogen binding energy to lower, resulting in an enhancement of catalytic activity. One of the most intriguing aspects of this study is the use of ALD technology to overcome the limitations of reducible oxides in high-temperature reducing atmospheres, such as particle encapsulation or consolidation that can diminish the catalytic activity of nanoparticles. Compared to state-of-the-art Ru-based catalysts with rare-earth metal oxides such as Y_2O_3 and La_2O_3, the Ru/ALD-TiO_2/γ-Al_2O_3 catalysts developed in this study demonstrated superior catalytic performance as well as cost competitiveness due to minimized utilization of functional oxide. The promising results of this study indicate that the use of ALD technology catalysts has the potential to significantly advance the establishment of ammonia-based hydrogen value chains, leading to enhanced efficiency in the hydrogen reconversion process and ultimately reducing the levelized cost of hydrogen.

3:15pm **AA1-TuA-8 Atomic Layer Depositied Silver Catalysts for Anion Exchange Membrane Fuel Cells***,* ***Gwon Deok Han,*** *H. Han, F. Prinz,* Stanford University*; J. Shim,* Korea University, Republic of Korea

In the automotive industry, the paradigm shift from internal combustion engine vehicle to electric vehicle is accelerating to respond to the global climate crisis. Fuel cell electric vehicles (FCEVs) powered by hydrogen are one of the zero-emission means of transportation, and its advantages are long mileage and fast charging time. However, proton exchange membrane fuel cell (PEMFC), which is the propulsion system of FCEVs, requires the use of precious metal catalysts such as Pt. This is a decisive factor hindering the popularization of FCEVs in terms of economic feasibility. Anion exchange membrane fuel cell (AEMFC) is receiving considerable attention as a next-generation technology due to its unique advantage of operating in an alkaline environment that allows the use of Pt-free catalysts. In this study, a high-performance AEMFC cathode containing carbon nanotubes surface-modified with Ag particulates was fabricated using plasma-enhanced atomic layer deposition (PEALD). HEMFC cathode coated with ALD Ag particulates delivers a maximum power density of 2,154 $mW \cdot mg_{Ag}^{-1}$ in an alkaline environment. The AEMFC cathode decorated with ALD Ag contributed to reducing the polarization energy loss by improving the cathodic oxygen reduction reaction. Through the application of PEALD, it was successfully demonstrated that an optimized microstructure design is possible while minimizing the load of the Ag catalyst at the cathode. This study is significant in that it successfully demonstrated the potential applicability of ALD in the manufacture of high-performance AEMFC cathodes.

ALD Applications
Room Grand Ballroom H-K - Session AA2-TuA

Emerging Materials

Moderators: Joel Molina Reyes, Instituto Nacional de Astrofísica, Óptica y Electrónica (INAOE), Tero Pilvi, Picosun Oy

4:00pm **AA2-TuA-11 Unfolding the Challenges to Prepare Epitaxial Complex Oxide Membranes by Chemical Methods***, **Mariona Coll**, P. Salles,* ICMAB-CSIC, Spain **INVITED**

Epitaxial transition metal complex oxides have raised enormous interest to be integrated in next-generation electronic devices envisaging distinct and novel properties that can deliver unprecedented performance improvement compared to traditional semiconductors. However, this step demands for ease heterointegration in mature semiconductor device technology including bendable, wearable and light-weight devices. The possibility to fabricate free-standing single crystal complex oxides has revolutionized this field stimulating new research from synthetic procedures and uncommon combination of materials to fundamental physics, foreseeing an even broader spectrum of applications.[1]

Motivated by the use of cost-effective chemical deposition approaches to prepare high quality complex oxide epitaxial films and investigate the influence of defects on its properties, here it is presented our most recent studies towards the fabrication of epitaxial complex oxide membranes using the sacrificial layer approach. First, it will be introduced a facile chemical route to prepare $Sr_3Al_2O_6$ (SAO) sacrificial layers [2] and how to overcome its instability in air. Then, it will be discussed the preparation of bendable and magnetic $CoFe_2O_4$ [3] and $La_{0.7}Sr_{0.3}MnO_3$ membranes with special focus on the influence of the sacrificial layer composition on the membrane crystallinity and physical properties. Advanced X-ray diffraction analysis (XRD), reflection high energy electron diffraction (RHEED) and scanning transmission electron microscopy combined with electron energy loss spectroscopy (STEM-EELS) are used to unfold and start solving the challenges to prepare free-standing epitaxial membranes by chemical methods. This approach here presented offers a new opportunity to work with crystalline oxide membranes, easy manipulate them and fabricate new artificial heterostructures allowing future investigations of novel physical phenomena that can bring new opportunities for high-performance oxide electronic devices.

[1]*Synthesis of freestanding single-crystal perovskite films and heterostructures by etching of sacrificial water-soluble layers*, Di Lu, Harold Y Hwang et al. **Nature Materials**, 15, 11255-1260 **(2016)**

[2] *Facile Chemical Route to Prepare Water Soluble Epitaxial $Sr_3Al_2O_6$ Sacrificial Layers for Free-Standing Oxides* Pol Salles, Ivan Caño, Roger Guzman, Wu Zhou, Mariona Coll* et al.**Advanced Materials Interfaces**, 8, 2001643 **(2021)**

[3]*Bendable Polycrystalline and Magnetic $CoFe_2O_4$ Membranes by Chemical Methods P*ol Salles, Roger Guzmán, David Zanders, Anjana Devi, Mariona Coll* et al. **ACS Applied Materials Interfaces***.* 14,10 12845-12854**(2022).**

4:30pm **AA2-TuA-13 Tailoring Lattice Match by Cation Substitution in a Functional Ternary Oxide***, M. Rogowska, L. Rykkje, **Henrik Sønsteby**,* University of Oslo, Norway

Integration of functional complex oxide thin films can push the boundaries of electronic device performance. Functionality can be enhanced by implementing materials with tailored properties, or completely new functionality may be achieved by *e.g.* making use of ferroic characteristics. Model systems have been predicted, designed, and found to be interesting, but their realization often comes to a halt due to the difficulty of preparing samples under conditions feasible for ICT industry.

One example is the integration of $SrTiO_3$ (STO) as a high-κ material in transistor architectures. The dielectric constant of defect-free STO is among the highest known, but integration of the material very often leads to structural defects that hamper its functionality. High-quality STO can be deposited by high-temperature techniques, but these are seldom compatible with device manufacturing. Furthermore, the properties of STO are sensitive to strain and the quality of epitaxy at the interface, which is often hard to control when applying a high thermal budget. A functional template layer deposited under industrially relevant conditions, that can mitigate strain effects while working as an electronic conductor, would be a significant step towards harnessing the attractive properties of STO. One such material could be $LaNiO_3$ (LNO). LNO is structurally similar to STO while being a metallic conductor and ALD epitaxy has already been shown. Unfortunately, LNO imposes a 1.7 % strain on STO, which again hampers the dielectric properties by inducing structural defects and pinholes.

In this work, we use the unique strengths of ALD to deposit a lattice matched and conductive material that may act as a template for implementation of STO. The material is based on $LaNiO_3$, but utilizes substitution of Sc on B-site to increase the lattice size to match STO. We show that the lattice parameters can be continuously tailored from those of $LaNiO_3$ to $LaScO_3$, albeit exhibiting a critical substitution level at which the metallic properties of are lost. Luckily, at lattice matched substitution levels (a_{pc} = 3.905 Å), low resistivity is maintained. We show that direct epitaxial integration of this quarternary compounds is achievable by ALD, and that the interfacial quality towards STO is of high quality. We also pinpoint a crucial advantage of the low thermal budget of ALD: The mixed compound seems to be metastable and decomposes into binary/ternary constituents at higher temperatures.

We believe this is a large step towards integration of functional complex oxides in future ICT, while at the same time showcasing the fantastic opportunities of using ALD to deposit complex oxides.

4:45pm **AA2-TuA-14 *In situ* Atomic Layer Doping of Epitaxially Grown β-Ga_2O_3 Films via Plasma-enhanced ALD at 240 ℃***, S. Ilhom,* Univerisity of Connecticut*; A. Mohammad, N. Ibrahimli, J. Grasso, B. Willis,* University of Connecticut*; **Ali Okyay**,* Stanford University*; N. Biyikli,* University of Connecticut

Wide and ultrawide bandgap (WBG/UWBG) semiconductors make the backbone of high-power high-frequency electronics, used in electric vehicles, 5G and beyond wireless communication systems, and smart power grids. However, the relatively complex growth reactors and typical growth temperatures around 1000 °C lead to increased production costs and limited application space. Gallium oxide (Ga_2O_3) is an emerging UWBG semiconductor showing superior material properties particularly ideal for harsh environments (high temperature, high-energy radiation, corrosion) applications. Reducing the growth and doping process temperatures for Ga_2O_3 would potentially enable a wider integration platform towards post-CMOS integration and flexible electronics.

Hence, we report on the low-temperature as-grown crystalline β-Ga_2O_3films on Si, glass, and sapphire via hollow-cathode plasma-enhanced atomic layer deposition (HCPA-ALD). The films were deposited using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Additionally, we have employed in situ atomic layer doping to n-type dope β-Ga_2O_3films where tris-dimethylaminosilane (TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. Growth experiments have been performed at 240 °C under 50 W rf-power. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Additionally, eachunit ALD-cycle was followed by an *in situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both in-situ and ex-situ ellipsometry were employed to measure the thickness and optical properties of the films. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial Ga_2O_3 films with monoclinic β-phase. On the other hand, GIXRD of the samples grown on Si and glass displayed polycrystalline β-Ga_2O_3 films. HR-STEM imaging and EDX elemental analysis confirmed the epitaxial relationship of the β-Ga_2O_3films grown on sapphire substrates and displayed successful incorporation of dopant elements. Preliminary electrical conductivity measurements showed highly resistive samples. Therefore, *ex situ* thermal annealing studies are ongoing to explore possible dopant activation. Further studies from our XPS characterizations will provide additional insight about the chemical bonding states of the dopant species. A significant effort will be devoted for the comparison of Si and Sn-doping strategies and potential suggestions will be provided to overcome the challenges in achieving device quality undoped and doped β-Ga_2O_3 layers at low growth temperatures.

5:00pm **AA2-TuA-15 Plasma Enhanced Atomic Layer Deposition of Niobium Nitride for Scalable Quantum Device Fabrication***, Yi Shu,* Oxford Instruments Plasma Technology, UK*; C. Lennon,* University of Glasgow, UK*; Z. Ren,* Oxford Instruments Plasma Technology, UK*; H. Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands*; F. Morini, A. Kurek, T. Hemakumara,* Oxford Instruments Plasma Technology, UK*; R. Hadfield,* University of Glasgow, UK

Superconducting niobium nitride (NbN) thin film has gained extensive attention in quantum computing and quantum communication applications[1,2] due to its high transition temperature (T_c) and high critical current. Highly uniform NbN films over whole processed wafers are essential to improve device scalability and fabrication yield. Moreover, superconducting through silicon vias (TSV) is one of the key technologies enabling 3D quantum integration where highly conformal NbN liners inside TSVs are required for interconnection between quantum and control/readout circuits[3]. Plasma enhanced atomic layer deposition (PEALD) of superconducting NbN is a promising option to meet all these requirements.

In this work, we firstly present PEALD NbN films grown at 250 ºC on 200 mm Si wafers, utilizing (t-butylimido)-tris(diethylamido) niobium (TBTDEN) and H_2/Ar plasma, carried out on an Oxford Instruments Plasma Technology FlexAL ALD tool equipped with an independent-controlled RF-biased electrode table (13.56 MHz, substrate biasing up to 100 W power, -350 V resulting DC bias voltage). By optimizing the substrate bias used in plasma steps, NbN films were produced at much faster speed (plasma exposure time in each ALD cycle was reduced from 60 s[4] to 5 s) with excellent film quality and uniformity. Characterization of T_c with a series thickness of NbN thin films (5 nm, 8 nm, 15 nm, 20 nm, and 30 nm) has demonstrated excellent film quality: T_c was as high as 10.2 K with the ultrathin 5 nm film and approached 13.5 K with the 30 nm film, as illustrated in Figure 1. Also, uniformity of the 8 nm NbN film was explored by investigating the thickness and superconducting properties spread up to a wafer size of 200 mm. Unparalleled uniformity over the whole 200 mm wafer was observed for both film thickness (±2.8%) and transition temperature T_c (±3.1%), as illustrated in Figure 2 and 3. A comparison of our parameter spread with literature data[4] is summarized in Table I.

In addition, superconducting TSV with conformal NbN coating was also explored by respectively depositing 50 nm PEALD NbN films on frontside and backside of a perforated TSV sample. Preliminary tests on such sample have revealed superconducting interconnections between the frontside and backside NbN films, provided by the NbN coated TSVs at ~10.7 K.

1. Yan et al., Supercond. Sci. Technol. 35, 065004 (2022)
2. Taylor et al., Appl. Phys. Lett. 118, 191106 (2021)
3. Yost et al., npj Quantum Inf 6, 59 (2020)
4. Knehr. et al., J. Vac. Sci. Technol. A 39, 052401 (2021)

5:15pm **AA2-TuA-16 Superconducting NbN Thin Films Deposited by Plasma Enhanced Atomic Layer Deposition***, Jakob Zessin,* SENTECH Instruments GmbH, Germany*; M. Hagel, T. Reindl, L. Freund,* SF Nanostructuring Lab, Max Planck Institute for Solid State Research, Germany*; P. Plate,* SENTECH Instruments GmbH, Germany*; J. Weis,* SF Nanostructuring Lab, Max Planck Institute for Solid State Research, Germany

Niobium nitride (NbN) is a superconductor with a critical temperature up to 16 K[1]. The application of NbN as a superconductor has already been demonstrated in superconducting nanowire single-photon detectors in the near infrared range[2] and resonators[3].

Atomic layer deposition (ALD) is an advanced technique used to deposit thin films with precisely controlled thickness in the sub-nanometer range, high conformality on complex 3D structures and the possibility of uniform deposition for large area fabrication.

With the Nanostructuring Lab of the Max-Planck-Institute for Solid State Research Stuttgart, we developed a plasma-enhanced ALD (PEALD) process of NbN. The depositions have been carried out in a SENTECH PEALD tool. Tris(diethylamido)(tert-butylimido)niobium(V) (TBTDEN) was used as a precursor and H_2 and Ar as plasma gas mixture. The influence of the most critical process parameters, such as temperature and plasma exposure time on room temperature resistance and critical temperature will be discussed. The highest achieved critical temperature was 9.6 K.

[1]Hazra et al. *Supercond. Sci. Technol.***2016**, 29, 105011.

[2]Cheng et al. *Appl. Phys. Lett.***2019**, 115, 241101.

[3]Sheagren et al. *J. Low Temp. Phys.***2020**, 199, 875.

5:30pm **AA2-TuA-17 Work-Function Modulation using Atomic Layer Deposited TaN and Ternary TaAlN Metal Gate***, Moonsuk Choi, B. Ku, S. Kim, C. Chung, C. Choi,* Hanyang University, Republic of Korea

With the disruptive scaling in semiconductor technology, high-k/metal gate (HKMG) stacks have been introduced to overcome direct tunneling in gate leakage current and reliability issues associated the conventional poly-Si/SiO_2 stacks. To implement a wide range of threshold voltage (V_{TH}) in MOS devices, work-function modulation is required. There are several factors that govern V_{TH}, which is significantly influenced by metal gate. The selection of suitable metal electrodes to modulate their work function remains still a challenging task. Considering 3D structure in FinFET and Gate-all-around FET (GAAFET) with the narrow dimensional margin, atomic layer deposition (ALD) is the promising process to form the advanced gate electrodes due to the excellent thickness control, outstanding film quality, and applicable complex structure with high aspect ratio.

In this study, we characterized ALD TaN and TaAlN and their relevant work functions were investigated. The different metal precursors were used such as metal-organic (tertbutylimide tris-diethylamido tantalum, TBTDET) and metal-halide (tantalum(V) chloride, $TaCl_5$) precursors as Ta source and tri-methylaluminium (TMA) as Al source, respectively, with reacting ammonia (NH_3) gas and deposition temperature was 350 °C. The chemical structures of the metallic precursors as well as the specific sequence in the ALD process are illustrated in Figure 1 (a)-(b). After the deposition process, the films were treated by forming gas annealing (FGA) treatment to confirm the effects of the thermal budget. Figure 2 (a)-(b) shows the resistivity of these metal gates. Their low values are a promising feature even at the thinner thickness as well as the increased amounts of Al element. MOS devices in the structure of p-Si/HfO_2/metal gate electrodes (TaN and TaAlN)/capping metal (either W or Al) were fabricated. The capacitance-voltage (C-V) characteristics are estimated in Figure 3 (a)-(b). The increase of sub-cycle ratios and pulse time of TMA in ALD induces the positive flat band voltage (V_{FB}) shift with enhancing Al incorporation into TaN films. In figure 4 (a)-(b), the work function of both films was summarized V_{FB} as a function of parameters. The effect of Al incorporation into TaN can provides the modulation of the work function from the mid-gap to the valence band of Si. The FGA process presents another option for tuning the work function in both thin films by reducing the amounts of carbon under a hydrogen ambient. These results can contribute to a better understanding to a feasible application for HKMG stacks with improved electrical properties such as engineering of the work function as well as multiple V_{TH}.

ALD Applications
Room Evergreen Ballroom & Foyer - Session AA-TuP
ALD Applications Poster Session

AA-TuP-1 Improved Properties of the $SrRuO_3$ Electrode by Controlling Annealing Conditions and Adopting Al-doping*, Junil Lim*, *C. Hwang,* Seoul National University, Republic of Korea

This study reports on the properties of $SrRuO_3$ (SRO) thin films used as a bottom electrode of $SrTiO_3$ (STO) dielectric film with a good lattice match[1]. SRO film was grown via atomic layer deposition of SrO and pulsed-chemical vapor deposition of RuO_2 using the $Sr(^iPr_3Cp)_2$ ($^iPr_3Cp$ means 1,2,4-trisisopropyl-cyclopentadienyl) and RuO_4 (product name ToRuS) precursors, respectively. Because oxygen-deficient SRO film was deposited, annealing in an O_2 atmosphere was necessary for its crystallization. During annealing, the Ru of SRO film reacted with oxygen to form the volatile RuO_4 (gas). In addition, many voids formed during the annealing by the agglomeration hindered its use as a bottom electrode. Al was doped in the SRO films to improve these properties, of which the optimal annealing conditions were searched. The effects of Al on the formation of the volatile RuO_4 were experimentally and theoretically investigated. The theoretical calculation confirmed that the Al substituted with Ru (Al_{Ru}) in the SRO film improved the crystallinity of cubic-SRO. Thus, Al-doped SRO (ASRO) film had a larger grain size, higher crystallinity, and improved surface morphology. Furthermore, surface morphology improvements improved resistance properties (~ 1000 μΩ·cm at a thickness of 25 nm).

Figure 1. (a) Resistivity of SRO and ASRO films after PDA as a function of thickness. (b) The internal energy (E) differences between crystalline (*xtal*) and amorphous (am) structures in pure, Al_{Ru}, and $2Al_{Ru}$ + oxygen vacancy (V_O) SRO.

Acknowledgments This work was supported by the National Research Foundation of Korea (2020R1A3B2079882).

References [1] Jeong Hwan Han et al., Chem. Mater., 24, 4686-4692 (2012)

AA-TuP-2 Yttrium-doping in TiO_2 Films for DRAM Capacitor Applications*, Tae Kyun Kim*, *C. Hwang,* Seoul National University, South Korea

This work reports on the electrical and structural behavior of Yttrium-doped TiO_2 (YTO) thin film as a dielectric layer for a capacitor of dynamic random-access memory. Yttrium (Y) is one of the well-known doping elements for dielectric materials such as ZrO_2 [1] and $SrTiO_3$ [2] for improving their electrical performances. It could be anticipated that the doped Y ions in TiO_2 thin films might reduce leakage current density by forming acceptor defects, as the doped Al in TiO_2 did [3]. However, the doping effect of Y in TiO_2 thin films appeared differently depending on the amount of dopant in one Y atomic layer deposited cycle. The doping concentration of Y ions was controlled by decreasing Y-source feeding time (Y F.T.) from its saturated feeding time (10 s) during the atomic layer deposition (ALD). Among different Y F.T.s, the best electric performance was observed when Y F.T. is 4s achieving equivalent oxide thickness (EOT) of 0.5 nm at physical oxide thickness (POT) of 8 nm (Fig. 1a) on the Ru bottom electrode. Moreover, the dielectric constant of YTO films increased when Y F.T. is 2s compared to TiO_2 films. This effect was ascribed to the relaxation of lateral tensile strain in the TiO_2 layer, induced by different thermal expansion coefficients of the TiO_2 ($8\text{-}11\times10^{-6}$/K) and Si substrate (2.6×10^{-6}/K). The size of Y^{3+} (Ionic radius: 104 pm) is larger than that of Ti^{4+} (74.5 pm), so tensile strain can be relaxed when the Ti ions are substituted with Y ions. However, Y_2O_3 particles were formed after 2s of Y. F.T. due to the low solubility of Y in TiO_2, which decreased the dielectric constant (Fig. 1b). The relaxation of strain and Y_2O_3 formation can be supported by the change in the position of rutile TiO_2 peaks from XRD data (Fig. 1c). These results indicated that the highly doped Y ions did not diffuse into the TiO_2 layer well but formed Y_2O_3 particles, which limited the diffusion and increased EOT. Therefore, careful control of Y-doping concentration and profile is necessary to optimize the capacitor dielectric performance.

