ALD Fundamentals: Growth and Characterization
Room Tampa Bay Salons 5-9 - Session AF-MoP

ALD Fundamentals: Growth and Characterization Poster Session

AF-MoP-1 Novel In/Ga Precursors for Atomic Layer Deposition of IGZO Thin Film Transistors*, **Eunsu Kang**, Hyunkyung Lee, Ki-yeung Mun, Kyu Hyun Yeom, Hyunkee Kim, Dae Won Ryu,* Hansol Chemical, Republic of Korea*; Jin-Seong Park,* Hanyang University, Korea

Recently, amorphous oxide thin film transistors(TFTs) have been widely studied for applications such as wearable electronics, large scale displays, optical sensors and etc., owing to their promising properties: high mobility, uniformity, and good transmittance.[1]

In this work, we developed non-pyrophoric indium precursor (DMITN) and gallium precursor (DMGTN), which are thermally stable and implemented wide atomic layer deposition (ALD) windows. The physical characteristics were investigated by differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA). The non-volatile residues of indium and gallium precursors were about 3.5% and 1%, respectively.

The oxide films (In_2O_3 and Ga_2O_3) were deposited by ALD using O_2 plasma and ozone as oxygen sources. The deposited oxide films were studied via ellipsometer, XPS, XRD, and TEM. In O_2 plasma system, self-limiting growth properties of DMITN and DMGTN were observed 0.9 Å/cycle at 100–250 °C respectively. In particular, the ALD of In_2O_3 film using ozone as an oxygen source was also showed wide ALD window of 250–320 °C and growth rate of 1.0 Å/cycle (Figure 1). In addition, no carbon and nitrogen impurities were detected at all growth temperatures for all films.

The Indium-Gallium-Zinc-Oxide Thin Film Transistors (IGZO TFTs) were fabricated using DMITN, DMGTN, and commercially available for zinc precursor as the n-channel active layer by ALD. The electro-properties of oxide TFTs, compared to oxide TFTs using representative In and Ga precursor, were observed equal or above figures in terms of mobility, threshold voltage, and subthreshold gate voltage swing (Figure 2). The new indium and gallium precursors have demonstrated potential as n-channel active layer materials in oxide semiconductor transistors.

AF-MoP-2 Optimization of Ferroelectric Ga-Doped HfO_2 Thin Films via Peald for Enhanced Phase Stability and Memory Performance*, **Jiseop Byeon**, Suhyeon Park, Minjae Kwon,* Kyungpook National University, Republic of Korea*; Roy Byung Kyu Chung,* Kyungpook National University

The rapid expansion of Artificial Intelligence (AI) workloads has intensified the demand for high-performance, low-power nonvolatile memory devices. HfO2-based ferroelectrics, particularly Hafnium Zirconium Oxide (HZO), have attracted significant attention due to their excellent CMOS compatibility.[1] However, challenges such as the wake-up effect, limited endurance, and leakage current necessitate further materials and process optimization.To enhance ferroelectric performance, suppressing the non-polar monoclinic phase while promoting the polar orthorhombic (o)-phase is critical. Recent AI-driven and DFT-based screening studies identify Ga as a promising dopant for stabilizing the o-phase.[2] The incorporation of Ga effectively modulates lattice parameters, facilitating phase stabilization through controlled lattice strain. In this study, we deposit o-phase Ga-doped HfO2 (HGO) thin films using plasma-enhanced atomic layer deposition (PEALD) and investigate their phase stability and ferroelectric properties for device applications. Specifically, we report on the impact of Ga/Hf sub-cycle ratio during the PEALD process on the remnant polarization and coercive field.Furthermore, integrating optimized HGO thin films into practical architectures, such as Ferroelectric Field-Effect Transistors (FeFETs) and FeNAND, is expected to enable wide memory windows and improved endurance. Therefore, we conclude by evaluating the performance of HGO/IGZO devices and their compatibility with back-end-of-line processing.Reference[1] Cheema, S.S., Kwon, D., Shanker, N. et al. Enhanced ferroelectricity in ultrathin films grown directly on silicon. Nature 580, 478–482 (2020). [2] Yan, S., Xu, P., Li, G. et al. Artificial intelligence-driven phase stability evaluation and new dopants identification of hafnium oxide-based ferroelectric materials. npj Comput Mater 11, 2 (2025)