AA-TuP-3 Non-Diffusive Phenomenon of Al and Y Doping in the ZrO_2/Al_2O_3 and ZrO_2/Y_2O_3 Bilayer Thin-Films and Its Influence on the Field-Induced Ferroelectric Properties*, Haengha Seo*, *J. Shin, J. Lim, T. Kim, H. Paik, C. Hwang,* Seoul National University, Republic of Korea

The emergence of the ferroelectric phase in the non-polar ZrO_2 or doped-ZrO_2 (e.g., $Hf_xZr_{1-x}O_2$) thin films under a sufficiently large electric field, which corresponds to the field-induced ferroelectric (FFE) transition, has led to a promising breakthrough to the future dynamic random access memory (DRAM) capacitor. A large extra charge can be stored reversibly in the DRAM capacitive layer by carefully manipulating the FFE materials. However, the leakage current control for such a thin film (sub-10 nm) must be a bottleneck for using the FFE material in mass production. Therefore, inserting layer or p-type doping (e.g., Al_2O_3) technique has been introduced for leakage current suppression. However, there is a lack of research on how the FFE characteristic of the ZrO_2 film would change in the presence of those aliovalent dopants.

It was reported that when the inserted Al_2O_3 layer was thicker than 0.3 nm (~monolayer) in the atomic-layer-deposited $ZrO_2/Al_2O_3/ZrO_2$ stack, the Al ions no longer diffused into the ZrO_2 lattice but formed a separated Al_2O_3 layer.[1] On the other hand, Y_2O_3 layer insertion in the ZrO_2 resulted in the full Zr-Y inter-diffusion even up to ~ 1 nm of the Y_2O_3 layer.

However, recent research showed that when the thin insertion layer was located on top of the ZrO_2 (i.e., bilayer system), diffusion of the dopant did not occur regardless of the doping element. Furthermore, it was found that only a small amount of diffusion occurred in the ZrO_2/Y_2O_3 case when the underlying ZrO_2 was extremely thin (~ 4 nm). This finding is interesting because even a low density of Al or Y ions could stabilize the tetragonal-ZrO_2 phase, thus eliminating the film's FFE hysteresis loop at a given electric field. Indeed, introducing a thin Al_2O_3 or Y_2O_3 layer in the middle region of the ZrO_2 film removed the FFE hysteresis loop of the film completely within the breakdown voltage range. On the contrary, both the ZrO_2/Al_2O_3 and ZrO_2/Y_2O_3 bilayer stacks showed the hysteresis loop with its magnitude of which the shape corresponds to the pristine ZrO_2 layer of the same thickness.

Therefore, introducing a thin capping layer on the ZrO_2 film rather than adding it in the middle should be a promising technique for controlling the leakage current issue while maintaining the FFE performance. The non-diffusive phenomenon also occurred when the layer was present underneath the ZrO_2 layer. However, this bottom-layer structure did not guarantee the thickness or quality of the crystalline structure of the ZrO_2 due to its different growth behavior on the insertion layer.

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AA-TuP-4 Promoted Crystallization of $SrTiO_3$ Thin Film for DRAM Capacitor by Inserting GeO_x Buffer Layer in $Ru/SrTiO_3/RuO_2$ Capacitor*, Heewon Paik*, *C. Hwang,* Seoul National University, Korea

$SrTiO_3$ (STO) is a perovskite material with an ultra-high dielectric constant(~300)[1]. However, STO has relatively low bandgap energy(3.2eV)[1] and is vulnerable to the formation of micro-crack during annealing at high temperatures, which could lead to high leakage current[2]. Therefore, carefully controlling the leakage current while securing high capacitance is necessary for STO to be used as a dynamic random access memory (DRAM) capacitor layer. This study presents the enhanced crystallization behavior of the STO thin film by inserting GeO_x buffer layer between the STO and the underlying Ru bottom electrode. The STO film and GeO_x buffer layer were deposited via atomic layer deposition (ALD) at 350℃, using $Sr(^iPr_3Cp)_2$, $Ti(CpMe_5)(OMe)_3$, $Ge(NMePh)(NMe_2)_3$ as Sr-, Ti-, and Ge- precursors, respectively. Post-deposition annealing at 475~650℃ was conducted to form a perovskite crystal structure.

The crystallization of STO was initiated at a lower temperature (475℃) with the aid of GeO_x buffer layer. As a result, the STO film with GeO_x buffer layer (b-Ge-STO) crystallized at 575℃ with a *k* value of ~159. In contrast, STO without the buffer layer showed a mixed structure of amorphous and crystalline phase(*k*~71.7), which required a higher annealing temperature of 650℃ for better crystallization (*k*~129.5). As the leakage path formation mainly occurs during high-temperature annealing[2], the lowered annealing temperature could efficiently suppress the leakage current without any degradation of crystallinity. However, when GeO_x buffer layer was inserted in the middle of the STO film (m-Ge-STO), it separated the upper and lower STO layers, and only the upper STO layer crystallized well at 575℃. As a result, the minimum equivalent oxide thickness values of b-Ge-STO annealed at 575℃ were 0.43nm, which could meet the leakage criteria for DRAM capacitor($<10^{-7}A/cm^2$ at a capacitor voltage of 0.8V). The significance of this study is that GeO_x buffer layer enabled controlling leakage current of STO without the conventional 2-step process involving the thin STO seed layer[2].

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AA-TuP-5 Laterally Resolved LEIS for Surface Coverage Analysis in Porous Materials*, **Thomas Grehl**, P. Brüner,* IONTOF GmbH, Germany*; S. Saedy,* Chemical Engineering Department, Delft University of Technology, Netherlands*; J. Järvilehto, C. Gonsalves, J. Velasco,* Department of Chemical and Metallurgical Engineering, Aalto University, Finland*; J. van Ommen,* Chemical Engineering Department, Delft University of Technology, Netherlands*; R. Puurunen,* Department of Chemical and Metallurgical Engineering, Aalto University, Finland

One of the essential advantages of ALD is in many applications of minor importance – its ability to deposit on rough and porous materials far beyond the classical semiconductor applications. This is already exploited for heterogeneous catalysts and similar material systems. However, the characterization is challenging for many of the analytical techniques when it comes to judging the surface coverage and film thickness on internal surfaces. Still the coverage, nucleation behaviour/dispersion, thickness distribution etc. need to be assessed even inside the pores, much like for the planar surfaces in classical thin film deposition.

The surface sensitivity of Low Energy Ion Scattering (LEIS) is key to determining these properties on planar films. The same properties can be determined also on rough and insulating surfaces like catalyst supports, which are often porous oxides. In combination with cross-sectioning of these support materials and laterally resolved LEIS analysis, essential information is gained.

In this contribution, we will illustrate the approach by reporting results from cross-section analysis of mesoporous γ-alumina spheres which were impregnated with Pt in an ALD process. Depending on the conditions, the deposition extends more or less deep into the sphere. LEIS can quantify the surface coverage of the Pt, which is the active phase of many catalysts, in a laterally resolved way and therefore allows to study the precursor exposure inside the porous material.

Another application of this approach is the analysis of deposition on PillarHall$^{\text{TM}}$ chips, which are used as a vehicle to study the precursor transport and exposure in general. Also here, not only the deposited amount of material, but more precisely the coverage and thickness of the (incomplete) film is evaluated as a function of diffusion length.

AA-TuP-6 Group III-Nitride Semiconductor Materials Made by Plasma Atomic Layer Deposition*, **Noureddine Adjeroud**,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

III-N semiconductors are largely present in the industry, through chemical vapor deposition (CVD) techniques such as Metalorganic vapour-phase epitaxy (MOVPE). Those deposition techniques use conventionally the reaction of ammonia (NH3) with industrially relevant precursors such as trimethylaluminum (TMA), trimethylgallium (TMG) or trimethylindium (TMI) at high temperatures (750-900 °C) [1]. Plasma-assisted Atomic Layer Deposition (PA ALD) is becoming a trustworthy alternative to the standard CVD deposition techniques, and it appears as a solution for highly conformal coating and low temperature processing as two important assets to tackle growth temperatures of the nitride films not interfering with CMOS circuitry.

This work is based on the optimization and engineering of the plasma ALD of c-axis highly oriented aluminium nitride (AlN) films we proposed [2]. The pathway was further extended to facilitate low temperature (<450 °C) deposition of other III-N materials, such as GaN and InN semiconductors with wide and small bandgap respectively. In this work we utilized a gas mixture of H2/Ar/N2 as nitrogen precursor for nitride thin films initiated by a plasma source. The mix of Ar and H2 allows both to stabilize the plasma phase and to induce an optimized reducing of the ligands of the organometallic precursors reducing the carbon contaminants measured in the materials. We observed by XPS stoichiometric III-N films with no detectable carbon contaminants and also a low level (<5%) of oxygen contaminants in the nitride films. The XRD and TEM analysis confirm privileged hexagonal crystalline structure of the thin film below 100 nm thickness.

Insights on the ALD set-up and specific sequence of the deposition process will be presented for the growth of aluminium nitride (AlN), gallium nitride (GaN), indium nitride (InN), and ternary III-N films.

Those results have the potential to pave a way for both buffer-oriented seed films for post-growth, and also films with tailor made electronics properties for the next-generation of III-Nitride/CMOS components and functional coatings with piezoelectric and semiconducting properties for MEMS applications with transducing capabilities.

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AA-TuP-7 High-Temperature High-GPC SiO_2 Gap-Filling by Thermal ALD Using Novel Si Precursors*, **Wonyong Koh**, J. Kim, B. Kim, J. Choi,* UP Chemical Co., Ltd., Republic of Korea

SiO_2 gap-filling by high-temperature ALD are used for semiconductor device manufacturing, especially for 3D-NAND Flash memory devices. Excellent step coverage is necessary to fill gaps with very high aspect ratio. Stress control and other requirements necessitate high deposition temperatures over 600°C. Newly developed Si precursors show high ALD growth-per-cycle (GPC), which is stable over wide temperature range between 600 and 800°C. It is in contrast of ALD using tris(dimethylamino)silane (3DMAS), of which GPC is smaller and the GPC is not maintained at temperatures higher than 750°C. Novel Si precursors show better step coverage than 3DMAS despite of more than twice larger GPC than 3DMAS. SiO_2 ALD films from novel precursors also show the same or better film characteristics such as wet etch rate, shrinkage, density, etc. compared against SiO_2 ALD films from 3DMAS at same temperatures using tube furnace type ALD reactor with O_3. Experimental results are presented and compared against those of 3DMAS.

AA-TuP-9 Molecular Layer Deposition of Lithium-Containing Polymeric Coatings for Superior Lithium Metal Batteries*, X. Wang, **Xiangbo Meng**,* University of Arkansas

Lithium (Li) metal is currently among the most attractive anodes of rechargeable batteries, ascribed to its extremely high capacity of 3860 mAh/g and the lowest negative electrochemical potential (-3.04 V versus the standard hydrogen electrode).[1] However, the dendritic growth and continuous formation of solid electrolyte interphase (SEI) have prohibited Li metal from commercialization. Surface coating remains as a facile and effective route to secure stable Li metal anodes. Recently, we for the first time designed and developed a novel cross-linked lithium-containing polymeric coating (LiGL, GL = glycerol) via molecular layer deposition (MLD), enabling excellent protection effects over Li metal anodes.[1] MLD features its controllable film growth with excellent uniformity and conformality.[2] Our results revealed that the Li anodes coated by this MLD-LiGL polymeric layer can achieve a superior cycling stability, accounting for an extremely long cyclability up to ten thousands of Li stripping/plating cycles without failures in Li/Li symmetric cells.[1] Not limited to LiGL, we have been developing other new polymeric coatings via MLD, which have shown promising applications in lithium metal batteries. The excellent protection over Li anodes by these MLD coatings are commonly ascribed to their exceptional ionic conductivity, flexibility, and chemical stability. They are representing a new pathway to address the issues of lithium metal batteries.

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AA-TuP-10 Suppression of Interfacial Layer Formation in ZrO_2-Based Capacitors with TiN Electrode by Adopting MgO Thin Films as an Oxygen Diffusion Barrier*, **Seungwoo Lee**, D. Han, H. Seol, M. Nam,* Kyung Hee University, Republic of Korea*; D. Kim, H. Oh, H. Kim, Y. Park,* SK Trichem, Republic of Korea*; W. Jeon,* Kyung Hee University, Republic of Korea

ZrO_2-based capacitors with TiN electrodes are typical high-*k* materials applied to dynamic random-access memory capacitors. However, when ZrO_2 is grown on the TiN electrode by atomic layer deposition (ALD) using ozone as a reactant, it forms an undesirable TiO_xN_y interfacial layer due to the high reactivity of the TiN bottom electrode (BE). [1] This TiO_xN_y interfacial layer may have been formed by oxygen diffusion toward TiN BE during ZrO_2 ALD and the subsequent annealing process. It accompanies the formation of an oxygen-deficient ZrO_2 phase and creates oxygen vacancy-related defects, which influence the electrical properties degradation of the metal-insulator-metal capacitor. [2] Also, TiO_xN_y interfacial layer can decrease the capacitance density by increasing the thickness of the dielectric film. These interfacial properties can be improved by inserting an oxygen diffusion barrier such as Al_2O_3. [3] However, the crystallinity of tetragonal ZrO_2 deposited on the amorphous Al_2O_3 may deteriorate. Therefore, in this presentation, we investigated the effect of adopting MgO thin films as an oxygen diffusion barrier on TiO_xN_y interfacial layer formation. MgO thin films were used as oxygen diffusion barriers due to high chemical and thermal stability and did not show oxygen scavenging effects when interfaced with TiN. [4, 5] In addition, MgO has a larger bandgap (~7.8 eV) and higher dielectric constant (~10) than Al_2O_3 (~8) and does not degrade ZrO_2 crystallinity due to a low lattice constant mismatch with tetragonal ZrO_2. We fabricated ZrO_2/MgO capacitors with TiN using ALD and evaluated their electrical properties to analyze the effect of MgO insertion. The insertion of MgO significantly reduced leakage current density and improved C-V nonlinearity and frequency-dependent capacitance degradation. The capacitance density decreased because of the lower dielectric constant of MgO. However, for a specific MgO thickness, it was similar to the equivalent oxide thickness of a ZrO_2 single layer. The results of chemical state analysis by X-ray photoelectron spectroscopy showed that MgO suppresses the formation of an interfacial layer by preventing oxygen diffusion.

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AA-TuP-11 Improvement in Dielectric Properties of ZrO_2 Thin Film by Employing Thermal Stability Enhanced Zr Precursor in High-Temperature Atomic Layer Deposition*, Yoona Choi, A. Lee,* Kyunghee univ., Republic of Korea*; H. Oh, Y. Park,* SK trichem, Republic of Korea*; W. Jeon,* Kyunghee univ., Republic of Korea

Currently, ZrO_2 film is deposited by the atomic layer deposition (ALD) method, it can be used as the dynamic random-access memory (DRAM) capacitor material with a high dielectric constant (high-*k*) and excellent film quality [1]. However, as a size scaling down of the DRAM device is continued, a thinner dielectric film with high-*k* and low leakage current is required. To improve the electrical properties as described, a high-temperature atomic layer deposition is considered. And a precursor with high thermal stability is also required to withstand high deposition temperatures.

The ZrO_2 thin film deposited at a high temperature can produce more nuclei before the annealing process. Because the film contains many nuclei, the grain size is smaller than a film that is deposited at a low temperature after post-deposition annealing (PDA) treatment. The thin film with a small grain size has a long leakage path, so it can contribute to a decrease in the leakage current [2]. Also, at a high deposition temperature, it can reduce impurities by increasing the reactivity of the precursor. And it can improve electrical properties such as a dielectric constant through an increase in crystallinity [3]. In this study, using thermal stability enhanced Zr precursor, it is deposited a ZrO_2 film by ALD at a wide range of temperatures (270–400 °C) on a TiN substrate. Compared to Cp-Zr, the representative Zr precursor, the differences in electrical properties and crystallization were confirmed at a high deposition temperature. And it discussed the advantage of the dielectric film using the high-temperature ALD method.

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AA-TuP-12 Enhancing the Electrical Characteristics of ZrO_2-TiSiN Based MIM Capacitor by Introducing Y_2O_3 Inserting Layer*, JongHwan Jeong, A. Lee, W. Jeon,* Kyung Hee University, Republic of Korea

Dynamic Random Access Memory (DRAM) is one of the representative semiconductor memory devices and is used importantly in various industries due to its wide application range. In the process of scaling to improve DRAM performance, it is required to have a smaller area and a thinner thickness. So, a high aspect ratio structure was formed. However, collapse of the pattern occurred in the high aspect ratio structure because of the weak mechanical strength. [1] Therefore, to solve this problem, this study attempted to introduce TiSiN as a bottom electrode of DRAM capacitor, which has a good mechanical property and is considered advantageous to endure a structure with the high aspect ratio. But, when ZrO_2 films deposited on Si, the interfacial layer that contained a Zr-silicate phase and/or a SiO_x phase was formed. [2] Interfacial layer degrades the electrical properties. So, it was concerned that the degradation of electrical properties of TiSiN because of Si doping. To prevent this concern, this study introduced Y_2O_3 inserting layer. To compare with to the electrical properties of the pristine sample, Y_2O_3 inserting layer having various thicknesses was deposited. After analyzing the electrical properties according to thickness of Y_2O_3 inserting layer, additional analysis of electrical properties was performed by changing other variables. By using these results, the advantages of Y_2O_3 inserting layer were discussed.

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AA-TuP-13 Atomic Layer Deposited Vanadium Oxides with Various Crystallinity for Uncooled IR Sensor Application*, Hyeon Ho Seol,* Kyung Hee University, Republic of Korea*; S. Lee, W. Jeon,* Kyung Hee university, Republic of Korea

Vanadium oxide has been studied as a material used for the microbolometer of uncooled infrared sensors.In the previous study, vanadium oxide is known to exhibit high reactivity through the high temperature coefficient of resistance (TCR) value at room temperature.[1] Vanadium dioxides have various crystallinity, which includes monoclinic phase, brookite phase, and rutile phase.[2] The most stable phase in vanadium dioxide is a monoclinic phase, where semiconductor to metal transition occurs by mott transition at 67 ℃, which is not suitable for use as an infrared detection layer for microbolometers in a wide temperature range.[2] However, brookite phase which is metastable phase and amorphous state vanadium oxides can be alternative. Because, in the case of brookite phase and amorphous state, mott transition does not occur in a wide range of room temperature, so it is suitable for use as an infrared detection sensor.

In this study, we suppressed the expression of monoclinic phase so that vanadium oxides had a uniform TCR value over a wide temperature range. Vanadium oxides was deposited by atomic layer deposition (ALD)with TEMAV as a precursor and ozone as a reactant. The deposition process temperatures was 140 °C, 200 °C, and 250 °C. We evaluated the vanadium oxides thin film through XRD, XPS, and XRF.TCR evaluation was conducted through resistance measurement for each temperature from 30 ℃ to 100 ℃.

It was confirmed that the brookite phase was dominantly expressed at high temperature deposition. At low temperature deposition, the amorphous state was maintained even when the annealing process was conducted. The XPS and XRD data supported the result. TCR values were measured from -1.5 to -2 %/K in the case of brookite phase, and from -2 to -2.5 %/K in the case of amorphous state.

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AA-TuP-14 Self-Isolation Electrode Formation by Selective Deposition Behavior of MoO_2/MoO_3 Thin Films by Atomic Layer Deposition*, Yewon Kim, J. Park,* Kyunghee university, Korea*; S. Moon, T. Youn, Y. Jung, E. Han, Y. Jang, M. Lee,* SK Hynix, Korea*; W. Jeon,* Kyunghee university, Korea

For the DRAM capacitor application, a metal–insulator–metal (MIM) capacitor should meet the requirements of a sufficiently high capacitance density as well as a low enough leakage current to ensure robust device operation.[1] Especially, MoO_2 has been proposed as a conductive oxide electrode for TiO_2-based MIM capacitors. Owing to the highly crystallized MoO_2 structure, deposited TiO_2 films also exhibited high rutile crystallinity. By employing MoO_2, a rutile TiO_2 thin film exhibiting a dielectric constant value as high as 150 was obtained. And high work function of MoO_2 was also attributed to leakage current suppression in the MIM capacitor. The minimum equivalent oxide thickness of 0.35 nm, the lowest ever reported, was achieved.[2]

Thus, MoO_2 is the most promising capacitor electrode for further improving electronic applications. To apply actual DRAM application, it is important to have different deposition behavior depending on the substrate. Because, in the real devices, oxide layers exist between the electrodes to separate each electrode. Molybdenum oxide thin films have various stoichiometries of $MoO_x (2 \le x \le 3)$. MoO_2 is conductive oxide, but MoO_3 is insulator. MoO_x thin films should be deposited MoO_2 on the electrode and MoO_3 on the oxide layer.

In this study, we examined selectively growing of MoO_x thin film as the electrode application for demonstrating the MoO_2 electrode implicated DRAM capacitor. The characteristic crystallization behavior of MoO_2 on the TiN resulted in self-isolation between bottom electrodes by the formation of MoO_3 on the mold oxide. To confirm the selective formation of MoO_x in the DRAM capacitor structure, various analyses methods were employed. Therefore, the proposed MoO_2 ALD is applicable to developing next-generation DRAM devices.

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AA-TuP-15 Formation of Mo Thin Film from ALD-Mo_2N Using Subsequent Reduction Process with Introducing a Mechanical Strain Applying Layer

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It is necessary that the metal interconnects has low resistivity to connect devices to devices by acting as current-carrying. However, the resistivity of the interconnects are gradually increasaing as intergrated circuits were downscaling by the design rule. The resistivity increase as the size of interconnects decreased to nano-scale because scattering increase at the interface and grain boundary. Therefore total resistivity is proportional to ρ_o (bulk resistivity) × λ (mean free path), which is called resistivity size effect. Mean free path of Cu and Mo are 39 nm and 17 nm, respectively. So we can use Mo metal instead of Cu as a new interconnect material [1]. Mo has a benefit that is has a lower $\rho_o \times \lambda$ and thermal expansion coefficient ($\alpha = 4.8\times10^{-6}\ K^{-1}$). Among the Mo compounds, molybdenum carbide and molybdenum nitride also have low resistivity, but Mo metal has the lowest resistivity, so it is most suitable as interconnect material [2], [3].