AF-MoP-3 $AlPO_4$ and AlPxOy by Dual-Source and Supercycle PEALD Approaches*, **Florian Preischel**,* Leibniz Institute for Solid State and Materials Research, Germany*; Karl Rönnby, Michael Nolan,* Tyndall National Institute, University College Cork, Ireland*; Harish Parala, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany

Aluminum phosphate ($AlPO_4$) is a dielectric material with high chemical and temperature resistance[1,2] making it suitable for use as a protective coating in lithium-ion batteries[3,4] and for high-temperature applications.[5-7] It features a microporous structure of PO_4 and AlO_4[1] and has been proposed to exist as a stable two-dimensional (2D) bilayer form with inherent, molecular-sized pores and no covalent bonds to its substrate.[8] With such a structure and high stability, bilayer $AlPO_4$ could serve as a selective gas-separation membrane. Atomic layer deposition (ALD) is a powerful technique for depositing thin films with high quality, conformality, and precise thickness control, which are essential for achieving the bilayer structure. Utilizing plasma as the co-reactant in plasma-enhanced ALD (PEALD), enables deposition at lower temperatures and provides an additional parameter to modify and control the material composition. For the deposition of ternary materials by ALD, different strategies are viable.[9] In a previous study, Blomme et al. employed PEALD supercycles of $P(NMe_2)_3$ and TMA, both with O_2 plasma as the co-reactant, demonstrating the applicability of this approach for the deposition of AlP_xO_y with tunable composition.10 In this study, we compare two approaches: using a dual-source precursor that introduces both Al and P, versus combining two individual ALD cycles into a supercycle.

We have identified trimethylaluminum triisopropylphosphine (TMAPIP) as a promising dual source precursor with favorable thermal properties (**Figure 1a**). However, a PEALD process using TMAPIP and O_2 plasma resulted in AlP_xO_y layers with only a few percent P incorporation (**Figure 1b**), indicating a chemisorption pathway involving the loss of the phosphorous adduct.

In a second approach, in conjunction with density functional theory (DFT) calculations, we developed a supercycle process that combines individual PEALD cycles of trimethylaluminum (TMA) and $P(NMe_2)_3$ from 60 °C to 240 °C (**Figure 2a**). This route enables controlled tuning of the AlP_xO_y composition by varying the deposition temperature and supercycle sequence, as shown by Rutherford backscattering spectrometry (RBS) (**Figure 2b**) and XPS. By combining two $P(NMe_2)_3$ sub-cycles with one TMA sub-cycle, the deposition of stoichiometric $AlPO_4$ is achieved (**Figure 2c**). Using the optimized PEALD process in initial downscaling experiments, we deposited $AlPO_4$ with an approximate thickness of 3 nm in a continuous, homogeneous thin film, as revealed by transmission electron microscopy (TEM) (**Figure 2d**). This finding provides a strong foundation for further exploring the bilayer structure of $AlPO_4$.11

AF-MoP-4 Correlative AFM-SEM for ALD Characterisation*, **Satyam Ladva**,* Quantum Design inc.

Background. Atomic Layer Deposition (ALD) provides sub-nanometer thickness control and excellent step coverage in 3D device architectures, but ultra-thin films and spatial variability often make single-technique metrology inconclusive.

Approach. We demonstrate a correlative workflow that couples Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) using Quantum Design's FusionScope AFM-with-SEM platform and the AFSEM®nano AFM insert for Cryo-SEM/FIB systems. SEM is used to rapidly localize thin-film defects (pinholes, particles, seam voids, trench-edge non-uniformity), followed immediately by AFM on the identical region for quantitative height and roughness, plus functional contrast when needed.

Key capabilities. FusionScope enables AFM-SEM-EDS correlation through a shared coordinate system and real-time overlay, minimizing the common "find it again" failure mode in thin-film analysis. Relevant operating ranges include a closed-loop 22 × 22 µm AFM scan with 11 µm Z range and <50 pm imaging noise, alongside a thermal field-emission SEM operated from 3.5–15 kV with pA–nA probe currents under high vacuum. Beyond standard contact/dynamic AFM, advanced modes (e.g., stiffness/adhesion mapping) and interchangeable probes support conductive and magnetic measurements.

In-chamber extension. AFSEM®nano brings closed-loop AFM into existing Cryo-SEM/FIB tools for in situ AFM inside the SEM chamber, with compatibility for nanomanipulators and device biasing. This is particularly valuable on FIB-prepared cross-sections, where sidewall thickness, interfacial roughness, and localized conduction pathways can be mapped at the same coordinates where SEM provides microstructural context.

Outcome. The combined approach shortens the loop between ALD process changes and actionable metrics (step height/thickness, RMS roughness, defect density, stiffness/adhesion contrast, localized conductivity) across planar films and complex 3D semiconductor structures.

Keywords: ALD, correlative microscopy, AFM, SEM, EDS, thin films, failure analysis, 3D semiconductors

AF-MoP-5 A Versatile Low-Temperature Pathway for Epitaxial Integration of Functional Nitrides via Hydrogen-Manipulated Atomic Layer Epitaxy*, **Kuan-Cheng Huang**, Fong-Jyun Jhong, Yu-Sen Jiang, Miin-Jang Chen,* Department of Materials Science and Engineering, National Taiwan University, Taiwan

High-quality epitaxial growth of nitride thin films remains a critical challenge in conventional low-temperature atomic layer deposition (ALD) due to limited surface kinetics and steric hindrance from precursor ligands. To address this challenge, we introduce a novel strategy referred to as Hydrogen-Manipulated Atomic Layer Epitaxy (HM-ALE), which enables low-temperature epitaxial growth of diverse functional nitride materials at a low temperature of 300 °C by reconfiguring the ALD cycle to precisely control surface reactions at the monolayer scale. For GaN and AlN growth, an H_2 plasma step is introduced prior to N_2 plasma exposure, which mitigates steric hindrance from organic ligands (e.g., methyl groups from TMA or TMG) and enhances adatom mobility and surface reconstruction. This synergistic effect facilitates long-range atomic ordering prior to the reaction with nitrogen species. The ω-2θ XRD patterns demonstrate a pronounced enhancement of the (0002) diffraction signal, while high-resolution TEM images further confirm high-quality epitaxial AlN and GaN films with well-resolved lattice fringes on sapphire substrates. For TiN growth, the HM-ALE method yields low resistivity and high crystalline quality with a well-defined epitaxial relationship and a sharp interface with sapphire substrates as confirmed by high-resolution TEM. Overall, HM-ALE provides a robust low-temperature pathway for epitaxial integration of functional nitrides, ranging from wide-bandgap nitride semiconductors to metallic nitride conductors, and offers new opportunities for nitride-based heterostructures under stringent thermal budget constraints.

AF-MoP-6 Study of the Chemical Stability of Precursors Used for ALD of Lithium-Containing Films by Structural and Thermal Analyses*, **Nicolas Massoni**, Manon Letiche, Sylvain Poulet,* CEA/LETI-University Grenoble Alpes, France*; Pierre-Alain Bayle,* CEA-University Grenoble Alps, France*; Névine Rochat,* CEA/LETI-University Grenoble Alpes, France*; Rodica Chiriac, François Toche,* Université Claude Bernard Lyon 1, LMI, UMR CNRS 5615, France*; Messaoud Bedjaoui,* CEA/LETI-University Grenoble Alpes, France

Lithium-based batteries are well-known and robust energy storage solutions for portable devices. The widespread electrolyte material employed for microbatteries is a LiPON thin film [1]. It can be deposited by ALD with organic precursors permanently heated into tanks, during several weeks. In this study, the impact of ageing of lithium hexamethyldisilazide (LiHMDS) and diethylphosphoramidate (DEPA) precursors, *i.e.* the time elapsed in their storage tanks, on their chemical stability is reported. It was already shown that LIHMDS was stable and only DEPA chemically degrades after 14 days of ageing [2].

Three DEPA suppliers, designated by the letters A, B and C, were compared, and significant differences were found, before and after ageing. The as-supplied DEPA purity was identical (98%) for all. However, their ^{1}H NMR spectra revealed that B and C shared the same structure, which was different for A. After 30 days of ageing at 90°C in a heated tank, significant differences were observed. For supplier A, the powder has agglomerated and turned in brown, whereas it remained white and flowable for suppliers B and C. As shown by FTIR, the brown aged DEPA has lost most of its NH_2 bonds. And ^{31}P NMR DOSY experiment has confirmed the agglomeration. When LiPON is deposited with the A DEPA, its ionic conductivity progressively drops over ageing time, with an overall loss of one decade between the as-supplied and the most aged precursor. Since the amine group is known to be involved in the conduction mechanism of LiPON, this is a direct consequence of the amine loss. For suppliers B and C aged in the same conditions, they kept their initial color and texture. Moreover, FTIR revealed that the NH_2 group was no impacted at all by ageing. This different ageing behavior may lie in the composition of the as-supplied products (currently investigated by DSC), or in the starting structure as already evidenced by NMR.