Mo metal is deposited mainly by sputtering. However, the film deposited through the sputtering method is limited to use on nano-scale or 3D structrures because the step coverage is poor. If the roughness of the film deposited by sputtering is poor [4], the resistivity and capacitance of the metal increase and RC delay occurs [5]. Therefore, it is neccesary to deposit conformal metal by atomic layer deposition (ALD).

In this study, we deposit Mo metal by plasma enhaced atomic layer deposition (PE-ALD) for interconnect.

Because Mo film is not possible to directly deposit Mo metal by ALD, it was deposited molybdenum nitride and then reduced to metal film. However, in this process, agglomeration occurs, resulting in morphology degradation. Therefore, in order to suppress agglomeration, we suppress agglomeration with capping layer through applying mechanical strain.

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AA-TuP-16 Novel Cyclopentadienyl-Based Yttrium Precursor for Atomic Layer Deposition of Y_2O_3 Thin Films

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The high dielectric constant (high-*k*) materials has been attracted a lot of attentions for improving the operation characteristics of various electronic applications, such as gate dielectric in metal oxide semiconductor field effect transistors, and insulator of metal-insulator-metal capacitors. However, the intrinsic property of high-*k* materials, a trade-off relationship between *k* value and bandgap, induces the leakage current problem, inevitably.

Among the various high-*k* materials, yttrium oxide (Y_2O_3) has been investigated one of the candidate for the gate dielectric and the insulator applications due to its relatively high *k* value (~12) with large intrinsic bandgap (5.5 - 5.8 eV). In this regard, various yttrium precursor complexes have been developed, but most of these compounds have solid phases[1-2] or liquid phases, which have high viscosity[3], making them difficult to apply to the actual atomic layer deposition (ALD) process.

Herein, we developed a novel cyclopentadienyl-based yttrium precursor with very low viscosity, good volatility, and thermal stability for demonstrating a reproducible thermal ALD process of Y_2O_3 thin film. By employing the newly designed yttrium precursor and ozone, the typical saturation behavior was obtained within an ALD window of 180 to 320 °C on SiO_2 substrate and a growth per cycle (GPC) up to 0.081 nm/cycle at 320 °C. The deposited Y_2O_3 films exhibited a cubic phase crystalline structure without any carbon and nitrogen contamination.We fabricated a metal-insulator-metal capacitors with Y_2O_3 and TiN electrode using ALD and evaluated their electrical properties such as dielectric constant and leakage current.

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AA-TuP-17 Novel Amidinate-Based Yttrium Precursor for Atomic Layer Deposition of Y_2O_3 Thin Films

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Yttrium oxide (Y_2O_3) thin film is one of the strong high dielectric constant (high-*k*) candidates for various electronic applications, such as a gate dielectric in metal oxide semiconductor field effect transistor or an insulator in the metal-insulator-metal capacitor, because of its valuable dielectric properties of the dielectric constant of around 12 with a relatively large intrinsic bandgap (Eg = 5.5-5.8 eV).

Therefore, various yttrium compounds for the precursor application in the thin film deposition process have been reported. Most of the reported compounds had a solid phase or highly viscous liquid phase, which was induced to obtain certain thermal stability.[1] However, these phases are not favorable as the precursor application, because they would result in difficulties in the actual deposition process, such as too low vapor pressure or low reactivities.[2]

Herein, we developed a novel amidinate-based yttrium precursor with low viscosity, excellent thermal stability, and high vapor pressure for the thermal atomic layer deposition process (ALD) application. The ALD process of Y_2O_3 thin film deposition utilizing newly designed amidinate-based yttrium compound and ozone was investigated. The ALD process exhibited a typical saturation growth behavior with a growth per cycle of 0.099 nm/cycle at 300 °C on SiO_2 substrate. Moreover, the high vapor pressure and low viscosity allowed for achieving a robust and reproducible ALD process of Y_2O_3 thin film. Finally, the crystallinity and dielectric properties of the Y_2O_3 thin film deposited on TiN electrode were examined.

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AA-TuP-18 Tailoring the Surfaces of Atomic Layer Deposited Metal Oxides for Metal Ion Removal from Aqueous Solutions

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The quality of water has worsened due to a wide range of contaminants from industrial waste, pesticides, and pharmaceuticals. These contaminants, including heavy metal ions and organic pollutants, can have adverse effects on human health even at low concentrations. Here we developed a method for functionalizing the surfaces of porous and flat adsorbents for enhanced metal ion removal from aqueous solutions. Atomic layer deposition (ALD) of metal oxides is utilized for the uniform and conformal coating of flat and porous substrates followed by vapor phase grafting of functional silanes. Here, we investigated the monolayer grafting of six different silanes with amine, thiol, nitrile, and ester functionalities. It is demonstrated that the density of reacted silanes and surface hydrophobicity varies depending on the reaction temperature and functional groups on the silane agents. Next, we extended the study onto porous substrates by coating mesoporous silica with ALD metal oxide thin films followed by grafting with monolayer functional silanes. We then studied the adsorption properties of surface-functionalized mesoporous silica to evaluate the removal of metal ions from aqueous solutions. The functionalized surfaces exhibited enhanced selective adsorptive removal efficiency towards a wide range of metal ions.

AA-TuP-20 ALD for Lead-Free Microchannel Plate Fabrication: Optimization of the Thermal Coefficient of Resistance by Modification of the Resistive Layer*, **Stefan Cwik**, M. Aviles, S. Clarke, M. Foley, C. Hamel, A. Lyashenko, M. Popecki, D. Mensah, S. Shin, M. Stochaj,* Incom Inc.*; A. Mane, J. Elam,* Argonne National Laboratory, USA*; A. Tremsin, O. Siegmund,* UC Berkeley*; M. Minot,* Incom Inc.

Microchannel plates (MCPs) have a negative thermal coefficient of resistance (TCR) which leads to challenges in non-temperature-controlled environments. Rising device temperatures lead to thermal runaway, while the increased resistance under cooling results in reduced detection performance including gain depletion. In contrast to conventional hydrogen-fired lead glass MCPs, the ALD-GCA-MCP technology from Incom Inc allows the optimization of the resistive properties independently of other performance characteristics like gain. The TCR improvements are expected to have a high impact on in-field and space flight applications of MCP based photodetectors as the temperature related resistance changes become less prominent.

The glass capillary array (GCA) substrate is comprised of a physically and chemically robust silicate glass with high resistance which enables large area MCP fabrication. For the functionalization, a resistive nanocomposite and an emissive layer are deposited on the electroded GCA via ALD. The tunability of the resistive layer is based on the nanocomposite mixing of metallic and insulating components. For improved thermal performance stability, the ratio of both components in our baseline resistive material (Chem1) is optimized to yield an improved TCR of ALD-GCA-MCPs on level with conventional MCPs. However, on large area (up to 400 cm^2) MCPs the large number of parallel conductors requires a higher resistivity on the layer limiting the tunability. This motivated the development and implementation of new resistive nanocomposites in the pilot scale production environment to achieve even lower TCR values for a given resistivity.

Herein, we present the performance characteristics of our TCR optimized Chem1 MCPs fabricated with our baseline resistive technology that are the foundation of our Large Area and High Rate / Resolution Picosecond Photodetectors (LAPPD and HRPPD). Moreover, the performance of low TCR resistive layers developed together with colleagues at Argonne National Laboratory (ANL) is discussed in prospect of integrating the technological advance in the ALD-GCA-MCPs production process. Implementation and commercialization of these developments to large area ALD-MCPs and Incom MCP based picosecond photodetectors will be discussed.

AA-TuP-21 New Secondary Electron Emissive Technologies for MCP-PMTS: Optimization of Water and CO_2 Adsorption on Microchannel Plate Surfaces*, **Melvin Aviles**, S. Clarke,* Incom, Inc*; S. Cwik, M. Foley, C. Hamel, A. Lyashenko, M. Popecki, D. Mensah, S. Shin, M. Stochaj,* Incom, Inc.*; A. Mane, J. Elam,* Argonne National Laboratory, USA*; M. Minot,* Incom, Inc.

Incom's ALD-GCA-MCP technology for the fabrication of large area microchannel plates (MCP) relies on the performance of the ALD secondary electron emissive (SEE) film. This technology provides MCP functionality by combining resistive and emissive films with glass microchannel substrates. The use of glass and films makes possible mechanically robust MCPs, of any shape and resistance required by the application. MgO is the state-of the-art SEE coating for open MCP instruments and UHV sealed microchannel plate photomultiplier tubes (MCP-PMT), due to high gain and long-term performance stability. Earlier studied alternative SEE layers, including Al_2O_3, offered initially high secondary electron yield (SEY) but suffered from declining gain as adsorbed water was scrubbed out of the channels. This effect reduces detection efficiency with extracted charge, potentially to an unacceptably low level.

However, the strong adsorption of water and CO_2 on the air-exposed MgO surface makes the integration of MCPs into photodetectors challenging, since residual adsorbed species contribute to ion afterpulsing. Such afterpulsing leads to the degeneration of the photocathode, therefore reducing the detection efficiency, and leading ultimately to device failure. Additionally, applications requiring open-MCP instrumentation, where the MCP chamber gets routinely vented, also have to consider the reversable adsorptions of moisture and CO_2, Thes adsorptions then require extended evacuation and may create gain variations.

A series of ALD thin films have been evaluated and optimized by Incom and colleagues from the Argonne National Laboratory to develop application tailored SEE coatings with acceptable gain and gain stability, together with reduced gas adsorption. We will report SEE based MCP performance demonstrating the relation between the material selection, film thickness and gain. While lower SEY can be deemed sufficient for the respective application, declining gain during operation renders a huge drawback for our customers. Therefore, the gain stability after extracted charge and the afterpulsing level are key parameters for newly developed and upcoming SEE technologies. The gain and afterpulsing performance of the new films will be evaluated and discussed as a function of extracted charge and deliberate exposures of water and CO_2.

AA-TuP-23 ALD-based Catalysts with TiO_2 Interlayer for Ammonia Decomposition and LOHC Dehydrogenation Reactions*, **Yu-Jin Lee**,* Korea Institute of Science and Technology (KIST), Republic of Korea*; Y. Kwak,* University of Delaware*; S. Moon,* Ecole Politechnique Fédérale de Lausanne, Switzerland*; H. Sohn, H. Jeong, S. Nam, Y. Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea

In this work, we demonstrate the use of atomic layer deposition (ALD) to fabricate catalysts that can accelerate the production of green hydrogen through ammonia decomposition and liquid organic hydrogen carrier (LOHC) dehydrogenation reactions. The ALD-based catalysts were designed with tailored surface properties, including the deposition of a TiO_2 interlayer, to enhance the catalytic activity, selectivity, and stability for these reactions. We tested the catalysts in a series of experiments and observed a significant improvement in the reaction rate and lower activation energy for ammonia decomposition and LOHC dehydrogenation, compared to conventional wet chemistry-based catalysts. Our study demonstrated significant improvements in catalytic activity for both ammonia decomposition and LOHC dehydrogenation reactions. These improvements can be attributed to the efficient modification of the electron structure of metal nanoparticles, which was facilitated by the uniform TiO_2 interlayer introduced onto a 3D-shaped substrate using the ALD technique. Our results suggest that ALD with TiO_2 interlayer is a promising technique for developing efficient catalysts for green hydrogen production, which can help accelerate the transition to a sustainable energy future.

AA-TuP-24 A Co-Design Approach to Optimize Neuromorphic Architectures for High Temperature Computing Integrating Novel ALD Materials*, **Angel Yanguas-Gil**, S. Madireddy, J. Elam, A. Mane,* Argonne National Laboratory

There is a need to broaden the temperature range of microelectronics. For applications such as enhanced geothermal systems, relevant downwell temperatures can exceed 300℃, which is well above the limits of VLSI and even high temperature Silicon on Insulator technology. In this work we demonstrate an application-driven codesign methodology that leverages machine learning techniques to identify optimal materials that maximizes the performance of architectures for an application-relevant task.

In particular, we have explored the integration of ALD materials based on metal/metal oxide nanolaminates for threshold logic-inspired architectures. An advantage of threshold logic approaches is that they minimize the number of transistors required to carry out complex operations, something relevant for high temperature computing, where the footprint of a transistor can be four orders of magnitude larger than the leading edges. Our approach integrates two different approaches: first, we cast the threshold logic circuits as models in deep learning frameworks such as pytorch or tensorflow. This allows us to use stochastic gradient descent approaches to identify the optimal values of the resistive elements in our architecture. We then use an asynchronous model-based search algorithm to explore and find optimal configurations in terms of accuracy and other criteria such as power consumption. Finally, we apply quantization approaches to minimize the number of processing steps required to realize the proposed architecture and identify the right ALD processes.

In addition to demonstrating the performance on baseline machine learning tasks such as MNIST, FashionMNIST, and KMNIST, we have explored the robustness of the proposed approach to process variability, noise, and shifts on the threshold voltage. Finally, we provide a realistic exemplar case where we use this approach to implement convolutional kernels for image processing applications.

This research has been supported through Argonne National Laboratory's Laboratory Directed Research and Development Program and Threadwork, a project funded through DOE Office of Science.

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AA-TuP-25 Forming Voltage-Free Memristive Hafnium Oxide Devices for Non-Polar Switching Applications*, **Minjong Lee**, Y. Hong, J. Kim, H. Hernandez-Arriaga,* University of Texas at Dallas*; R. Choi,* Inha University, Republic of Korea*; J. Kim,* University of Texas at Dallas

Resistive memory-devices, the memristors, have received great amount of attentions for future memory applications. Among memristor devices, a resistive random-access memory (ReRAM) has been widely studied with its high on/off current ratio and applicable for compute-in memory applications. However, conventional ReRAM based on a filamentary switching mechanism requires electrochemical formation of filaments which causes reliability issues in ReRAM. This challenge issue must be addressed to achieve an advanced memory behavior.[1] In this regard, C. A. Paz de Araujo *et al*. reported the universal non-polar switching behavior in carbon-doped transition metal oxide (TMO) films deposited by spin-on fabrication, in which reliable operation and immunity from forming voltage were observed.[2]

In this work, we demonstrate the forming voltage-free memristive hafnium oxide (HfO_x) devices based using the conventional low-temperature atomic layer deposition (ALD) technique, which is high compatible for 3D structure and back-end-of-line (BEOL) process. For the ALD process, tetrakis(dimethylamino) Hf (TDMA-Hf) and carbonated hydroperoxide (H_2O_2) were utilized as the Hf and oxygen precursors, respectively. For activating the conductive carbon bond states, rapid thermal annealing (RTA) at 450 °C for 1 min was performed. By adopting the carbon composited HfO_2 films, the switching and memory behaviors were observed without any high forming voltage. It is noted that the first reset operation of the demonstrated devices is different from ReRAM forming in terms of the magnitude of switching voltage and current level. Although the high-resistance states are quite low due to the carbon composition, the set and reset voltages are reliable respectively as ~1.6 and ~0.6 V with similar high- and low-resistance states (HRS and LRS) in cycle-to-cycle variation. In addition, the intriguing operation in the carbon composited HfO_2 devices is non-polar switching behavior, showing programmable HRS and LRS regardless the polarities of operation voltage. These phenomena enable the devices to exhibit both unipolar and bipolar operation, which would be highly compatible for the further circuit applications. Detailed experimental procedure and results will be discussed.

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AA-TuP-26 Impact of Oxygen Source and Cocktail Precursor on Ferroelectricity of ALD $Hf_xZr_{1-x}O_2$ Thin Films*, **Jin-Hyun Kim**, Y. Jung, M. Lee, D. Le, S. Lee,* University of Texas at Dallas*; J. Spiegelman, M. Benham,* RASIRC*; S. Kim,* Kangwon University, Republic of Korea*; R. Choi,* Inha University, Republic of Korea*; J. Kim,* University of Texas at Dallas

The ferroelectricity in Zr-doped HfO_2 (HZO) film has attracted great interest for memory applications. Generally, HZO thin films can be deposited by super-cycle process with Hf and Zr precursors (e.g., TEMA-Hf/Zr and TDMA-Hf/Zr) via thermal atomic layer deposition (tALD) technique.[1]

In this work, we demonstrated the ferroelectricity of ALD HZO thin films without using a super-cycle process, in which TEMA-Hf/Zr cocktail precursor was employed. The great merit of the cocktail precursor is to achieve a higher throughput based on their simple ALD cycles. To comprehensively understand the proposed precursor, the effects of different oxidants (O_3, H_2O, H_2O_2) and deposition temperature on the growth characteristics and film properties were investigated. At 250 °C, the deposited HZO thin films using different oxygen sources exhibited ALD saturated growth characteristics. Although H_2O_2-based thin films exhibited higher growth per cycle (GPC) compared to other oxidants, HZO deposited with O_3 showed the lowest nonuniformity percentage. Unlike H_2O- and H_2O_2-based processes, the growth rate of O_3-based HZO remained constant between the deposition temperature of 200–300 °C. Furthermore, the etch resistance of deposited thin films was evaluated using 200:1 HF diluted solution. While exhibiting higher GPC than H_2O-based HZO, the films deposited with H_2O_2 showed a similar wet etch rate compared to H_2O process (~0.99 nm/ min). Interestingly, O_3-based HZO showed the lowest wet etch resistance. The observed results indicated that $H\text{-}_2O$ and H_2O_2 delivered HZO thin films with higher density compared to $O\text{-}_3$-based process. To extend our studies to device applications, the TiN/HZO/TiN capacitors are fabricated by ALD at 250 °C with various oxygen precursors. The device fabrication flows were similar to our previous studies,[1] except using TEMA-Hf/Zr cocktail precursor. As a result, the H_2O_2-based devices exhibit a higher remanent polarization (P_r) and higher dielectric constant than those with H_2O- and O_3-based processes, due to the higher density of H_2O_2-based process. Overall, we thus believe that the combination of TEMA-Hf/Zr cocktail precursor and H_2O_2 would deliver HZO thin films with improved growth characteristics, film properties, and enhanced electrical performance.

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AA-TuP-29 Multifunctional Carbon Textile Prepared by Carbothermic Reduction for Energy Materials*, D. Lam, J. Kim, **Seung-Mo Lee**,* Korea Institute of Machinery and Materials (KIMM), Republic of Korea

Carbothermic reduction in the chemistry of metal extraction (MO(s) + C(s) → M(s) + CO(g)) using carbon as a sacrificial agent has been used to smelt metals from diverse oxide ores since ancient times. Here, we paid attention to a new aspect of carbothermic reduction that remained unnoticed till now to prepare activated carbon textiles for high-performance energy materials. Based on the thermodynamic reducibility of metal oxides reported by Ellingham, we employed not carbon, but metal oxide as a sacrificial agent to prepare activated carbon textile. We conformally coated ZnO on bare cotton textile using atomic layer deposition (ALD), followed by pyrolysis at high temperature (C(s) + ZnO(s) → C′(s) + Zn(g) + CO(g)). We figured out that it leads to concurrent carbonization and activation in a chemical as well as mechanical way. Particularly, the combined effects of mechanical buckling and opening-mode fracture that occurred between ZnO and cotton turned out to play an important role in carbonizing and activating cotton textiles. This effect significantly increased surface area (nearly 10 times) compared with the cotton textile prepared without ZnO. The battery and supercapacitor using the carbon textiles prepared by carbothermic reduction as an electrode showed impressive combination properties of high power and energy densities (over 20 times increase) together with high cyclic stability.

AA-TuP-31 Comparison between Doped and Undoped Ferroelectric HfO_2*, **Liliane Alrifai**, E. Skopin, N. Guillaume, P. Gonon, A. Bsiesy,* Univ. Grenoble Alpes, CNRS, LTM, France

The recent discovery of ferroelectric behavior of doped hafnium oxide (HfO_2) has led to a renewed interest in this material for its potential use in CMOS technology, such as integrated FeRAM ferroelectric non-volatile memory. Indeed, since HfO_2 was used in CMOS as an insulating layer, its elaboration process, physical and chemical properties are largely mastered even at ultrathin layers. Following the HfO_2 ferroelectric discovery, much effort has been devoted to the understanding of the role of doping. Different dopants have been investigated since it is widely believed that doping allows the stabilization of HfO_2 non-centrosymmetric orthorhombic phase which is the origin of the HfO_2 ferroelectric behavior. However, a number of reports showed experimental evidence of ferroelectricity in HfO_2 undoped layers. These results cast the light on the origin of the ferroelectric behavior and the role of doping in stabilizing it.

In this work, the ferroelectric properties and crystalline structure of doped [1] and undoped HfO_2 layers in TiN/HfO_2/TiN stacks were studied as a function of the layer thickness. For high conformity, precise thickness control and deposition at low temperatures, HfO_2 (or doped HfO_2) layers and TiN contacts were deposited by Plasma Enhanced Atomic Layer Deposition (PEALD) in the same chamber without getting exposed to air.

To clarify the role of doping, the crystalline and electric properties of undoped HfO_2 layers were compared to that of doped layers. For doped and undoped ultrathin HfO_2 layers, the increase of ferroelectric crystalline phase as well as the ferroelectric behavior were found to be similar. Indeed, the remnant polarization was linearly increasing as a function of thickness but this trend started splitting at 6.5nm. Above this thickness, a slight increase of the monoclinic phase was noticed in undoped layers until it dominated and led to a drop in the remnant polarization above 14nm thick layer. In contrast, for doped samples, the remnant polarization kept increasing linearly with thickness. These results were analyzed in the light of possible role of mechanical stress in stabilizing the ferroelectric phase in ultrathin HfO_2 layers.

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AA-TuP-32 Control of the Electrical Resistivity and Stress of ALD W for 3d Nand Word Line Applications

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Since 3D NAND products were mass-produced, the number of stacking layers with W word lines has been increasing to achieve higher cell density. The total height of 3D NAND is also increasing with the increased number of W word lines, causing technical challenges such as channel-hole etch with a high aspect ratio and a high wafer warpage. As one of the solutions to overcome these technical challenges, the vertical pitch of the word line has been scaled down. However, in the aspect of W metallization, the gap fill at a reduced WL pitch becomes more challenging. Therefore excellent properties of W thin film with very low electrical resistivity and high step-coverage are required. Also, extremely low mechanical stress of W thin film is one of the important requirements because the word line W, which occupies more than 30% volume of the 3D NAND structure, causes a high wafer warpage.

ALD W process has been applied to the word line metallization of 3D NAND to meet the process requirements. Based on sequential alternating gas precursors with self-limiting reactions, ALD W film has excellent step-coverage on high-aspect ratio structures of 3D NAND. In addition, ALD W film generally has an electrical resistivity and mechanical stress of 50% or less compared to CVD W films. The most practical use of ALD W is that it is easy to control thin film properties with various process factors.

In this study, the effect of W nucleation layer on the electrical resistivity and stress of ALD W thin film is investigated. W nucleation layer using sequential pulses of B_2H_6 and WF_6 gases affects the bulk growth of ALD W, resulting in lower resistivity at higher nucleation thickness. In addition, the surface condition of TiN substrate affects the surface coverage of W nucleation on it. This leads to changes in the thin film properties of ALD such as electrical resistivity and stress. The effect of the surface condition of TiN substrate on W nucleation and ALD W films and their growth mechanism will be presented.

AA-TuP-33 Low-Temperature Atomic Layer Deposition of Indium Oxide and Tin Doped Indium Oxide using Ozone

***Huazhi Li**, D. Gorelikov,* Arradiance LLC.*; A. Agrawal, W. Zhu,* NIST

Indium oxide (In_2O_3) and tin-doped indium oxide (ITO) are well known transparent conducting oxides (TCO). Due to their high optical transmittance and excellent electrical conductivity, they are used in various optical, electrical and photo-electric device technologies such as heat mirrors, antistatic coatings, electrochromic devices, flat panel displays, light-emitting diodes and solar cells. For optimal performance and utilization of the expensive indium, most of the above-mentioned applications need precise control over the conductive film thickness and composition. In addition, many applications require the ability to deposit thin In_2O_3 or ITO layers onto very high aspect ratio structures or high surface area materials. That makes atomic layer deposition (ALD) more advantageous over other deposition techniques such as chemical vapor deposition and physical vapor deposition. 100 °C temperature or below growth of In_2O_3 or ITO ALD films [1,2,3] recently gained more attention due to the need of using low temperature budget sensitive substrates like halide perovskites and polymers.

Arradiance desired to provide industry a low-cost solution for conformal In_2O_3 or ITO ALD films over substrates at or below 100 °C utilizing the GEMStar^{TM} platform. In this work, we studied the growth kinetics, crystalline structure, resistivity, and purity of ITO and In_2O_3 thin films as grown using O_3 as the primary reactant gas in combination with the most cost efficient In and Sn ALD precursors on the chemical market: trimethylindium (TMIn) and tetrakisdimethylaminotin (TDMASn). Electrical measurements were performed using a four-point probe, and optical measurements (for growth rate and non-uniformity) using spectroscopic ellipsometry (SE). We found both films conductive at 100 °C growth temperature with the conductivity in tens mOhm range. Our findings prove that low-temperature ALD processing of ITO and In_2O_3 is feasible and scaleable utilizing existing ALD and supporting hardware solutions on the market like that from Arradiance.

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AA-TuP-34 Thin Titanium Oxynitride Film as Alternative to ITO for Optoelectronic Devices

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Transparent and conductive films (TCF) are critical parts of current and future optoelectronic devices (e. g. solar cells or displays). The most commonly used is In-doped SnO_2 (ITO) that exhibits satisfying transparency and conductivity. Due to indium scarcity, it is necessary to propose alternative TCFs. Another approach consisting of turning into transparent a conductive material by decreasing its thickness to nanometric scale should be highlighted and developed. It can extend significantly the variety of promising material available. Therefore, atomic layer deposited (ALD) titanium nitride as a metal-like material is an interesting candidate. However, from literature and our previous studies, as-grown ALD TiN films contain an oxynitride contribution[1,2]. The obtained films present a rather high resistivity for a metal but remains in TCFs range (10^{-4} Ω·cm). Depositions from 10 to over 100 nm have been performed to assess their optical and electrical properties.

TiO_xN_y layers are grown on fused silica by thermal and plasma-enhanced ALD using TDMAT (tetrakis(dimethylamido)titanium) and two different N-sources (NH_3, N_2). This enables to investigate their impact on the layer characteristics. Highest transmittance measured for thermal and N_2-plasma routes are highly satisfactory for 10 nm-thick films (87%) while NH_3-plasma one is slightly lower (83 %). Those values are compared to commercial ITO used as benchmark[3]. In visible range, the transmittances are very closed while, in the IR region, TiO_xN_y layers remain transparent and ITO exhibits a non-negligible absorption. Since numerous photons of the solar radiation are emitted in this region, the use of TiO_xN_y can result in a huge enhancement in photocurrent and then a better photoconversion yield of photovoltaic cells. The resistivity depends as well on the thickness, down to 1608 and 578 10^{-4} Ω.cm for both plasma routes (100 nm) while it remains stable for the thermal process around 550 10^{-4} Ω.cm. In the case of NH_3-plasma, after a thermal treatment at 700°C in nitriding atmosphere, the resistivity drops to 137 10^{-4} Ω.cm (10 nm) while the transmittance remains at 80%. Additional investigations are currently carried out to characterize the roughness and the crystallinity of the TCFs but current results are already very interesting. In addition, ALD can be used to conformally coat structured substrates that could be highly suitable for antireflective coatings and metasurfaces.

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AA-TuP-36 Advanced $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ Cathodes by Sulfide Coating via Atomic Layer Deposition

***Xin Wang**, X. Meng,* University of Arkansas

Layer-structured $LiNi_xMn_yCo_{1-x-y}O_2$ (NMCs, 0< x, y <1) cathodes are among the promising cathodes for next-generation lithium-ion batteries (LIBs). However, these cathodes suffer from severe issues, which hinder them from commercialization, mainly in two aspects: performance degradation and safety hazard. They are reflected as cation mixing, oxygen evolution, phase transition, transition metal ion dissolution, and microcracking. In tackling these interrelated issues, surface coating has been proved being a facile and effective strategy. In recent years, atomic layer deposition (ALD) has emerged as an accurate tool to apply uniform and conformal coatings over NMCs at the atomic level, which have shown remarkable effects on battery performance improvement.$^{1-4}$ Recently, we for the first time discovered that lithium sulfide as surface coating via ALD could remarkably improve the performance of NMC811^{5}. The ALD sulfide coating has dramatically enhanced the cyclability and rate capability of NMC811 cathodes. In exploring the protective mechanism of the ALD coating, we utilized a suite of characterization tools including X-ray diffraction, scanning electron microscopy, high resolution transmission electron microscopy, and synchrotron-based transmission X-ray microscopy. Our results revealed that the ALD sulfide coating has evidently helped sustain the NMC structure during cycling and thereby significantly mitigated the formation of cracks. More importantly, X-ray photoelectron spectroscopy measurements have further revealed that the sulfide coating has experienced some transformations to sulfite or/and sulfate. Such transformations could remove oxygen released from NMC811 during cycling, protect electrolytes from oxidation and further degradation, and thereby contribute to the battery's improved performance. This work is significant, for it paves a new technical avenue for addressing the issues of NMCs and the like and has some important implication on other sulfide coatings in LIBs and beyond.

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AA-TuP-37 Improved Performance of Li||Nmc Batteries by a Novel Polymeric Coating via Molecular Layer Deposition*, **Kevin Velasquez Carballo**, X. Wang, X. Meng,* University of Arkansas

Abstract:

Lithium-metal batteries (LMBs) have received considerable attention for their great potential to achieve much higher energy densities than those of lithium-ion batteries (LIBs). [1-3] Among them, Li||NMC LMBs are very promising and could realize an energy density up to 500 Wh/kg, in which Li is the lithium metal anode and NMC is one variant of $LiNi_xMn_yCo_zO_2$ (x + y + z = 1) as the cathode. Although promising, they suffer from a series of issues, which hinder them from commercialization and are rooted in the Li anode and NMC cathode. Aimed at addressing these issues of Li||NMC LMBs, recently we developed a novel polymeric film, LiGL (GL = glycerol) via molecular layer deposition.[1] We revealed that LiGL as a surface coating could produce exceptional effects on the Li anode in Li||Li symmetric cells and enabled long-term cyclability. Inspired by this discovery, we adopted LiGL-coated Li chips (i.e., LiGL-Li) to couple with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) cathodes. We prepared NMC811 cathodes with different mass loadings, varying from 2 to 14 mg/cm^2. Compared to bare Li||NMC811 cells, in all the cases, LiGL-Li||NMC811 cells enabled much better performance, in terms of sustainable capacity and rate capability. We ascribed the improvements of LiGL-Li||NMC811 cells to the excellent protection effects of the polymeric LiGL coating, i.e., inhibiting SEI formation and mitigating Li dendritic growth. All these results are encouraging, for they clearly indicate that MLD could be an effective pathway for us to address the issues of Li||NMC LMBs rooted in the Li anode. This study also clearly revealed that it is critical to address the issues rooted in both the Li anode and NMC cathode simultaneously for ultimately commercializing Li||NMC LMBs.

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AA-TuP-39 Resistivity Engineering of Atomic Layer Deposited Tungsten Carbonitride Thin films *via* Carbon Concentration Control for 3D VXP Electrodes Applications*, **Seunggyu Na**, T. Kim, S. Park,* Yonsei University, Korea*; M. Kim,* SK Hynix, Korea*; S. Chung, H. Kim,* Yonsei University, Korea

As a demand for data storage and processing has been exponentially increased, phase change memory (PCM) with fast speed and non-volatility is attracting huge attention. In particular, three-dimensional (3D) vertical cross-point (VXP) array architecture is one of the most promising technologies for fabricating PCM with increased integration density due to its cost-effective vertical structure with narrow holes realized by atomic layer deposition (ALD) compared to the conventional planar memory structures. This 3D VXP structure requires selectors to suppress undesirable sneak current from unselected cells, such as ovonic threshold switching selector (OTS). However, the switching behavior of OTS selector depends heavily on electrodes, which are essential part of the OTS device, depending on the electrode material and interface. Thus, detailed engineering of electrode material is required to obtain desirable properties for 3D VXP. Electrodes for 3D VXP require moderate resistivity because of the trade-off between thermal efficiency and power consumption. As a matter of fact, resistivity of film can be shifted by carbon incorporation. Even though ALD is essential technique for depositing conformal film on sidewalls in 3D VXP structure, studies on ALD process and resistivity control for electrodes applications are insufficient. Tungsten nitride is mainly used as an electrode due to its high thermal stability and conductivity.

Herein, we developed thermal ALD tungsten carbonitride process with intentional carbon control in films for effective tuning of film properties including resistivity by changing process parameters, such as deposition temperature, purge gas flow rate, and reactant flow rate. Subsequently, various ALD process parameters of tungsten carbonitride were controlled to observe changes in growth characteristics and film characteristics to investigate the effect of carbon concentrations in films. This opened the possibility of tuning the characteristics of the electrodes in detail, which will eventually help control the electrical characteristics of the devices.

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AA-TuP-40 Broadband Anti-Reflective Coatings on Plastic Optics Using Graded Refractive Index Alumina by Atomic Layer Deposition*, **Philip Klement**, L. Gümbel, I. Müller, J. Schörmann, S. Chatterjee,* Justus Liebig University Giessen, Germany

Plastic optics from acrylic glass or polycarbonate find widespread applications in eyeglasses, cell phone cameras, windows and displays as they are lightweight, cheap and easy to manufacture. All these applications require broadband, omni-directional and durable anti-reflective (AR) coatings which are difficult to achieve for plastics using conventional deposition methods. Typical problems are the low limit in process temperatures, modifications of the surface through the process plasma or the lack of rigid chemical bonding between the coating and the plastic.

Here, we present nanoporous alumina on plastic optics with a graded refractive index to produce broadband, omni-directional and durable AR-coatings. Atomic Layer Deposition (ALD) of alumina on poly (methyl methacrylate) or polycarbonate and the subsequent immersion in hot water forms grass-like alumina. Using this approach, we achieve an excellent AR-performance with a reduction of the residual reflectance to 0.4% in the visible range (400–900 nm) for a single-sided coating. Angular spectral reflectance (0–70°) confirms the omni-directional characteristic of the AR-coating with a minimal residual reflectance under all angles of incidence. Further, infiltration of the polymer substrate with inorganic precursors during ALD forms rigid chemical bonds and allows for durable coatings. The combination of excellent AR-performance, facile processing with strong adhesion to many relevant optical plastics and compatibility with commercial deposition systems should enable a multitude of practical use for this AR-technology.

AA-TuP-41 Revelation of Ferroelectricity of ALD ZrO_2 Thin Films through a Trace of Ge Incorporation*, **Seonyeong Park**, S. Na,* Yonsei University, Korea*; W. Choi, B. Kim, C. Jung, H. Lim,* Samsung Electronics Co., Inc., Republic of Korea*; S. Chung, H. Kim,* Yonsei University, Korea

Since the research on ferroelectricity of doped HfO_2 was first announced in 2011, a lot of research on $Hf_{1-x}Zr_xO_2$ (HZO) has been conducted due to its low crystallization temperature and high remanent polarization. However, HZO has problems such as high intrinsic coercive fields and electric fields cycling instability, and La doping has become a promising solution to improve ferroelectric behavior of HZO films. Recently, ferroelectricity of

ZrO_2 is highly promising because of its compatibility with CMOS technology. Although undoped ZrO_2 thin film is generally known to have antiferroelectricity, it exhibits ferroelectricity in very thin films of 2 nm. However, as the film becomes thinner, there is a possibility that device characteristics may be deteriorated due to inter-cell interference. In order to exhibit ferroelectric properties in ZrO_2 thin films of 10 nm or more, lattice distortion is required. According to the DFT calculation result, crystallinity can be improved when doping an element with a small atomic radius in the HfO_2 thin film. Therefore, we selected Ge as a doping element, which has smaller atomic radius than Zr and has good compatibility with Si.

In this study, super-cycle ALD method was used to incorporate Ge. Controlling the number of ALD GeO_X process cycle, we varied the proportion of Ge from 0.1 % to 2.7 %, which was examined by XPS analysis. In particular, through XRD analysis, it was found that the crystallinity of the ZrO_2 thin film significantly increased when Ge was doped at less than 1%. It was also confirmed that ferroelectricity appeared in about 13 nm thin film with only 0.1 % doping, and it is predicted that the increased crystallinity affected the revelation of ferroelectricity. If further research is conducted, it is expected that this film can be applied to real industry.

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AA-TuP-43 Atomic Layer Deposited TiN Capping Electrode for sub-10 nm $Hf_{0.5}Zr_{0.5}O_2$ Gate Oxide in Ferroelectric Transistors with 8 nm Gate Length Defined by Helium Ion Beam Lithography*, **Yu-Sen Jiang**, C. Wang, T. Chang, Z. Huang, M. Chen,* National Taiwan University, Taiwan

Since the discovery of ferroelectricity in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films, they have attracted considerable interest in a variety of devices including ferroelectric field effect transistors, ferroelectric random-access memory, ferroelectric tunneling junctions, and neuromorphic computing. The scaling of the HZO thickness down to the sub-10 nm region, along with a low thermal budget while maintaining pronounced ferroelectric (FE) properties, is of significant importance in practical applications. In this study, the TiN capping electrode deposited by atomic layer deposition (ALD) is used to enhance the ferroelectric properties of sub-10 nm $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films. Compared with the TiN prepared by sputtering, the ALD TiN facilitates the crystallization into the orthorhombic phase in HZO without any post-annealing treatment. With the ALD TiN capping electrode, high remnant polarization ($2P_r$), low thermal budget (<300°C), low operation voltage, and high endurance are demonstrated in the ferroelectric HZO thin films with the thickness scaling from 10 to 3 nm. A maximum $2P_r$ as high as ~50 $\mu C/cm^2$ is reached in the 6 nm HZO, and the ferroelectricity still remains robust with a good $2P_r$of 21.6 $\mu C/cm^2$ in HZO with a thickness of only 3 nm. The wake-up effect is almost negligible when the HZO thickness is above 5 nm, which could be attributed to the dependence of the stability between tetragonal and orthorhombic phases on the film thickness. On the other hand, high endurance (10^{11} cycles) is achieved in the 3 nm HZO thin film due to the increasing dielectric breakdown strength with the decreasing thickness. The distinguished ferroelectric properties can be ascribed to the formation of the TiO_xN_y mixed phase and a large in-plane tensile strain in HZO by the ALD TiN capping electrode. Finally, a Si junctionless transistor with a short gate length (~8 nm) and 6 nm HZO gate oxide is also demonstrated by using helium ion beam lithography based on the hydrogen silsesquioxane (HSQ) resist. Owing to the ferroelectric negative capacitance effect, the HZO gate oxide contributes to the suppression of the off-state current by around two orders of magnitude and the reduction in the subthreshold swing to ~33 mV/dec. All the results demonstrate the enhancement of ferroelectricity and the alleviation of short-channel effects in nanoscale transistors by the ferroelectric HZO thin films capped with a TiN top electrode deposited by ALD.

AA-TuP-45 Metal Oxide ALD Overlayers Enhance Thermal Stability and Activity of Platinum Catalysts in Propene Oxidation Reaction*, **Bang T. Nhan**, S. Bent,* Stanford University

The transportation sector is a major contributor to greenhouse gas emissions in the U.S. In the efforts to reduce the amount of toxic pollutants found in exhaust gas that is released into the atmosphere, many diesel and gasoline-powered vehicles are equipped with catalytic converters comprised of platinum-based catalysts. These catalysts contain platinum-group nanoparticles (NPs) dispersed on metal oxides such as alumina that have been shown to be highly effective at oxidizing harmful exhaust emissions containing CO, NO, and hydrocarbons. However, under harsh conditions (high temperature, oxidizing environment, steam), these NPs often sinter to form large particles, leading to a reduction in active surface area and, consequently, decreased catalytic activity.

One way to prevent particle sintering is to encapsulate the metal NPs within porous oxide layers. The oxide layers act as a cage around the NPs, reducing their mobility at elevated temperatures and thus limiting particle migration and coalescence. Encapsulation techniques such as chemical vapor deposition (CVD) and sol-gel chemistry have successfully formed stable core-shell particles. However, these techniques often lead to a stability-activity tradeoff where catalytic activity is compromised by mass transfer resistance of gaseous emissions associated with the tens of nanometer-thick protective layers. Atomic layer deposition (ALD) can meet the needs for growing uniform thin films on metal nanoparticles with angstrom-level thickness control over surface composition, which allows for a better understanding of the catalyst surface for fine-tuning purposes.

In this work, we investigated how the stability and activity of catalysts comprised of Pt supported on Al_2O_3 that was nanocasted from polymer organic framework (POF) (Pt/Al_2O_3) materials changed with both TiO_2 and CeO_2 overlayers. These metal oxides were selected as overlayers due to their prominence as supports in heterogeneous catalysis. We found that Pt/Al_2O_3 catalysts modified by TiO_2 ALD showed improved stability and retained activity after aging at 800 ºC in propene oxidation reaction conditions compared to the unmodified Pt/Al_2O_3 catalyst control. Particle size analysis of the aged samples showed a significant reduction in NP size as the number of TiO_2 ALD cycles increased, suggesting less sintering. We also explore Pt/Al_2O_3 encapsulated in CeO_2 ALD layers. As a catalyst support, CeO_2 is known to be much more active compared to TiO_2 due to its unique surface chemistry. A comparison of the activity and stability for CeO_2 encapsulated Pt/Al_2O_3 catalysts with both the TiO_2-modified and unmodified Pt/Al_2O_3 catalysts will be presented.

AA-TuP-46 ALD for Spatial Control of Redox Reaction Selectivity*, **Wilson McNeary**,* National Renewable Energy Laboratory*; W. Stinson, D. Esposito,* Columbia University*; K. Hurst,* National Renewable Energy Laboratory

Photocatalytic water splitting holds great potential in the pursuit of the U.S. Department of Energy's Hydrogen Shot initiative to bring the cost of H_2 to $1/kg by 2031. A key challenge in the development of photocatalysts is increasing their overall solar-to-hydrogen efficiency by enhancing charge separation yields and redox selectivity. In this work, we use area selective ALD of oxide films to develop tunable interphase layers for selective oxidation and reduction reactions on a single substrate. This presentation details initial synthesis and characterization of Pt- and Au-based planar thin film electrodes in which Au regions were deactivated towards ALD growth through self-assembled thiol monolayers. The suppression of TiO_2 ALD selectivity of thiols was assessed through ellipsometry, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry. A patterned planar sample comprised of interdigitated arrays of Au and Pt, used as a surrogate for a photocatalyst particle containing two different co-catalysts, was exposed to ALD growth and removal of the inhibitor species. Scanning electrochemical microscopy (SECM) was used then to probe the local activity of different regions of the patterned surface towards the hydrogen evolution reaction (HER) and iron oxidation and correlated with the ionic and e^- blocking effects of the area selective ALD coating. We will also detail the application of these findings to the ongoing development of 3D, particle-based photocatalysts.