Finally, it is expected that LiPON deposited with DEPA from suppliers B or C, will not show any deleterious impact on its ionic conductivity (in progress).

[1] Sallaz et al, 2024, https://doi.org/10.1021/acselectrochem.4c00022

[2] Massoni et al, 2025, ALD/ALE 2025, talk #AA2-WeA-12

AF-MoP-7 Deposition and Electrical Characterization of Hafnia ALD Thin Films Using Cp–Based Precursors*, **Hyun Woo Jeong**,* CN1 Co.,Ltd, Republic of Korea

HfO_2 thin films were deposited by thermal atomic layer deposition (ALD) using a thermally stable cyclopentadienyl-based hafnium precursor (CpHf) and comparatively evaluated as a function of oxidant chemistry (H_2O vs O_3) for charge-trap memory (CTM) applications. Deposition was carried out on a 300 mm single-wafer ALD system (Atomic Premium, CN1 Co., Ltd.) at 320 °C and 0.45 Torr. GPC and RI were extracted by systematically varying precursor/oxidant pulse and purge times to establish optimized process recipes. For the H_2O process, saturated growth was achieved with CpHf 1 s and H_2O 1 s, and film uniformity significantly enhanced when purge times were increased to 20 s, yielding an average GPC of 0.058 nm/cycle and RI of 2.00. For the O_3 process, growth stability improved with longer O_3 exposure; the optimized recipe (CpHf 1 s / purge 20 s / O_3 5 s / purge 20 s) exhibited a higher average GPC of 0.068 nm/cycle with RI of 1.99. CTM capacitors with a Si/SiO_2 (2 nm)/HfO_2 (10 nm)/Al2O3 (10 nm)/Au stack were fabricated and post-deposition annealed at 350, 400, and 450 °C. X-ray diffraction showed no crystallization of either Al_2O_3 or HfO_2 for all anneal temperatures.

Electrically, O_3-processed devices exhibited larger C-V memory windows than H_2O-processed devices under identical measurement conditions, with the largest difference after 350 °C annealing. Fowler–Nordheim analysis and constant-current stress indicated relatively minor degradation at 350 °C, the H_2O process yielded an overestimated apparent barrier suggesting defect-induced mixed conduction, whereas the O_3 process retained linear FN behavior consistent with dominant FN tunneling. Endurance cycling confirmed stable memory windows of ~6.0–6.2 V over 10^1–10^4 cycles for O_3-based devices, while H_2O-based devices degraded from 0.823 to 0.691 V. Overall, O_3 is a more favorable oxidant for CpHf-based HfO_2 ALD, improving both process efficiency (GPC) and CTM memory characteristics (window and endurance).

AF-MoP-8 Low-Temperature High-Quality Epitaxial Aluminum Nitride Films Deposited by Plasma-Enhanced Atomic Layer Deposition*, Pini Medved,* Ariel University, Ariel 40700, Israel*; Silvia Piperno,* Bar-Ilan University, Ramat Gan 5290002, Israel*; **Valentina Korchnoy**,* Technion Israel Institute of Technology, Israel*; Gili Cohen-Taguri,* Bar-Ilan University, Ramat Gan 5290002, Israel*; Asaf Albo,* Ariel University, Ariel 40700, Israel

Aluminum nitride (AlN) is an ultra-wide-bandgap semiconductor (6.2 eV) with applications in optoelectronics and high-power electronics due to its high thermal conductivity, low thermal expansion coefficient and high dielectric strength. Conventional deposition techniques for high-quality AlN, such as metal-organic chemical vapor deposition and molecular beam epitaxy, typically require temperatures exceeding 700 °C, limiting integration with temperature-sensitive materials and pre-existing layers.