AA-TuP-47 Influence of Oxygen Source on Ferroelectricity of ALD-$Hf_{0.5}Zr_{0.5}O_2$ Thin Films With and Without Capping Layer*, **Hye Ryeon Park**,* Kangwon National University, Republic of Korea*; S. Park,* Kangwon National university, Republic of Korea*; J. Kang,* Kangwon National University, Republic of Korea*; J. Kim, Y. Jung, J. Kim,* The University of Texas at Dallas*; S. Kim,* Kangwon National University, Republic of Korea

Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films have recently gained great attention in the semiconductor industry due to their high compatibility with standard CMOS processes, high dielectric constant, and high scalability.[1] Specifically, HZO thin films not only pave the way to overcome the scaling limitations that have been a chronic problem of conventional perovskite films, but also provide low thermal budget and availability of atomic layer deposition (ALD) processes. Since ALD is a chemical vapor deposition method that uses self-limiting and sequential surface reactions, the type of oxygen source used during the process can affect residues (e.g., carbon impurities or hydroxyl groups) in the deposited film.[2,3] Meanwhile, it is known that the ferroelectric properties of HZO originate from the non-centrosymmetric polar orthorhombic phase (o-phase).[1] In order to promote the formation of the o-phase in HZO, the films must undergo additional stress during crystallization process. One representative approach for inducing mechanical stress in the film involves the use of a capping layer, commonly referred to as the “capping layer effect”. Therefore, in this study, we comprehensively investigated the effect of an oxygen source on the ferroelectric properties of ALD-HZO thin films with and without a capping layer. 10-nm-thick HZO films were deposited on the TiN bottom electrodes by ALD using TDMA-Hf and TDMA-Zr as the Hf and Zr precursors and O_3 or H_2O or D_2O as the oxygen source. O_3-, H_2O-, and D_2O-based HZO samples were annealed in N_2 atmosphere at 400°C for 60 s by rapid thermal annealing before or after deposition of the TiN top electrode, respectively. As a result, the HZO samples annealed with the capping layer showed excellent ferroelectric properties regardless of the type of oxygen source, and the largest ferroelectric polarization was confirmed in the O_3-based HZO film. On the other hand, samples annealed without a capping layer showed ferroelectric properties only in H_2O- and D_2O-based HZO films, whereas O_3-based HZO film showed linear dielectrics properties. These results suggest that different types of oxygen sources should be used depending on the presence or absence of a capping layer in order to obtain and enhance the ferroelectric properties.

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AA-TuP-48 The Optimizing Mobility-stability Trade-off by Vertically Stacked IGZO/GZO TFT with Controlling of Indium-free GZO Layer via PEALD*, H. Oh, Y. Kim,* ***Jin-Seong Park,*** Hanyang University, Korea

Oxide semiconductor-based TFTs have already been commercialized for display backplane circuits based on advantages such as high mobility, large-area uniformity, low temperature processability, and low production cost[1,2]. In addition, oxide semiconductors, which have the advantage of low off-current ($\leq 10^{-18}$ A/μm), are drawing attention in recent application fields in ultra-high resolution display, AMOLED, DRAM, 3D-NAND and CMOS image sensors. However, mobility-stability trade-off is observed in oxide semiconductors, and it is important to find an appropriate compromise to apply them to various commercial applications.

In this study, we fabricated an PEALD IGZO/GZO TFT with a stacked indium-free GZO layer on the front channel to solve the mobility-stability trade off relationship. We focused that control of the cation composition of the GZO layer via PEALD enables (1) interface engineering through defect density control and (2) band alignment modulation. In addition, it was confirmed that these effects greatly affect the improvement of the electrical performance and stability of the IGZO/GZO TFT. As a result, the optimized IGZO/GZO TFT has high electrical characteristics with mobility (μ_{FE}) of 31.86±0.74 cm^2/Vs, threshold voltage (V_{th}) of -0.14±0.12 V, and subthreshold swing (S.S.) of 0.20±0.01 V/decade. In addition, it has excellent stability compared to IGZO TFT with ΔV_{th} = 0.00 V and -3.46 V under PBTS (60 ℃, 2 MV / cm stress) and NBIS (1000 lux, -2 MV / cm stress) conditions, respectively. Our study shows that the electrical performance and stability of TFTs can be effectively enhanced by applying an In-free GZO layer with an appropriate composition to the interface between GI and active by PEALD.

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AA-TuP-50 Interface Engineering of Porous Cathodes by Spatial ALD for Improved Cycle Retention in Liquid Electrolyte*,* ***Diana Chaykina****, N. Huijssen, W. Manders, F. van den Bruele, A. Kronemeijer, M. Ameen,* TNO/Holst Center, Netherlands

Lithium ion batteries are an important component to the energy transition, enabling widespread deployment of e.g. electric vehicles. To achieve societal targets for performance and sustainability, research has been focused towards finding cobalt-less (NMC), and nickel-less (LMNO) cathode chemistries. In addition, some of these cathode materials are considered “high-voltage” cathodes (e.g., NMC811), leading to a higher cell voltage, and ultimately, energy density[1]. However, these new cathode chemistries are often incompatible with the currently used liquid electrolytes, resulting in electrolyte oxidation/degradation and a number of parasitic side reactions during battery operation[2]. These unfavorable interactions between the cathode and electrolyte ultimately lead to capacity fade and cell death.

To mitigate this, we engineer the interface between the high voltage cathode and liquid electrolyte by depositing an ultrathin (<2 nm) passivation layer on the porous cathode by spatial atomic layer deposition (sALD)[3]. With this technique, we can deposit thin conformal coatings with atomic control of many different materials (e.g., metal oxides) at atmospheric pressure and at a high growth rate (throughput), which renders sALD a scalable manufacturing process for integration in the battery manufacturing process flow.

We assessed the effect of different deposition parameters/conditions, such as precursor dose, oxidator nature and purge times, on the electrochemical performance of battery cells using NMC811. As well, we studied the impact of the sALD process on the full electrode stack and investigated, among other aspects, the penetration depth of the coating throughout the thick porous cathode. Combining the device performance with physical analysis, we optimized the cathode passivation and showed that the use of an sALD barrier is beneficial for capacity retention.

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AA-TuP-51 Study of Nb_2O_5 high-k Dielectric Material Deposited by Atomic Layer Deposition for Metal-Insulator-Metal Capacitor*,* ***Kou Ihara****, C. Labbé, J. Cardin, C. Frilay, M. Philippe,* CIMAP Normandie Université, France*; M. Leménager,* Murata Integrated Passive Solutions, France

The application of new high-k materials can help improve the properties of modern capacitors such as capacitance density. However, it is necessary to understand the deposition conditions of both electrode and dielectric materials in order to master the dielectric properties in future capacitors. One potentially interesting high-k material is Nb_2O_5 deposited by Atomic Layer Deposition (ALD) using NEO as niobium precursor and H_2O as reaction agent and oxygen source. Nb_2O_5 films are deposited directly on a silicon (Si) substrate or on a titanium nitride (deposited by ALD on Si substrate). Their structural properties are characterized by spectroscopic ellipsometry, scanning electron microscopy and atomic force microscope. Subsequently, a MIM structure ($Ti/Nb_2O_5/TiN$) is produced by adding a second titanium layer deposited on a $Nb_2O_5/TiN/Si$ stack by the sputtering method. The electrical properties of Nb_2O_5 dielectric layer such as dielectric constant, breakdown field and leakage current at possible user voltage are measured on this last structure. These measurements indicate that the electrical properties of the Nb_2O_5 material produced by ALD with specific settings are promising for the application in capacitors. These results provide new insight into our understanding of the application of Nb_2O_5 realized by ALD for the MIM capacitor.

AA-TuP-52 Cathode Electrolyte Interphase Development and Residual Lithium Compound Removal via Chemical Vapor Treatment on Nickel-Rich Cathode*,* ***Rajesh Pathak****, V. Rozyyev, A. Mane, J. Elam,* Argonne National Laboratory, USA

The cycling performance of lithium-ion batteries depends greatly on the interface between the cathode and the liquid electrolyte.With the industry shifting towards higher capacity nickel-rich cathode materials, methods are needed to remove residual lithium compounds (RLCs) from the nickel-rich cathode surface and create a robust cathode electrolyte interphase (CEI). In this study, we utilized an ALD-like process, chemical vapor treatment (CVT), to remove RLCs such as LiOH and Li_2CO_3 from the surface of NMC811 cathode powders. We investigated the process using in situ Fourier transform infrared (FTIR) spectroscopy and ex situ X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR) measurements.These measurements revealed the conversion of LiOH and Li_2CO_3 surface contaminants into Li_3PO_4 via self-limiting surface chemical reactions. Following the CVT, the NMC811 powders were integrated into coin cells to evaluate the effect of the Li_3PO_4 coating on the cycling performance.We found that the removal of the RLCs maintained the cathode structural integrity and improved the Li-ion transport. In addition, the Li_3PO_4 CEI not only acts as a physical barrier between the cathode and liquid electrolyte but also provides strong covalent bonding of the PO_4^- group enabling high thermal stability. As a result, CVT Li_3PO_4 on NMC811 yielded more stable cycling, lower voltage hysteresis, and higher-rate capability compared to the bare NMC811 during electrochemical cycling.

AA-TuP-53 Pt-Al2O3 Metamaterial with Tunable Resistivity, ***Ritwik Bhatia***, Veeco Instruments Inc.

Films of intermediate resistivity in between semiconductors and insulators are needed to prevent static build up while minimizing/controlling current discharge. Atomic layer deposition (ALD) has been used to create such materials using a blend of transition oxide semiconductors and insulators [1,2]. This approach is problematic due to lack of stability of these materials [2]. An alternate approach with ALD of molybdenum or tungsten nano-dots in an Al2O3 matrix has been developed in the context of micro channel plates [3] and has also been applied to electro-optical MEMS devices [4].

Deposition of Mo (MoF6+Si2H6) or W (WF6 + S2H6) requires a high level of engineered safety since S2H6 (disilane) is a highly flammable gas and the reaction produces hydrogen fluoride as a byproduct. In this work, we have replaced Mo/W with platinum as the material in the nano-dots. Platinum is deposited using the metal organic precursor MeCpPtMe3 with molecular oxygen as the co-reactant. Managing environmental health and safety for platinum deposition is much easier than for molybdenum or tungsten. Further the low growth per cycle (GPC) of Pt (~ 0.05nm/cycle) allows finer control of the resistivity compared to Mo or W (GPC ~ 0.5nm/cycle)

We show that resistivity can be varied by several orders of magnitude by either changing the size of nanodots (holding the ALD Al2O3 cycles constant and varying the number of Pt cycles) or by changing the spacing between the nanodots (holding the number of Pt cycles constants and varying the number of Al2O3 cycles). The resistivity range accessed to date is 1e3 to 1e10 ohm.cm. We also discuss stability of the material in response to electrical and thermal stresses and the thermal coefficient of resistance.

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AA-TuP-54 Effect of Ar Purge Step Condition on PEALD-TiN Film Properties, ***Ju Eun Kang***, *S. An, S. Hong,* Myongji University, Republic of Korea

The role of the metal diffusion barrier become more crucial for the low power consumption and high reliability in the metallization process. TiN thin film has been a conventionally preferable material for Cu diffusion barrier using atomic deposition layer (ALD). Despite of the purge steps in time-divided cyclic ALD, undesired residues of precursor and reactants remained inside the process chamber may turns into unexpected particles in the film which can jeopardize the film quality. Extending purge time can avoid the presence of the particle, but it also decreases the manufacturing throughputs due to the extended process time. Therefore, we investigated the relationship between purge time and characteristics of the TiN thin film quality. The TiN films deposited in 6-inch PEALD system with varyied purge conditions was inversigated with repect to the thickness, sheet resistance, and surface composition with ellipsometry, a 4-point probe, and X-ray photoelectron spectroscopy, respectively. The by-product production, with respect to the flow rate of the purge gas and flow time, was also investigated using Employing Chemkin simulation study.

As the longer Ar flow time, the N 1s peak of 300 sccm as the Ar flow rate and thickness decrease because the screening effect increases and it means that residual Ar atoms are intervened between the adsorbents to block the adsorption of the precursors and reactants. As shown in Fig. 1, through chemical reaction simulations, we found that the production rate of hydrocarbon increased as the Ar flow rate increased because Ar as inert gas increases the collision between chemical species in the chamber, making the production rate increase. We found that when the Ar flow rate increased, the reaction between the desorbed ligands increased to form an unstable compound (CH_3), and as the material was formed, the carbon component increased. Especially, in low Ar flow rate, the C_3H_6 production rate increased. Carbon 1s peak decreased at a lower Ar flow rate because the stable compound (C_3H_6) is easily removed from the chamber by the pump. Thus, we concluded that inducing the generation of these compounds can reduce the removal of the incorporation of materials into the thin film surface. In the past ALD process cycle optimization research, the focus has been on optimizing the flow time of precursors and by-products rather than purging. However, in this study, the effect of the purge condition on the characteristics of the TiN thin film was confirmed was proposed. This can be a novel approach to prevent by-product incorporation through purge conditions in terms of controlling the surface composition of thin films.

AA-TuP-55 Probing the Structural and Chemical Evolution of Interfacial SiO_x Layers Formed During ALD and Post-Deposition Processing, ***Ben M. Garland***, *N. Strandwitz,* Lehigh University

Atomic layer deposited (ALD) aluminum oxide (AlO_y) has been investigated to increase silicon solar cell efficiency by decreasing carrier recombination as a passivating interfacial tunneling layer, as well as a non-tunneling active layer in passivating emitter and rear contact (PERC) cells. When subjected to post-ALD annealing, a negative fixed charge forms at the interface with silicon oxide (SiO_x) to provide field-effect passivation. Post-ALD annealing also promotes chemical passivation of dangling bonds near the interface from the diffusion of residual hydrogen left over from the ALD process. The interfacial SiO_x chemistry is impacted by the Si surface preparation, ALD growth parameters, and post-preparation or post-deposition annealing. Previous work in x-ray photoelectron spectroscopy (XPS) and computational studies has indicated that the suboxides of SiO_x, where x=1-3, exist at interfaces and in ultrathin layers along with the dominant SiO_2. These suboxides could promote trap-assisted carrier tunneling in layers < 3 nanometers thick and/or change passivation characteristics.

In this work, we investigated the thickness and composition of interfacial SiO_x layers using XPS in $Si|SiO_x$ and $Si|SiO_x|$ALD AlO_y structures to provide a comprehensive understanding of the interface. Hydrogen-termination, oxide grown with the Radio Corporation of America (RCA) process, ultraviolet ozone-grown oxide, and nitric acid-grown oxide were explored as silicon preparations often used in industry processing. The annealing condition (425°C in N_2 for 20 minutes) was chosen since it is in the range often used to promote passivation by ALD AlO_y. The Si 2p core level location associated with the primary SiO_x component was observed to shift to lower binding energy after AlO_y deposition, implying a change in the chemical structure that was examined through peak fitting. The Al 2p core level position and relative intensity to Si 2p was also studied, H-terminated silicon having the smallest intensity of Al 2p due to inhibited initial nucleation of ALD AlO_y. 2-bin and 5-bin peak fitting models were used to quantify the SiO_x layer thickness and composition. Between the two models, a ~0.2-0.3 nm difference in SiO_x thickness was seen depending on processing conditions; for example, with Si|nitric acid-grown $SiO_x|$ALD AlO_y, the SiO_x thickness was 0.9 nm in the 2-bin model and 1.1 nm in the 5-bin model. Silicon preparation, the presence of AlO_y, and post-preparation/deposition annealing influenced the SiO_x thickness and composition. Our findings may shed light on the SiO_x conditions that arise from processing and yield knowledge useful in silicon device manufacturing.

AA-TuP-57 Ultraviolet Bandpass and Wedge Filter ALD Coatings for Astrophysics Instruments, ***John Hennessy***, *R. Rodriguez, A. Jewell,* Jet Propulsion Laboratory (NASA/JPL)

We report on the use of atomic layer deposition (ALD) for the development of metal-dielectric bandpass filters that can be integrated directly onto back-illuminated imaging sensors for operation at far ultraviolet wavelengths (FUV, 90-200 nm). These coatings utilize previous developments in ALD metal fluoride processes for materials like MgF_2 and AlF_3, which are then combined with evaporated aluminum layers in multilayer structures. Planar coatings can produce an FUV bandpass response that allows broadband silicon CCD or CMOS imaging sensors to operate with visible and solar blindness, this enhances the utility of these devices for use in astrophysics sensing applications. We describe the fabrication and optical characterization of these coatings, and describe the development of detectors integrating these coatings that are planned to be delivered to upcoming NASA CubeSat and Explorers Missions.

We also report on the extension of this concept to include graded thickness dielectric layers deposited by ALD. We show that a graded lateral thickness can be engineered in a variety of thermal ALD processes by depositing into a shallow horizontal cavity. Process parameters like delivered dose, and background pressure can influence the lateral extent of the grading effect and therefore allow the slope of the graded thin film to be tailored without the need for moving parts inside the vacuum chamber. This allows for the fabrication of detector-integrated filter coatings with a spatially-varying response that can be matched to the spectral dispersion of spectrometer instruments. At visible and near infrared wavelengths this is used to produce graded dielectric anti-reflection coatings on silicon with R<1% over a wavelength range of 300–1000 nm. Metal-dielectric variants provide order-sorting and long-wavelength rejection for FUV applications. Prototype graded coatings are demonstrated over areas up to 4 x 4 cm, and characterized for optical performance and environmental stability.

AA-TuP-58 Internal Photoemission (IPE) Spectroscopy Measurement of Interfacial Barriers in Fatigued ALD Ferroelectric Hafnium Zirconium Oxide MFM Devices*, **Jessica L. Peterson**,* Oregon State University*; T. Mimura, J. Ihlefeld,* University of Virginia*; J. Conley,* Oregon State University

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) is under intense investigation for its potential ease of integration into advanced CMOS memory and logic applications. Atomic layer deposition (ALD) is the preferred method of depositing HZO. Inducing ferroelectric behavior in HZO typically requires "wake-up" – repeated voltage cycling above the coercive field.[1] Once woken, there is a period of stable behavior. Eventually, additional voltage sweeps fatigue the HZO, degrading ferroelectric performance.[2] Here we study the impact of cycling fatigue on metal/HZO band offsets and IPE yield in metal/ferroelectric/metal (MFM) devices.

20 nm of ~$Hf_{0.5}Zr_{0.5}O_2$ was deposited on TaN/Si substrates at 150 °C via ALD in an Ultratech S100 using 102 1:1 supercycles of TDMAH / H_2O and TDMAZ / H_2O. Next, 20 nm of sacrificial TaN was sputtered and the structure was annealed at 600 °C for 30 seconds. Following the anneal, the top TaN was stripped and replaced by an optically transparent 5 nm TaN/5 nm Pd top electrode. The completed MFM devices were "woken" using 5k cycles of a 10 kHz +/- 5 V square wave and then stressed at increasing intervals of cycles up to 500 k cycles. Band offsets and photoemission yield were measured using a lab-built IPE system.[3] Voltage applied to the bottom electrode was swept from -1.5 to 1.5V in 0.1 V steps. Simultaneously, monochromatic light focused onto the top electrode was swept from 1.7 to 5.5 eV. IPE thresholds were extracted at each voltage from plots of the square root IPE yield vs. photon energy. Zero field HZO/electrode zHHZOband offsets were extracted from plots of IPE thresholds vs. square root electric field.

Compared to pristine devices, the initial 5k waking cycles had little impact on band offsets but slightly reduced yield. An additional 5k cycles (total 10k) (i) reduced band offsets from 2.6/2.9 eV to 2.2/2.3 eV for top/bottom electrodes, respectively, with no further significant change up to 100k cycles, and (ii) reduced yield for both electrodes. Continued cycling up to 40k total did not significantly impact yield, indicating a regime of stable operation. Beyond 40k cycles, decreasing photon yield and increased leakage with increasing cycles was observed, consistent with fatigue. At 500k cycles, the devices were no longer functional. The decrease in yield, especially between 4-5 eV, accompanied by increased leakage is consistent with fatigue related to oxygen vacancy generation and movement.[4]

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AA-TuP-59 Understanding the Reactions of ALD Precursors on Lithium Metal and Its Application to Lithium Metal Batteries*, **Donghyeon Kang**, A. Mane, J. Elam,* Argonne National Laboratory

Trimethylaluminum (TMA) is a widely utilized aluminum precursor for atomic layer deposition (ALD) in various aluminum-based coatings. For example, TMA produces Al_2O_3 with H_2O,[1] AlF_3 with HF-pyridine,[2] and Al_2S_3 with H_2S [3] by well-defined ALD mechanisms. These ALD processes have been widely applied into various substrates to introduce ultra-thin Al-based coating layers, including energy storage materials such as battery cathodes, anodes, and solid electrolytes. Our group demonstrated that the Al_2O_3 ALD process using TMA can be used for Li-metal anode coating to improve electrochemical stability and reduce Li-dendrite formation during battery cycling.[4]

Although many studies about ALD on Li metal anodes have been reported using TMA, most of them focus on Li-metal battery performance, instead of ALD chemistry. During deep investigation on ALD chemistry of TMA, we recently discovered an interesting chemistry between TMA and reactive metal substrate (i.e., Li metal). Based on our observation, TMA reacts with Li-metal during ALD cycles then producing a carbon composite layer on the top of Li metal, not following conventional ALD mechanisms. It may come from highly reactive nature both of TMA and Li metal. Despite of wide use of TMA, this phenomenon has not been reported to date because Li metal is passivated by several layers such as Li_2CO_3, LiOH and Li_2O even stored in glovebox environment. In this presentation, we will discuss the chemistry between TMA and Li metal found by in-situ QCM, high-resolution XPS, SEM, and Raman studies. Then we will also demonstrate how this unexpected 'side reaction' can be utilized in Li-metal battery applications using liquid and solid electrolytes.

AA-TuP-61 Magnesium-doping in TiO_2 Dielectric Films for DRAM Capacitor Applications*, **YU-KYUNG PARK**, C. Hwang,* Seoul National University, South Korea

This work reports the electrical and structural behavior of Mg-doped TiO_2 (MTO) thin film as a dielectric layer for a dynamic random-access memory capacitor. As a successor of the current ZrO_2-based high-*k* (*k* ~ 40) capacitor dielectric thin film, rutile-structure TiO_2 film with a *k*-value > 100 draws great attention [1]. However, its low band gap (~3.1 eV) incurs concerns about the leakage current. Al-doping decreased the leakage current significantly by the acceptor-doping effect [1]. However, Al-doping degrades the -*k*-value of the TiO_2 film to 70 - 90, depending on its concentration. This work exploits another acceptor-type dopant, Mg, as an alternative to Al to decrease the leakage current while minimizing the *k*-value degradation. Figure 1(a) shows the variations in the equivalent oxide thickness (EOT), which is the physical thickness of the film multiplied by 3.9/*k*, grown on the Ru substrates. The bulk *k*-values of the TiO_2 film and MTO can be calculated from the slopes of the linear fit graphs and are ~113 and ~90 for the films, respectively. MTO exhibits a higher *k*-value than ATO, which is known to be ~80. This effect was ascribed to the relaxation of oxygen sublattice caused by oxygen vacancies, and the reduction of Mg^{2+} ions can promote the rutile phase transformation of TiO_2. When Mg^{2+} ions are doped into TiO_2, they are successfully incorporated at the substitutional site of Ti^{4+}, and one oxygen vacancy is formed [2]. Furthermore, because the ionic radius of Mg^{2+} (86 pm) is larger than that of Al^{3+} (67.5 pm), tensile strain can be relaxed when the Ti^{4+} (74.5 pm) ions are substituted with Mg ions. In contrast, the inhibition of the phase transformation by Al doping is known due to the lattice constraint effect [3]. The best electric performance of MTO was observed at an equivalent oxide thickness (EOT) of 0.44 nm and a physical oxide thickness (POT) of 8 nm with a J value of 6.7×10^{-8} A/cm^2 at +0.8V. Figure 1(b) compares the J-V curves of 20-nm-thick MTO and ATO samples in both the positive and negative bias regions. The MTO sample shows lower leakage current than the ATO sample at +0.8V, with a remarkable difference of nearly two orders of magnitude, is observed in the high-voltage region. The shift in band offsets caused by Mg doping may be more effective than that induced by Al doping due to the lower number of valence electrons of Mg ions than Al ions. Therefore, Mg doping in the TiO_2 film is a promising approach to improve the capacitor dielectric performance.

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AA-TuP-62 Electrical Characteristics Modification of Dual Gate Oxide Semiconductor Thin-film Transistor*, **Sehun Jeong**, S. Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Thin film transistors (TFTs) are a critical element in the development of next-generation displays, and oxide semiconductor TFTs have garnered considerable attention due to their advanced electrical properties. Specifically, oxide semiconductors have high electron mobility, low leakage current, and remarkable electrical stability, making them suitable for use as active channel materials in TFTs.[1] To further control the electrical characteristics of oxide semiconductor TFTs, we propose using dual gate structures, which offer controllable subthreshold swing and rapid hard saturation. Our research has shown that the capacitance ratio between the top gate insulator and the bottom gate insulator in dual gate structured oxide semiconductor TFTs can be used to control the subthreshold swing and that the voltages needed to switch between the on and off states can be adjusted by changing the subthreshold swing.[2] Furthermore, we have demonstrated that hard saturation, a crucial characteristic for TFTs used in display applications, can be achieved by applying voltage bias to both gates.[2] In addition to their electrical advantages, dual gate structures also offer structural benefits, such as the ability to block external light from both the top and bottom gates. Our findings suggest that by tuning the gate insulators in dual gate structured oxide semiconductor TFTs, we can achieve ultra-rapid switching properties with hard saturation, making them a promising candidate for advanced TFTs in next-generation displays. Overall, our work highlights the potential of dual gate structured oxide semiconductor TFTs as a new and exciting avenue for the development of advanced displays.

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AA-TuP-63 Control of Hydrogen Content via Super-Cycle ALD Deposited Al_2O_3 Gate Insulator

Hwayoung Kim*, S. Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Oxide thin film transistors (TFTs) have gained much attention in the display market due to their outstanding properties such as high mobility and low off-current. Of the various types of oxide semiconductors, InGaZnO (IGZO) and InSnZnO (ITZO) deposited through atomic layer deposition (ALD) are being actively studied. Because ALD can precisely control the film thickness and enables conformal deposition, it is one of the best methods for depositing oxide semiconductors that are sensitive to the number of carriers, and even it can form complex structures. In addition, multi-component oxide semiconductors can be deposited through the super-cycle method.

In oxide TFT, carrier concentration is a major factor determining device characteristic; and hydrogen, of which content is difficult to control, greatly affects the carrier concentration. The hydrogen diffused into the semiconductor can act as a donor, but it can also act as a defect passivator. Therefore, it is important to optimize the interface between semiconductor and gate insulate layer, where the hydrogen diffusion occurs a lot. For the gate insulate layer, ALD-deposited Al_2O_3 with a high dielectric constant and excellent barrier properties for moisture and air, was used. The Al_2O_3 layer can be grown by plasma-enhanced ALD (PE-ALD) and thermal ALD (T-ALD) that uses O_2 plasma and H_2O as an oxygen reactant respectively. Therefore, it results in distinct hydrogen content and characteristics[1]. In studies so far, the ALD super-cycle method has been used only for active layers to control the carrier concentration. In this study, the hydrogen content in gate insulator was controlled through the super-cycle of PE-ALD and T-ALD. One super-cycle consisted of n cycles of T-ALD and m cycles of PE-ALD, and the ratio (n:m) was varied between 0:1, 1:1, 1:4, and 1:8. As the number of T-ALD cycle in super-cycle increases, the mobility gradually increases by 100 cm^2/Vs. Furthermore, damage on semiconductor during the gate insulator deposition was reduced as the PE-ALD cycle ratio decreases. Since the carrier concentration differs depending on the oxide semiconductor, it would be possible to fabricate a TFT with an appropriate number of carriers by finding an optimized super-cycle ratio for each type of semiconductors.

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AA-TuP-64 Atomic Layer Deposited ZnO and Al_2O_3 on Nonwoven Fibre Materials – Improving Antimicrobial Properties and Moisture Resistance

Laura Keskiväli, VTT Technical Research Centre of Finland*; P. Porri,* University of Helsinki, Finland*; S. Salo, K. Heinonen, A. Harlin,* VTT Technical Research Centre of Finland

Atomic layer deposition (ALD) is an excellent technique to produce different inorganic-organic hybrid materials. Self-terminating nature of ALD cycles helps attaining reliable coverage of the complex nonwoven fibre structures. Low-temperature deposition of metal oxides can be used to improve antimicrobial properties of the hybrid materials and to enable effective decontamination and moisture resistance.[1,2] These properties are beneficial in personal protective equipment, such as technical masks.

In this study we deposited zinc oxide (ZnO) and aluminum oxide (Al_2O_3) on nonwoven viscose (Lyocell) and foam-formed cellulose fibres (JKL, from VTT Jyväskylä pilot plant).[3]The 75-400 cycles of ALD ZnO were produced with Picosun R-200 ALD reactor from diethyl zinc (DEZ) and H_2O at 80 °C. Furthermore, additional 7 cycles of Al_2O_3 (TMA, trimethylaluminium + H_2O) on ZnO coatings were studied. The visual appearance and distribution of ZnO was analysed by SEM-EDS. Hydrophobicity (contact angle measurement) was tested with deionized water. Furthermore, antimicrobial properties, filtration efficiency and particle shedding were studied. For antimicrobial properties, modified ISO 22196, MS2 virus and S.Aureus bacteria were used.

According to the contact angle measurements, Lyocell with 150 c and 300 c of ZnO and additional 7 c of Al_2O_3 were hydrophobic. With JKL cellulose samples no proper hydrophobicity was reached. ALD coatings did not affect on filtration efficiency, even though the ZnO coating penetrated throughout the fibre sample sheets and the amount of ZnO was equivalent on both sides according to SEM-EDS results. Particle shedding results revealed the differences in stability of the ZnO and Al_2O_3 treatments between the two fibre substrates. In the case of Lyocell, the ALD coating seems to be firmly attached and prevents the fibre particle shedding as well. In the case of JKL samples, the number of shedded particles exceeds the reference sample with 150 cycles or more of ZnO ALD, indicating the shedding of the ALD coating material. Antimicrobial efficiency was notable since both fibre types performed well already with 75 cycles of ZnO. All samples were microbicidal for both bacterial and viruses, and many of the samples exceeded the microbicidal impact of 3 log cfu/sampe, which is considered as an excellent effectiveness (Figure 1). ZnO ALD coating seems to have stronger microbicidal impact when deposited on foam-formed cellulose (JKL) compared to viscose material (Lyocell).

AA-TuP-65 Evaluation of Encapsulation Characteristics of $Si_xSn_yO_z$ Thin Film for OLED

S. Jeon, Y. Kwone, S. Lee, T. Byun, Y. Im, ***Sang Ick Lee,*** DNF Co. LTD., Republic of Korea

The current display market is led by OLED(Organic Light Emitting Diodes), and mass production of QNED(Quantum Nano-Emitting Diode) and Micro LED is being attempted. Since these display devices are vulnerable to moisture and oxygen, encapsulation is essential. A low WVTR(Water Vapor Transmissiion Rate) is required for the encapsulation film, and an appropriate refractive index is required to increase light extraction efficiency.

In this paper, in order to confirm that WVTR characteristics can be improved by doping Sn into SiO_2 and the refractive index can be controlled according to the Sn concentration, a $Si_xSn_yO_z$ thin film was deposited through PEALD process and its properties as an encapsulation film were evaluated.

For Si and Sn precursors, NSi-01 and DTP-01 developed by DNF were used(Table 1), and N_2O was used as the reaction gas. After depositing the $Si_xSn_yO_z$ thin film by controlling the vapor pressure of each precursor, the basic characteristics were analyzed(Fig 1a). As a result, it was confirmed that the refractive index and concentration can be controlled by adjusting the vapor pressure(input amount) of each precursor(Fig 1b). Through TEM mapping analysis, there were confirmed that Si and Sn were evenly distributed(Fig 2). As a result of analyzing the stress and film density according to the Sn concentration, it was confirmed that as the Sn concentration increased, the stress changed from compressive stress to tensile stress and the film density increased.(Fig 3) For transmittance and WVTR analysis, $Si_xSn_yO_z$ was deposited on PEN (Poly Ethylene Naphthalate) film. The transmittance measured by UV-Vis. was close to 100%. The WVTR of the $Si_xSn_yO_z$ film measured using MOCON's AQUATRAN 2 equipment showed excellent characteristics compared to SiO_2 of the same thickness(Fig 4).

Through this, the possibility of encapsulation application of $Si_xSn_yO_z$, which can control the refractive index and has excellent properties as an encapsulation film, was confirmed.

ALD Applications
Room Grand Ballroom H-K - Session AA1-WeM

Memory RRAM, Neuromorphic, NVM

Moderator: Dr. Robert Clark, TEL Technology Center, America, LLC

8:00am **AA1-WeM-1 3D Integrated Device Applications of ALD-Grown Ferroelectric and Oxide-Semiconductor Materials***, **Masaharu Kobayashi**,* University of Tokyo, Japan **INVITED**

Ferroelectric memory is a candidate for lower power memory device. HfO_2-based ferroelectric (FE-HfO_2) has been recently discovered [1], which drives ALD-based ferroelectric (FE) material and opens pathway to high-capacity memory. Oxide semiconductor (OS) such as IGZO is now getting attention for BEOL-compatible transistor channel material [2]. 3D integrated device application requires ALD growth of OS. These two ALD-based materials have been intensively explored in R&D of LSI community as key enablers for energy-efficient computing devices. In this presentation, I will discuss challenge and opportunity of ALD process for 3D integrated device applications based on our recent research progress.

(1) Monolithic 3D integration of OS FET and $HfZrO_2$ FE-capacitor

HfO_2-based FE-capacitor can be formed at BEOL because of its low thermal budget. Monolithic integration of embedded FeRAM can be realized by FE-HfO_2 and OS FET, which enables high density and high bandwidth nonvolatile memory for xPU. High quality $HfZrO_2$ can be grown by ALD, where HfO_2 and ZrO_2 are alternatively grown layer by layer. After crystallization anneal, $HfZrO_2$ becomes orthorhombic phase and shows ferroelectricity. We found that OS capping layer helps to reduce anneal temperature and improves memory reliability. We demonstrated 1T1C FeRAM cell operation by Sn-doped IGZO (IGZTO) access transistor and HZO FE-capacitor with just 400℃ thermal budget [3].

(2) 3D vertical channel FeFET for high-density and low power FE storage memory.

Ferroelectric FET (FeFET) is an one-transistor memory device with FE gate insulator. Depending on its polarization, FET can be set as high V_{th} state or low V_{th} state. Similar to NAND flash memory, FeFET can also have 3D vertical channel architecture. We are interested in OS channel material instead of conventional poly-silicon channel for 3D FeFET because of its high mobility, low thermal budget, and potentially high reliability. We developed ALD growth process of InOx and applied it to 3D vertical channel FeFET integration process. We demonstrated memory operation of 3D vertical channel FeFET with 5nm-thick InOx [4].

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8:30am **AA1-WeM-3 Cross-Point Metal-Ferroelectric-Metal Capacitors Array for Compute-in-Memory Applications***, **Minjong Lee**, H. Hernandez-Arriaga, J. Kim, J. Kim,* University of Texas at Dallas

Rapid advancement of electronic technology has been a driving force towards the development of high-density and low-power processors, from a classical von-Neumann computing architecture to an interesting compute-in-memory (CIM) configuration. With the adoption of ferroelectric (FE) materials for CIM applications, most researchers have focused on the FE field-effect-transistors based vector-matrix multiplication (VMM) operation which can realize the analog conductance states;[1] however, the studies for metal-FE-metal (MFM) structure are rare to see.

In this work, we demonstrate a 2×2 pattern recognition system using a 4×2 cross-point array configuration of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) MFM capacitors. TiN/HZO/TiN MFM capacitors were fabricated following our previous work.[2] However, the finger shaped TiN top and bottom electrodes (TEs and BEs) were patterned by the photolithography and ICP metal etching, and the thicker TEs were adopted to reduce series resistance components in TE lines. Since the polarization-change in MFM capacitors induces the different amounts of stored charges, the current signal can allow binarized states, generally called as switching and non-switching currents. It should be noted that the feature of HZO MFM capacitors is particularly similar to a polarization-induced synaptic charge behavior unlike conventional resistance/capacitance ones. Furthermore, the devices enable an excellent VMM operation, eligible for the neuromorphic computing with binary weight, by implementing the readout of maximum current value. For the pattern recognition, we followed the experimentally demonstration-method of 2×2 pattern recognition, introduced in a previous report.[3] Each cell of 2×2 pattern was applied to the TiN TEs, in which the white pattern is regarded as positive polarization state by 2.5 V set-pulse while the black pattern implies a negative polarization state by –2.5 V set-pulse. The tested patterns are all occurrences in 2×2 patterns (total 16 patterns). As the pattern recognition results, the current readout has the recognition accuracy of 81.3%, which is comparable results with the previous report,[3] thus highlighting the promise of the simple MFM capacitors towards the neuromorphic computing applications. The detailed results will be presented.

This work is supported by GRC-NMP program (#3001.001) of SRCUT Dallas' Texas Analog Center of Excellence (TxACE). The ozone generator used in this work was provided by TMEIC.

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8:45am **AA1-WeM-4 Using ALD to Precisely Place Multiple Transition Metal Impurities to Defect Engineer MIM Diode Performance***, **Shane Witsell**, J. Conley,* Oregon State University

Metal/insulator/metal (MIM) diodes promise ultra-fast rectification for applications in THz energy harvesting and detection but simultaneously require low turn on voltage (V_{ON}), low zero bias resistance (ZBR), and reasonable current-voltage (*I-V*) asymmetry (f_{asym}). Methods for improving these parameters beyond the standard use of different work function metal electrodes ($\Delta\Phi_M$), include multiple insulators (MIIM, MIIIM) to promote resonant or "step" tunneling, geometric field enhancements (using, e.g., carbon nanotubes), and *intrinsic* defects to promote defect-enhanced conduction [1]. Recently, we applied atomic layer deposition (ALD) to precisely insert transition metals into the Al_2O_3 tunnel barrier of dissimilar electrode MIM diodes. These metals introduce *extrinsic* defect levels that enable conduction pathways not present in undoped Al_2O_3 [2]. Ni (D_{Ni}) defects placed nearer the smaller Φ_M electrode, improvedf_{asym}, but increased V_{ON}, likely due to negative charge trapped at defect levels lying energetically near or below the equilibrium Fermi level ($E_{F,equil}$) of the electrodes [3]. On the other hand, Ti (D_{Ti}) defects placed near the larger Φ_M electrode reduced V_{ON} due to positive charge trapped in levels above $E_{F,equil}$, but slightly increased f_{asym}. Results were consistent with asymmetric trap assisted tunneling (TAT). In this work, both Ni and Ti impurity defect layers were inserted at specific positions within the Al_2O_3 insulator thickness to allow for defect levels to align at specific applied voltages to promote asymmetric dual defect assisted tunneling.

ALD was performed using TMA/H_2O, $Ni(tBu_2DAD)_2/O_3$, and $TTIP/H_2O$. Two versions of doped structures were created: (i) "Dual Doped" in which the two ALD cycle Ni defect layer was positioned within the Al_2O_3 closer to the smaller Φ_M electrode and the two ALD cycle Ti layer inserted near the higher Φ_M electrode, and (ii) "Reverse Doped" in which the positions of the Ni and Ti layers were swapped. Electrode pairs with varying work functions were tested to investigate defect alignment. The Dual Doped $Pt/Al_2O_3/Al$ produced the largest increase in low voltage asymmetry over undoped MIM devices, while the Reverse Doped $Pt/Al_2O_3/Al$ device produced higher breakdown voltages and high voltage asymmetry. Both devices show lower ZBR. Additional results will be presented at the meeting including capacitance-voltage measurements on MIM and metal/oxide/semiconductor (MOS) devices. This work shows that ALD can be an effective tool for engineering device behavior.

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9:00am **AA1-WeM-5 The Impact of Oxygen Source on the Formation of TiN Interface at the Initial Stage ALD process of Hafnia-based Ferroelectrics: An *in-situ* Analysis***, **Jin-Hyun Kim**, S. Kim, D. Le, Y. Jung, S. Hwang, H. Hernandez-Arriaga, M. Lee, A. Khosravi, K. Tan,* University of Texas at Dallas*; J. Spiegelman, M. Benham,* RASIRC*; S. Kim,* Kangwon University, Republic of Korea*; J. Kim,* University of Texas at Dallas

Ferroelectricity in doped hafnia is widely studied with its promising capability for memory applications. However, despite the mature HfO2 ALD technology, hafnia-based ferroelectrics still have major reliability issues such as relaxation, imprint, fatigue, and breakdown.1 These reliability properties are deeply related to the interface condition between the ferroelectric film and the electrodes. Thus, many reports suggested ways to improve reliability and enhance ferroelectricity by modifying the interface states of the metal-ferroelectric-metal (MFM) capacitors.2 Furthermore, the interface becomes a bigger issue for the ferroelectric layer scaled down thinner than 5 nm due to series capacitance and difficulties in crystallization due to high surface energy.3 Therefore, it is crucial to understand the interface formation and the properties more carefully to further improve the reliability and scalability of the hafnia-based ferroelectric materials.

Herein, we investigated the effects of various oxidants on the interface layer using in-situ reflectance absorption infrared spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS). With these techniques, we monitored the surface reactions and interface formation in Hf0.5Zr0.5O2 (HZO) ALD process with TDMA-Hf/Zr and three different oxidants sources (H2O, O¬3, and anhydrous H2O2) on TiN substrate at 250 °C. As determined with in-situ IR absorbance spectra, all three oxidants effectively oxidized the TiN surface with just 1 exposure cycle. With additional pulses of O3, the intensity and peak area of features related to Ti–O and TiN–O continuously increased. However, in the case of H2O and H2O2, limited formation of oxygen bonds was observed on TiN surface. Interestingly, contrasting to H2O, H2O2 formed self-limiting peroxyl groups on the TiN surface with a minimum interface formation, resulting in superior film properties and robust reliability of H2O2-based HZO capacitors.

Moreover, the in-situ XPS data using H2O showed the formation of Ti–O bonds after the initial cycle more clearly, which strongly supports the RAIRS result. Extensive in-situ XPS analysis will be conducted to confirm these observations in the IR spectra.

We thank YEST and KEIT for supporting the project through ISTD Program (No.20010806). This work is also supported by GRC-LMD program (task#3001.001) through SRC. The BRUTE hydrogen peroxide was provided by RASIRC and the ozone generator was from TMEIC.

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9:15am **AA1-WeM-6 Performance Enhancement in HZO Based Ferroelectric Memory Devices*, Ranjith K. Ramachandran,*** *L. Lukose,* ASM Belgium*; A. Leonhardt, M. Surman,* ASM Microchemistry Ltd., Finland*; V. Koladi Mootheri,* ASM Belgium*; M. Ioana Popovici,* IMEC, Belgium*; M. Givens, A. Illiberi,* ASM Belgium

HfO_2 based ferroelectric (FE) materials have gained tremendous attention as a potential candidate for memory applications such as FeFET and FeRAM. Since its first demonstration as a FE material [1], immense research has been done to circumvent the challenges such as scalability, increasing the remnant polarization (Pr), and improving endurance. Among others, Zr-doped HfO_2, hafnium zirconate (HZO) is being intensively studied due to its compatibility with complementary metal oxide semiconductor (CMOS) processing and excellent scalability.

The ferroelectricity in HZO films is believed to originate from the presence of polar metastable orthorhombic phase (o-phase: Pca21). Several methods have been explored to stabilize o-phase in the films, such as annealing, doping, and interface engineering. This, in turn, depended on the advent of synthesis methods that offer atomic level control over the thickness, composition, and interface, i.e., Atomic Layer Deposition (ALD). In this report, using ALD, we demonstrate three different methods such as 1) precursor selection 2) doping, and 3) interface engineering to improve the FE performance of HZO. ALD of HZO and La:HZO films was performed in a 300mm, industrial scale, EmerALD ALD reactor at a substrate temperature of 275^{o}C. Both halide and MO-based precursors were used as the metal source with H_2O/O_3 as a co-reactant and their FE performances were compared via remanent polarization (2Pr) and endurance measurements.

First, the influence of ALD precursor and co-reactant on the performance of HZO devices is demonstrated. Halide-based precursor shows initially high 2Pr compared to the MO (with O_3 as co-reactant). However, the onset of fatigue is at 1x10^5 cycles due to the presence of possible Cl impurities. In the case of MO precursor, there is an observed wakeup effect which can be attributed to the transition from the tetragonal-orthorhombic phase (t-o phase) to the stable o-phase with increased cycling. The stable o-phase leads to higher 2Pr with the number of cycles and better endurance (fatigue at 3.5x10^7 cycles) compared to the halide-based precursor (**Fig. 1**). Together with low coercive field (2Ec) and high 2Pr, this MO-based process has useful applications in Fe-RAM. In addition, ozone as co-reactant shows improved 2Pr compared to water.

Furthermore, La doping on HZO was carried out to improve wake-up, max 2Pr, and endurance (Table 1). Subsequently, interface engineering with La-doped HZO resulted in record-high 2Pr (63 µC/cm^2), with high endurance and lower wake-up (**Table 1**) [2].

References

1. T.S. Boscke et al, Appl. Phys. Lett. 99, 102903 (2011)
2. M. I. Popovici and J. Bizindavyi et al, IEDM 2022

9:30am **AA1-WeM-7 Stabilization of Tetragonal Phase of Ti-doped ZrO_2 Deposited by ALD*, Seokhwi Song,*** *Y. Choi, E. Kim, K. Kim, H. Jeon,* Hanyang University, Korea

Manufacturing metal-insulator-metal (MIM) capacitors with high capacitance and low leakage current for dynamic random access memory (DRAM) has become a challenge as electronic devices rapidly decrease in size and distances between devices increase. Therefore, in this study, Ti-doped ZrO2 was investigated as a high-k material for DRAM capacitors. ZrO2 film has been widely studied as a high-k material for DRAM capacitors due to its high permittivity and wide bandgap. ZrO2 has monoclinic, cubic and tetragonal crystal phases. The dielectric constant of ZrO2 is highly dependent on the crystal structure (monoclinic: 19.7, cubic: 36.8, tetragonal: 46.6). However, a material with a higher permittivity than common ZrO2 was required, and a method of changing the crystal structure of ZrO2 through doping was studied. The same tetravalent element as Zr can stabilize the cubic/tetragonal phase of ZrO2 without introducing oxygen vacancies into the thin film. When the tetravalent dopant is replaced by a Zr atom, the distance between the dopant and the O atom is different from that of the Zr-O atom, so it is converted into a cubic or tetragonal phase. Among them, Ti dopant is a promising stabilizer to replace Zr atoms.

Atomic Layer Deposition (ALD) is an optimal deposition method for Ti-doped ZrO2 at a desired Ti dopant concentration. The concentration of Ti may be controlled through a super cycle ALD process in which n ALD cycles for the host material ZrO2 and 1 ALD cycle for the dopant material Ti are repeated. Through this ALD process, Ti-doped ZrO2 having a desired doping concentration can be deposited to a desired thickness. Ozone with high oxidizing power is essential to improve crystallinity. Since the crystallinity varies not only with the dopant concentration but also with the ozone concentration, Ti-doped ZrO2 is deposited at various ozone concentrations of 100 to 400g/m3 to check the crystallinity change.

In this study, Cyclopentadienyl Tris(dimethylamino)zirconium (CpZr(NMe2)3) was used as a precursor and titanium isopropoxide (TTIP) was used as a dopant. And ozone was used as a reactant. You want to deposit Ti doped ZrO2 and analyze the film with a supercycle ALD process. The core of this study is to confirm the change in the crystallinity of the thin film and the change in the physical properties of the thin film according to the Ti doping concentration.

9:45am **AA1-WeM-8 Three Terminal Synaptic Devices Employing ALD Grown Dual Dielectrics and Their Linear Learning Process*, Jung Wook Lim,*** Electronics and Telecommunications Research Institute, Republic of Korea*; J. Kim,* ETRI, Republic of Korea

To overcome the limitation of the von-neumann architecture, synaptic devices has been widely researched to emulate synaptic functions[1-2]. For this, synaptic devices with high stability and CMOS compatibility are required to overcome the barrier of commercial entry. Three terminal inorganic oxide transistors may be most suitable to satisfy these requirements. In our group, three terminal synaptic transistors employing ALD grown the TiO_2 channel layer and dual gate dielectrics were fabricated on Si n^{++} wafers (used as bottom gate electrodes) and the vertical structure is shown in Fig. 1. The synaptic behavior is performed by storing or capturing charges, and for this purpose, the interface trap sites were formed at the interface between channels and dielectrics by in-situ ALD process. We have used selectively deep traps among traps at different levels in the energy bandgap for capturing holes, resulting in negative shift of threshold voltages[3-4]. As a synapse device in which learning is performed by an electrical signal, a phenomenon in which the transfer curve moves in a negative direction by hole traps was observed after supplying an electrical pulse. Interestingly, when a voltage pulse of 10 V or higher is applied for 0.5 s, the conductivity increases abruptly and the metallic behavior was observed and the result is shown in Fig. 2. For confirming synaptic performance, paired pulse facilitation (PPF) curves were obtained, in which 0.4 s and 11.11 s of life times were obtained for the pulse times of 5 ms and 0.5 s (10 V), respectively. With electrical pulses of 10 V and 3 ms of short-term plasticity condition derived from PPF curves, long term plasticity was obtained with repeated pulses and the results are shown in Fig. 3. The 1024 conduction states (10 bit) was obtained with high linearity, which implies the high accuracy of recognition. The dual dielectrics are composed of ALD grown SiOx and AlOx films. The deep trap sites were formed at the interface of SiOx and TiO_2 channel layer, hence indicating that the in-situ plasma treatment is very important during the ALD growth. The AlOx films confirms the stability of devices and enhances the performance of transistors. In the further study, synaptic devices will implement the forgetting curves of human brains and their various phenomena.

References

[1] Y. Yang, Y. He, S. Nie, Y. Shi, Q. Wan, IEEE Electron Device Letters 39 (2018) 897-900.

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[4] J. W. Lim, M. A Park, J. Kim, Advanced Electronic Materials (2022) 2200494.

ALD Applications
Room Grand Ballroom H-K - Session AA2-WeM
Memory DRAM

Moderator: Prof. Parag Banerjee, University of Central Florida

10:45am **AA2-WeM-12 Opportunity of Atomic Scaled Materials in Revolutionary Memory Technologies*, Seiyon Kim,*** SK Hynix, Republic of Korea **INVITED**

The ALD technology has been widely utilized in modern nanometer scaled electronic due to the excellent uniformity, conformality, and thickness controllability.

The unique advantage of ALD is the “tune-ability” of the materials thanks to the freedom of changing concentration of elements and crystalline states. It makesALD films as versatile functional and structural materials with the capability to optimize electrical and physical properties for multiple applications spanning from logic to memory.

In DRAM storage node capacitor, without ALD technique, the metal electrode and the dielectric material cannot be deposited uniformly, considering the height of DRAM capacitor is more than 1μm, while the top opening of capacitor is just a few tens of nanometers. The aspect ratio of 3D NAND is even more severe than DRAM capacitor. Very conformal deposition with good uniformity is required in several critical steps, such as O-N-O charge trapping layer formation inside plug and thin metal deposition in replacement word line gates. In logic technology, Hf-based high K dielectric layer paired with ALD deposited work function metal has still been used for gate stacks since it revolutionized the transistor performance two decades ago. The low-k but robust SiOC film is key element of enabling gate pitch scaling and epi SD formation of Finfet devices.

As DRAM and NAND reaches sub-10nm node and 1000 layers respectively, many industries are afraid that the evolutionary approaches to extend the scaling would not work anymore. Therefore, revolutionary path technology such as stacked DRAM is taking more attention more than ever. The new revolutionary platform will require new devices, new integration schemes, and new materials. The requirement for new materials is expected to be very challenging, and more importantly, may require very different properties never asked in the past.

In this talk, I would like to illuminate how ALD materials have been utilized in ultra-scaled electrical devices, especially for DRAM and NAND. Then I will introduce emerging revolutionary memory technologies on the horizon. I also discuss about the requirement of structural and functional ALD materials to enable the future memory devices.

11:15am **AA2-WeM-14 Ultra High-k $HfZrO_4$ Thin Films Grown by Atomic Layer Deposition using Metal-Organic and Brute HOOH Precursors*, Harshil Kashyap,*** *A. Kummel,* University of California San Diego*; J. Spiegelman, M. Benham,* RASIRC

Lower leakage at low EOT is a requirement for DRAM application. Ferroelectric/antiferroelectric $HfZrO_4$ films have shown high-k at 10 nm but as the films are scaled, the dielectric properties of the films decrease[2,3]. The key to low EOT is to find a material with high-k at 5 nm or sub-5nm thickness with low leakage.

Metal-Insulator-Metal capacitors were[MB1] [#_msocom_1][HK2] [#_msocom_2] fabricated with $HfZrO_4$ thin films. 5nm $HfZrO_4$ was grown by ALD on sputtered TiN and W substrates at 275 °C using tetrakis(dimethylamino)hafnium (TDMAH), tetrakis(dimethylamino)zirconium (TDMAZ) (STREM) and H_2O_2 (Rasirc). $HfZrO_4$ thickness was determined by cross-sectional TEM and were between 5.0 and 5.5 nm. TiN and W electrodes were deposited by magnetron sputtering. Top electrodes were patterned by photolithography. Samples were annealed in N_2 at 600°C for 2 minutes. Control samples with H_2O were also fabricated for comparison with TiN and W electrodes.

C-V measurements were performed for $HfZrO_4$ films deposited with HOOH (Fig 1). Control samples made with H_2O were used for comparison. For $HfZrO_4$ using HOOH with TiN electrodes, there are 4 switching peaks in the C-V consistent with presence of the AFE phase (Fig. 1a). HZO with 1:1 Hf:Zr ratio is known to show FE switching; however, use of HOOH precursor may lead to Ti diffusion from TiN substrate into the HZO film. Small amounts of Ti are known to stabilize the AFE phase in HZO[4]. To study the impact of metal electrodes, samples with sputtered W electrodes were fabricated since W is known to show enhanced FE/AFE switching in HZO films. Undoped HZO with 1:1 Hf:Zr and W electrodes grown with HOOH (Fig 1b) shows only FE switching and no AFE switching.

When using HOOH, both the samples with TiN and W electrodes show record high capacitance for 5 nm films (> 10 mF/cm^2). Extrinsic contributions to k value from domain walls play an important role. A higher vol% of domain walls may be key to the extremely high-k observed in films fabricated using HOOH vs H_2O. A heuristic model of domain walls show surpassed polarization which are very susceptible to eternal stimuli and thus show high permittivity (Fig 2).

For DRAM application, it essential to have high-k near 0V. Both capacitors fabricated using HOOH show record high-k at (~58 with TiN, ~88 with W) 5 nm thickness which results in ultra-low EOT of ~3.5 A with TiN and ~2.5 A with W (Fig 3 a). The sample with W electrodes shows higher leakage in comparison with samples with TiN electrodes (Fig 4). This may be in part due to higher crystallinity in $HfZrO_4$ imparted by the W electrodes since major leakage pathway in crystalline $HfZrO_4$ thin films is grain boundaries.

11:30am **AA2-WeM-15 Achieving Ultra-High Mobility and Reliability of ALD-IGZO TFTs via Selective N2O Plasma Reactant for BEOL Applications*, Dong-Gyu Kim,*** Hanyang University, Republic of Korea*; H. Choi,* Chungnam National University, Republic of Korea*; Y. Kim, D. Lee, H. Oh,* Hanyang University, Republic of Korea*; J. Lee,* Chungnam National University, Republic of Korea*; J. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; S. Lee, B. Kuh, T. Kim,* Samsung Electronics, Republic of Korea*; H. Kim,* Chungnam National University, Republic of Korea*; J. Park,* Hanyang University, Republic of Korea

The semiconductor industry is expanding toward artificial intelligence (AI), cloud data centers, and high-bandwidth memory processing in memory (HBM-PIM). In these fields, atomic layer deposition (ALD) is indispensable for adjusting thickness control and high step coverage. The design of high-performance field-effect transistors (FETs) with low-voltage operation, high field-effect mobility (μ_{FE}), and low leakage current have propelled the development of relevant fields. Oxide-based thin-film transistors (TFTs) are garnering increased attention owing to their steep sub-threshold swing (SS) and extremely low leakage current. Although oxide-based TFTs are known to restrict μ_{FE} (~30 $cm^2/(V{\cdot}s)$), numerous research groups have demonstrated exceptional μ_{FE} values exceeding 100 $cm^2/(V{\cdot}s)$. However, the high stability of oxide-based TFTs is another prerequisite for their widespread application. Achieving high mobility and stability is challenging as the overall properties of oxide-based TFTs are compromised. Doping at oxide semiconductors with anions may resolve the issue of uniformity. Previous studies have confirmed that nitrogen (N) doping is promising for regulating oxygen vacancy (V_O) defect concentration. Because the atomic radius of N is comparable to that of oxygen (O), doped N is a suitable replacement for V_O defect sites.

In this work, we deposited plasma-enhanced ALD (PEALD)-IGZO TFT with O_2 plasma reactant using the super-cycle method at a set temperature of 200℃. For the In_2O_3, Ga_2O_3, and ZnO deposition, (3-dimethylaminopropyl)dimethylindium (DADI), trimethylgallium (TMGa), and diethylzinc (DEZ) precursors were utilized. To gain insight into N dopants for each cation of PEALD-IGZO, a nitrous oxide (N_2O) plasma reactant was selectively applied for each PEALD cation cycle. Our strategy here, the N_2O plasma reactant, is completely different from plasma treatment in that it participates in chemical reactions during the ALD process. Using a combinatorial study of experimental analysis and theoretical interpretation, the N-doping mechanism and the associated enhancement in the performance and stability of PEALD-synthesized IGZO TFTs were investigated. Based on these insights, high-performance with stable PEALD-IGZO TFTs could be obtained with minimal V_{TH} shifts of 0.35 V in difficult PBTS environments (temperature stress: 95℃, field stress: 2 MV/cm) despite a high μ_{FE} of 106.5 ± 2.7 $cm^2/(V\cdot s)$. Our results provide insights into the atomic precision optimization of the performance and stability of IGZO TFTs.

11:45am **AA2-WeM-16 Ultrathin and Highly Crystalline Indium Oxide Thin Films Using Novel Liquid In Precursor as a New Channel Material***, **Su-Hwan Choi**, R. Seong-Hwan,* Hanyang University, Korea*; C. Yeon, J. Jung, Y. Park,* Soulbrain, Republic of Korea*; J. Park,* Hanyang University, Korea

Oxide semiconductors containing indium oxides (InOx), such as IGZO, IGTO, and ITO, have been attracting attention for various applications, such as field effect transistors (FETs), catalysts, and active layers of memory devices because of their outstanding properties, such as high mobility, low off-current, and excellent uniformity. Among the oxide semiconductors, indium oxide is crucial because the electron carrier transport path mainly consists of In 5 s orbitals. The study of crystalline mechanisms and preferred crystal orientation of indium oxide were widely conducted because the characteristics of indium oxide, such as electrical and optical properties and reliability, are affected by InOx film crystallinity. Mengwei Si et al. reported an InOx channel FET with a thickness of 0.7 nm that can be applied to extended devices such as monolithic three-dimensional (3D) integration and dynamic random access memory (DRAM)[1]. However, the electrical properties of FETs were inferior because of the amorphous properties of 0.7nm thick InOx thin film. Since a constant thickness is required to crystallize the InOx film, the study of the critical thickness of crystallization is needed for further applications of InOx[2].

In this study, we developed a new liquid indium precursor with an ALD window from 200 to 350℃. To the best of our knowledge, this 350 ℃ is the highest ALD InOx deposition temperature using ozone as a reactant without impurities such as carbon and nitrogen. According to various analysis methods such as XRD and GIWAXS, 3 nm is the critical thickness of crystalline InOx films deposited by the ALD method using the SBIP-03 precursor. The authors studied the crystallinity effect of InOx in terms of thickness, deposition temperature, and post-annealing process. The crystallized 3 nm thick InOx film is adopted as the channel layer of FET. The FET has excellent transistor characteristics in terms of field-effect mobility (39.3 cm^2/Vs), threshold voltage (-0.7 V), subthreshold swing (310 mV/dec), and on-off current ratio (3.3×10^7).

[1] Si, Mengwei, et al. Nano Letters 21.1 (2020): 500-506. https://doi.org/10.1021/acs.nanolett.0c03967

[2] Macco, Bart, et al. Journal of Applied Physics 120.8 (2016): 085314. https://doi.org/10.1063/1.4962008

ALD Applications
Room Grand Ballroom H-K - Session AA1-WeA

ULSI, Display, Optics, Metamaterials, and Bio Applications
Moderator: Charles Dezelah, ASM

1:30pm **AA1-WeA-1 Synthesis of Low-k SiCNO Thin Films by Plasma-enhanced Atomic-molecular Layer Deposition with Tetra-isocyanate-silane (TICS) and Phloroglucinol (Phl)***, G. Baek, J. Park, G. Park,* ***Haelin Yang,*** Hanyang University, Korea

Recently, as the nanoelectronics manufacturing process is ultra-miniaturized, high-level patterning technology is increasingly required. The “edge placement error(EPE)” accumulated during the repeated patterning process in back-end-of-line (BEOL) causes shorting or high resistance. To solve the EPE problem, a fully self-aligned via (FSAV) design is essential, and FSAV can be realized by increasing the spacing between the via and the metal line by using low-k materials[1]. Two ways to reduce the dielectric constant k are to reduce the number of dipoles in the film and to reduce its polarizability. The dielectric constant can be reduced by fabricating a film with almost perfect non-polar binding (ex, C–C) through the hybrid of SiO_2 and organic polymer. Therefore, it is essential to research a new molecular layer deposition (MLD) thin film fabrication process that can hybridize with Si-based atomic layer deposition (ALD). For nano scale thin film deposition, various Si precursor synthesis results have been reported for ALD SiO_2 and SiN_x thin film fabrication, and high-quality thin film fabrication is being studied through plasma enhanced atomic layer deposition (PEALD) application. Development of the MLD process using Si precursors is difficult to secure due to very low reactivity with organic precursors.

In order to induce Si-based PEALD and MLD hybrid processes, the surface adsorption reactivity of organic precursors should be increased. In this study, PEALD and MLD hybrid processes were developed using Tetra-isocyanate-silane (TICS) as a Si precursor and Phloroglucinol (Phl.) as an organic precursor for low-k material fabrication. The activation layer was fabricated with PEALD SiN_x using N_2 plasma to improve the hydroxyl reactivity. Subsequently, the SiCNO thin film was successfully fabricated through the Phl. MLD process with tri hydroxyl group. X-ray photoelectronic spectroscopy (XPS) has been used for analyzing SiCNO film composition. As the process temperature increased, the SiN_x surface oxidation was induced more strongly, and the nitrogen composition in the thin film decreased while the oxygen composition increased. Through I-V and C-V measurement, SiCNO deposited at 300 °C has a leakage current (at 1MV/cm) of 1.02 10^{-9} A/cm^2 and dielectric constant k of 3.02 compared to SiO_2 (k of 3.9).

[1] Yu, Xiaoyun, et al. "Area-selective molecular layer deposition of a silicon oxycarbide low-k dielectric." Chemistry of Materials 33.3 (2021): 902-909.

1:45pm **AA1-WeA-2 Performance and Thermal Stability Improvement of Vertical-Channel Thin-Film Transistor by Controlling Deposition Temperature of Gate Stack Prepared by Atomic Layer Deposition***,* ***Dong-Hee Lee,*** Kyung Hee university, Korea (Democratic People's Republic of)*; Y. Kwon, N. Seong, K. Choi,* NCD. Co., Korea (Democratic People's Republic of)*; S. Yoon,* Kyung Hee University, Korea (Democratic People's Republic of)

Vertical-channel structure is one of the promising candidates for scaling down the oxide semiconductor thin-film transistors (TFTs), in which the active channel and gate stack are formed along the vertical sidewall, as shown in Fig. 1a. Thus, the channel length of vertical-channel TFT (VTFT) can be shortened to nanometer regime by reducing the spacer thickness. An ALD technique is completely compatible with manufacturing the oxide VTFTs in terms of conformal deposition, and the device feasibilities of VTFTs using the ALD In-Ga-Zn-O (IGZO) channels have been well demonstrated. However, in lots of works, the impact of deposition temperature (T_D) for the gate stack on device performance have rarely been investigated. Considering that the IGZO channels can be sensitively influenced during the ALD process of gate stack, the T_D is one of the most critical process parameters determining device operation as well as thermal stability of the IGZO VTFTs. In this work, we focused on the relationship between the T_D and VTFT performance from the perspective of thermal stability at various post-annealing temperatures.

For the fabrication of IGZO VTFTs, a vertical sidewall was formed by patterning the PECVD SiO_2 spacer (150 nm) intervening between the ITO source and drain layers. Then, an IGZO (In:Ga:Zn=1:1:2, 5 nm) was deposited by ALD using triethyl indium (TEIn), In-Ga bimetallic, diethyl zinc (DEZn), and O_3 as source of In, Ga, Zn and O, respectively. The gate stack composed of Al_2O_3 protection layer (PL, 5 nm) and gate insulator (GI, 15 nm) was prepared by ALD at different T_D’s of 200 (Dev. A), 250 (Dev. B), and 300 °C (Dev. C). Finally, gate electrode and contact pads were formed with Al-doped ZnO deposited by ALD. Figs. 1b and 1c show an optical image and a device layout of the VTFTs. To examine the thermal stability of the fabricated VTFTs, post-annealing was carried out in O_2 ambient with increasing the temperature up to 300 °C.

Fig. 2a shows the transfer curves of the fabricated VTFTs. The overall device performance was found to be enhanced with increasing the T_D and the Dev. C showed the highest current drivability (44 μA/μm). Even after post-annealing at 300 °C, all the VTFTs showed sound thermal stability (Fig. 2b) with excellent operational stability (Figs. 2c, 2d). It was noteworthy that the current drivability of Dev. C amounted above 55 μA/μm (Fig. 3a), which is remarkable improvement in the bench-mark plot shown in Fig. 3b. The T_D could be verified to have crucial impact on the current drivability of thermally-stable IGZO VTFTs. These achievements in device operation provide a path towards the highly-functional IGZO VTFTs.

2:00pm **AA1-WeA-3 Sequential Design of PEALD In-Ga-Zn-O Active Layer: Sub-cycle Engineering of Indium Oxide Layer for Highly Stable TFT***,* ***Taewon Hwang,*** *H. Yang, Y. Kim,* Hanyang University, Korea*; T. ONO, S. KAMIMURA, A. EIZAWA, T. TERAMOTO, C. DUSSARRAT,* Air Liquide Laboratories, Japan*; J. Park,* Hanyang University, Korea

Oxide semiconductors such as In-Ga-Zn-O (IGZO) are attracting considerable attention as active layers of next-generation displays such as AR/VR and automotive displays due to their excellent characteristics such as low leakage current, low deposition temperature, large area uniformity, and compliance mobility. For the application of 3D integration such as Fin-FET and memory/logic technology, atomic layer deposition (ALD) is a suitable method because it has the advantages of smooth surface, accurate thickness control in nanoscale, and conformal coating in complex structures due to its self-limiting characteristic. Furthermore, controlling the ALD sequence facilitates controlling the composition of the multi-component oxide semiconductor. In our previous study, we fabricated Indium-rich IGZO TFT with high mobility (≥70 cm^2/Vs) by controlling the indium sub-cycle of the ALD sequence[1]. However, it shows that excessive indium content can cause device degradation due to large carrier concentrations and crystallinity. This crystallinity-related device degradation needs to be solved for the application to future technology. We chose an advanced channel design to get the film with improved electrical properties by controlling the sub-cycle of the ALD sequence.
In this study, we suppressed the crystallinity of IGZO by inserting gallium and zinc layers into the indium layer through sequential design, and the electrical/reliability of the device was also evaluated. We confirmed that the indium crystallinity was suppressed as the interlayer of IGZO increased using the sequential design. As the indium crystallinity was suppressed, the roughness of the thin film was decreased by ~35 %, and the oxygen-related defect was also reduced. Furthermore, by adding an inter-layer to the Indium layer of IGZO, the S.S. reduced by ~45 % (from 0.42 V/decade to 0.23 V/decade), and the threshold voltage shift under PBS 3,600 s is decreased from 3.75 V to 0.83 V. The Sequential design method could be a breakthrough in improving the performance of the oxide semiconductor.

Reference

[1] Sheng, Jiazhen, et al. "Amorphous IGZO TFT with high mobility of∼ 70 cm2/(V s) via vertical dimension control using PEALD." ACS applied materials & interfaces 11.43 (2019): 40300-40309.

2:15pm **AA1-WeA-4 Bilayer Channel Combination Strategy via Atomic-Layer Deposition of In-Sn-O/In-Sn-Zn-O Structures for Highly-Functional Oxide Thin-Film Transistors***,* ***SHIN HO NOH,*** Kyunghee University, Republic of Korea*; Y. Kwon, N. Seong, K. Choi,* NCD Co. Ltd, Korea*; S. Yoon,* Kyunghee University, Republic of Korea

The introduction of a bi-layered channel structure is considered a highly effective approach to improve the device performance of oxide TFTs, which is composed of stacked ‘prompt’ and ‘prime’ channel layers with higher and lower carrier concentrations, respectively, owing to the impact of 2-dimensional electron gas (2DEG) formation at hetero-interfaces, leading to synergic roles in enhancing the carrier mobility and operation stability of the oxide TFTs. In this work, by means of ALD, a unique bilayer channel configuration exploiting In-Sn-O (ITO) prompt and In-Sn-Zn-O (ITZO) prime layers, where cationic compositions of each layer were carefully controlled and determined for realizing high-performance oxide TFTs showing both benefits of higher mobility and better stability.

Fig. 1 shows a schematic cross-section of the ITO/ITZO TFTs with overall process conditions of active channel compositions for single-layer and bilayer channel configurations. Bi-layered prime ITZO (7 nm) and prompt ITO (3 nm) thin films were successively deposited in ALD chamber at 150 ^{o}C. Cationic compositions of ITZO layers were adjusted by controlling the sub-cyclic ratios (TEIn:TDMASn:DEZn) to 2:1:2 and 2:1:4. Alternatively, the sub-cycles (TEIn:TDMASn) was fixed as 6:1 for the preparation of ITO layer.

Figs. 2a and 2b show the transfer characteristics of the fabricated ITZO and ITO/ITZO TFTs, respectively. Dev-C and Dev-D with bilayer channel configurations exhibited sound TFT operations, even though the turn-on positions were shifted in negative direction. While the field effect mobility (μ_{FE}) of the Dev-B was estimated to be only 23.0 cm^2/Vs, the μ_{FE} of the Dev-D was significantly improved above 30.8 cm^2/Vs. Figs. 3a-3d shows the variations in transfer curves with stress time evolution for the Dev-B and Dev-D, respectively. Noticeably, the Dev-D exhibited the shifts in threshold voltages of +0.05 and -0.07 V under positive- and negative-bias stress conditions, respectively, declaring stronger immunity against gate bias stress than the Dev-B. In other words, the implementation of hetero-junctions with 2DEG was verified to provide easier path of conduction electrons with simultaneously suppressing the charge-trapping events at front-channel interfaces. As results, the introduction of ALD-derived ITO prompt layer was found to enhance the device performance of conventional devices using ITZO single-layer channel.Consequently, the enhancement in device performance obtained from the ITO/ITZO bilayer channel TFTs clearly claim that the engineered bilayer channel configurations designed by the ALD process can extend the application fields of oxide TFTs.

2:30pm **AA1-WeA-5 Elaboration of Refractory Metamaterials by Atomic Layer Deposition for Tuning Thermal Emission at High Temperature***, **Syreina Sayegh**,* European Institute of Membranes, France*; A. NZIE,* CEMHTI, France*; M. Bechelany,* European Institute of Membranes, France*; O. ROZENBAUM,* CEMTHI, France*; Q. FLAMANT,* Saint Gobain, France

At high temperature, thermal radiation accounts for a large part of the heat transfer. Therefore, the ability to tune thermal emission is paramount to improve energy efficiency when heating and cooling. It is also one of the keys for converting efficiently heat into electricity in a thermophotovoltaic system.

Electromagnetic properties of natural materials are mainly determined by their chemical composition. The metamaterial approach provides additional degrees of freedom for tailoring these properties by playing on the internal structure. This accrued flexibility is of particular interest for the design of thermal emitters: it allows full spectral control and impedance matching with free space, thereby maximizing the emission for a chosen wavelength range.

Unfortunately, most existing metamaterials rely on metals with a low melting point such as gold or silver. So far, the attempts to realize refractory metamaterial emitters relied either on refractory metals (e.g. Ta, Mo, W) or on nitrides (e.g. TiN, AlN, ZrN). These materials do have high melting points but are prone to oxidation which limits their operating temperature in air.

In this presentation, we will show how using innovative fabrication approaches such as Atomic Layer Deposition (ALD) and making the proper choice for associating a conducting and a dielectric material allows elaborating refractory metamaterials with tunable emissivity in the near infrared (NIR) that can operate in air at temperatures exceeding 1000°C.

2:45pm **AA1-WeA-6 Optical Properties of Interconnected Plasmonic Nanostructures with sub-10 Nm Nanogaps by Area-Selective Atomic Layer Deposition***, **Brian Willis**, R. Raman, J. Grasso,* University of Connecticut

Nanostructures made of materials such as Cu, Ag, and Au have plasmonic resonances in the visible and near infrared spectral regions. These resonances enhance light - matter interactions by concentrating electric fields around nanostructures. Enhanced electric fields are useful for applications in spectroscopy, catalysis, and photodetection. Electric fields are especially strong in nanogaps between closely spaced particles, and there has been significant work to devise nanofabrication techniques to control interparticle distances with nanometer precision. The majority of work in plasmonics has investigated particles in solution or nanostructures deposited onto surfaces without electrical connections, but adding electrical contacts adds new functionality. In particular, adding electrical interconnects to plasmonic nanostructures provides opportunity for nanoscale light emitters and detectors, as well as energy harvesting. In this work, we investigate the design and fabrication of arrays of interconnected plasmonic nanostructures with sub-10 nm nanogaps. FDTD simulations model optical extinction properties of nanostructures fabricated on glass substrates, and ALD experiments create nanostructures with tunable nanogap spacing. We use glass substrates with nanostructure templates made by conventional nanofabrication methods, and subsequently coat those nanostructures with conformal layers of Cu by ALD to control interparticle distances. Cu ALD occurs selectively on Pd, and nanostructure templates are coated with Pd to promote growth. Selective area growth ensures that neighboring nanostructures remain electrically isolated. This configuration allows for electrical measurements during irradiation with light, see attached figure. Compared with Cu and Au, Pd is a poor plasmonic material, but Pd is necessary for promoting Cu growth. In this talk, we investigate several different approaches using both homodimers and heterodimers with different Au/Pd combinations. Optical extinction measurements reveal how plasmonic resonances evolve when Cu layers are added and nanogaps shrink. FDTD simulations provide insight to how complex changes of nanostructure size, thickness, and shape affect plasmonic properties. We also investigate how interconnect designs perturb plasmonic resonances compared to isolated nanorods. Our findings show that ALD can achieve sub-10 nm nanogaps for interconnected designs with plasmonic properties similar to isolated nanostructures, and that the process can scale to large arrays of devices. Results show that it should be possible to create electro-optic devices where intense electric fields from plasmonic resonances enable new functionality.

3:00pm **AA1-WeA-7 Electrochemically Active Antibacterial Electrodes for Neural Interfacing Applications***, **Shahram Amini**,* Pulse Technologies Inc.*; G. Feng, H. Khosla,* Villanova University

Miniaturization and electrochemical performance enhancement of electrodes and microelectrode arrays in emerging long-term implantable neural interfacing devices improves specificity, functionality, and performance of these devices. However, surgical site and post-implantation infections are amongst the most devastating complications after surgical procedures and implantations. Additionally, with the increased use of antimicrobial drugs, the threat of antimicrobial resistance is significant and is increasingly being recognized as a global problem. Therefore, the need for alternative strategies to eliminate post-implantation infections and reduce antibiotic consumption has led to development of medical devices with antibacterial properties. In this work, we report for the first time on the development of antibacterial platinum-iridium electrodes with ultra-high electrochemical performance using a two-step manufacturing process. Electrodes are first restructured using femtosecond-laser hierarchical surface restructuring technology yielding unprecedented performance values that significantly exceed those reported in the literature, e.g. charge storage capacity and specific capacitance were shown to have improved by two orders of magnitude and over 700-fold, respectively, compared to un-restructured electrodes. In the second step of the process, atomiclayer deposition was utilized to deposit conformal copper oxide thin films on the hierarchical surface structure of the electrodes to impart antibacterial properties to the electrodes. Electrochemical, morphological, compositional, and structural properties of the electrodes were studied using a suite of characterization techniques. Last, but not least, the antibacterial properties of the electrodes were also studied, particularly, the killing effect of the antibacterial electrodes on Escherichia coli and Staphylococcus aureus - two common types of bacteria responsible for implantation infections.

3:15pm **AA1-WeA-8 Ultrathin TiO_2 ALD Coatings Strongly Enhance Biological Response of Biomedical Materials***, **Jan Macak**,* University of Pardubice, Czechia

TiO_2 surfaces are in general recognized as excellent biocompatible materials owing to their low cytotoxicity, high stability, antibacterial properties, and wetting ability. Among various TiO_2 nanostructured surfaces that show very good cell interactions (various cell types) and osseointegration, anodized TiO_2 nanotube (TNT) layers have emerged as extremely suitable substrates. A pioneering work demonstrated that TNTs with diameter of 15 nm are the most suitable for the growth of various cells [1]. But numerous papers also showed that anodization is a very viable tool for nanostructuring of various biomedical alloys, including frequently used TiAlV.

Recently, we demonstrated that an ultrathin coating on TNT by suitable oxides (e.g. TiO_2) using Atomic Layer Deposition (ALD) can enhance cell growth and adhesion [2]. These properties make them excellent as final surfaces for medical and dental implants based on Ti alloys.

The presentation deals with the comparison of the influence of ultrathin ALD TiO_2 coatigs (achieved by few cycles of TiO_2 ALD process) on TNT layers, reference Ti foils and Ti biomedical alloys for the proliferation of fibroblast, osteoblast and neuroblasts cells. For that Ti sheets and anodized TNT layers with a distinct inner diameter of 12 nm, 15 nm, and 100 nm were used as substrates, as they appear to be the most suitable for cell growth in general [2,3,4]. We investigated the shaping, adhesion, proliferation, and cell density on these substrates.

Moreover, the single-cell adhesion of the cells to the TNTs was studied by the bio-atomic force microscopy (bio-AMF) technique [3]. Last, but not least, black form of TiO^2 nanotubes was investigated for cell proliferation in comparison to classical TNTs [4],

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2. Motola, M. & Rousar, T.; &Macak, J.M. Thin TiO_2 Coatings by ALD Enhance the Cell Growth on TiO_2 Nanotubular and Flat Substrates. ACS Appl. Bio Mater. 2020, 3, 6447–6456.

3. Baishya, K. & Macak, J.M. Bio-AFM exploits enhanced Response of Human Gingival Fibroblast (hGFs) on TiO_2 Nanotubular Substrates with Thin TiO_2 Coatings. 2022, Applied Surface Science, submitted.

4. Sopha, H. & Rousar, T. & Macak, J.M., et al. Comparison of cellular effects between white and black anodic TiO_2 nanotubes, Surface and Coating Technology, 2023, submitted.

ALD Applications
Room Grand Ballroom H-K - Session AA2-WeA

Energy Solar

Moderators: Mike McSwiney, Applied Materials, Shaibal Sarkar, ITT Bombay

4:00pm **AA2-WeA-11 Atomic Layer Deposition of Highly Stable and Efficient Perovskite Solar Cells (~ 24%)***, H. Park, S. Shin, P. Nandi, D. Pal,* ***Hyunjung Shin,*** Sungkyunkwan University (SKKU), Republic of Korea **INVITED**

Power conversion efficiency (PCE) of Perovskite solar cells (PSCs) is over 25.7%. Their operational/environmental instability remains to be solved and restrict commercialization.[1] The state-of-the-art PSC is used pure a-$FAPbI_3$ and Spiro-OMeTAD in *n-i-p* structure of PSCs. A chemical-driven transition from photoactive α-$FAPbI_3$ to non-photoactive δ-$FAPbI_3$ is pointed as a significant challenge. Much lower stability of Spiro-OMeTAD is critical for the device instability. As an interlayer in between top metallic electrodes and Spiro-OMeTAD/a-$FAPbI_3$, inorganic HTLs prepared by a low-temperature ALD provide bi-functionality to stabilize the PSCs during operation. Transition metal oxide (TMO) can be a strong candidate. Most of TMO layers generally require a high processing temperature and the lack of *p*-type characteristics inhibits application to PSCs as hole-transporting interlayers. We adopt ALD to fabricate TMO layers at low temperatures (~ 50 °C) and intentionally induce oxygen deficient traps to form empty *d*-bands and further enhance hole transporting properties. We fabricated n-i-p normal structure PSCs of a-$FAPbI_3$ and Spiro-OMeTAD with ALD grown TMOs on top of Spiro-OMeTAD to enhance device stability. We also adopt ALD to form ultra-thin NiO and SnO_2 as charge transport layers (ETLs).[2,3] As a result, highly efficient PSCs of PCE of over 24% with TMOs are fabricated with pin-hole free hole transporting and protection bi-functional ALD layers. [2,3] The environmental stability of PSCs is over 90% initial PCE after 600 hrs, while without the interlayer started to be degraded under 80% of initial PCE just after around 200 hrs without any special encapsulation. Furthermore, this study shows the possibility that ALD TMOs can be also applicable to tandem device fabrication with p-i-n type PSCs and stable PSCs' commercialization.

[1] High Efficiency Perovskite Solar Cells, *Chem. Rev.* (2020) [2] Perovskite Solar Cells with Inorganic Electron and Hole Transporting Layers Exhibiting Long – Term (≈ 500 h) Stability at 85 °C under Continuous 1 Sun Illumination in Ambient Air, *Adv. Mater.* (2018) [3] Atomic Layer Deposition for Efficient and Stable Perovskite Solar Cells, *Chem. Comm.* (2019) [4] Cyclohexylammonium-Based 2D/3D Perovskite Heterojunction with Funnel-Like Energy Band Alignment for Efficient Solar Cells (23.91 %), *Adv. Energy Mater.*(2021) [5]Amorphous TiO_2 Coatings Stabilize Perovskite Solar Cells, *ACS Energy Lett*(2021)[6] Hole Transporting Vanadium-Containing Oxide (V_2O_{5-x}) Interlayers Enhance Stability of a-$FAPbI_3$-Based Perovskite Solar Cells (~ 23%), *ACS Appl. Mater. & Interfaces,* (2022)

4:30pm **AA2-WeA-13 ALD of Niobium Oxide (Nb_2O_5) and Niobium-doped Titanium Oxide (Nb:TiO_2) for Solar Cell Applications***, T. VINCENT,* IPVF, France*; D. COUTANCIER,* CNRS, France*; P. Dally, M. AL-KATRIB, F. DONSANTI,* IPVF, France*; A. YAICHE,* EDF, France*; K. MEDJOUBI, M. PROVOST,* IPVF, France*; J. ROUSSET,* EDF, France*; M. BOUTTEMY,* ILV, France*;* ***Nathanaelle SCHNEIDER,*** CNRS, France

Atomic Layer Deposition (ALD) is increasingly contributing to the energy field and more specifically to the engineering of solar cells. Its conformity enables deposition on nanostructured substrates and its low growth temperature allows the deposition on temperature-sensitive substrates such as perovskite. Niobium oxide, Nb_2O_5, is a wide bandgap semiconductor that has been grown by different methods and has recently been used in solar cells. Its optical and electrical properties depend strongly of the technique used for its growth, opening access to a wide range of application, such as electron transport layer (ETL)or passivation layer [1,2]. It is also used for the doping of titanium oxide (TiO_2), a well-known ETL, to reach a better stability of the complete solar cell.

In this study, the growth of niobium-doped titanium oxide (TiO_2:Nb) thin films by atomic layer deposition (ALD) is reported. Films were obtained at 200°C from titanium (IV) i-propoxide (TTIP), (t-butylimido)tris(diethylamido)niobium(V) (TBTDEN), and water by introducing Nb_2O_5 growth cycle in a TiO_2 matrix. Process parameters such as the order of precursor introduction and the cycle ratio were optimized. The growth mechanisms and the effective Nb incorporation were investigated by in situ quartz crystal microbalance (QCM) and X-ray photoelectron spectroscopy (XPS). The as-deposited films were analyzed for their surface morphology, elemental stoichiometry, optoelectronic properties, and crystallinity using a variety of characterization techniques. Such as-deposited films are amorphous and a fine control of the Nb amount with the supercycle parameters along with a continuous evolution of their optical properties from the ones of TiO_2 to Nb_2O_5 bare oxides are observed. To allow a successful implementation in solar devices, a comprehensive annealing study under several temperatures and atmospheres was conducted and revealed an evolution of the optical bandgap after crystallization in the anatase phase. Ultimately, the incorporation of these 15 nm-thick films in mesoscopic perovskite solar cells (PSCs) as ETL shows an improvement of the cell performances and of their stability with increasing Nb amount, reaching power conversion efficiency (PCE) up to 19.8%.

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

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

4:45pm **AA2-WeA-14 Closing Remarks***,*

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