In this work, we demonstrate the deposition of single-crystal AlN films on gallium nitride (GaN) templates at a substrate temperature of 300 °C using plasma-enhanced atomic layer deposition (PEALD), without additional energetic plasma exposures or *ex situ* annealing. The deposition was carried out in an Ultratech Fiji G2 PEALD system on *c*-plane GaN-on-sapphire substrates. Prior to growth, the substrates were exposed to a remote N_2–Ar plasma to condition the surface. Each PEALD cycle consisted of a trimethylaluminum (TMA) precursor pulse followed by a remote N_2–Ar plasma co-reactant step under low-pressure conditions optimized for epitaxial growth.

High crystalline quality is evidenced by narrow X-ray diffraction rocking curves of 288 arc sec (0.08°) for 10 nm films and 497 arc sec (0.138°) for 70 nm films. Continuous epitaxial growth across the full film thickness is confirmed by high-resolution transmission electron microscopy and selected-area electron diffraction. Atomic force microscopy reveals smooth surface morphologies with sub-nm roughness.

This research demonstrates a PEALD-based approach for achieving high-quality, single-crystal AlN films at 300 °C, enabling III-nitride integration into low-thermal-budget platforms without additional *in situ* energetic plasma exposure or *ex situ* annealing steps that may degrade film quality.

This presentation discusses the results published in Ref. [1].

[1] Pini Medved, Silvia Piperno, Valentina Korchnoy, Gili Cohen-Taguri and Asaf Albo, "Low-temperature high-quality epitaxial AlN films deposited by PEALD," *Appl. Phys. Lett.*, vol. 127, no. 23, 232104, Dec. 2025, doi: 10.1063/5.0291492.

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The work is the subject of a pending U.S. patent application (No. 63/844,832).

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AF-MoP-9 ALD of Zinc Phosphate films with Tuneable Structure and Stoichiometry*, **Aditya Chalishazar**, Arpan Dhara,* Ghent University, Belgium*; Sylwia Klejna,* AGH University of Krakow, Poland*; Matthias Minjauw,* Ghent University, Belgium*; Eduardo Solano,* ALBA Synchrotron, Spain*; Frans Munnik,* Institute of Ion Beam Physics and Materials Research, HZDR, Germany*; Christophe Detavernier, Jolien Dendooven,* Ghent University, Belgium

Metal (M) phosphates are compatible with diverse applications that span battery technology, corrosion protection, electrocatalysis, and proton conduction. Phosphate polymorphs have multiple structures and stoichiometries, with the P/M ratio profoundly impacting their functional properties and applicability [1]. Atomic layer deposition (ALD) of metal phosphate films commonly combines metal oxide (MO) and phosphorus oxide (PO) cycles in supercycles. Trimethylphosphate (TMP) is the most-used P source for ALD, combined with H_2O, O_3 or O_2 plasma as oxidants [1-3].

In this work, we first investigated the ALD growth of PO using alternating TMP and O_2 plasma exposures. *In-situ* spectroscopic ellipsometry (iSE) and *in-situ* reflection Fourier transformed infrared (FTIR) spectroscopy revealed self-inhibited growth – an initially high growth on oxide surfaces, followed by rapid saturation with continuing film growth (Figure 1(a)).

Next, we developed a new plasma-enhanced ALD supercycle to grow zinc phosphate (ZnPO) films by combining one ALD cycle each of ZnO (DEZ/O_2 plasma) and PO (TMP/O_2 plasma) at 150 °C. The process demonstrated self-limiting film growth and resulted in the deposition of P-doped ZnO films, with improved (compared to [4]) but limited P incorporation of ca. 11 at.% (Figure 1(b)).

Increasing the number of PO cycles (n) from 1 to 5 in the [1·(ZnO) – n·(PO)] supercycle improved the P incorporation in the films, whose composition varied from P-doped ZnO to zinc metaphosphate ($ZnPO_3$) (Figure 2(a)). Our data also suggested that the PO interlayers impact the long-range order of ZnO layers within the as-deposited films, impacting their crystallinity (Figure 3(g)). However, we observed concurrent reduction in both the growth per supercycle (GPSC) as well as elemental Zn and P incorporation for the films for $n \geq 3$ (Figure 2(b,c)).

Experimental and computational data elucidated the dependence of film growth on the composition of the growth surface. ZnO growth is suppressed on a PO surface, resulting in self-inhibited film growth for the supercycle. This self-inhibited growth, in combination with nucleation effects for ZnO ALD on PO surfaces, results in the deposition of increasingly rough films, as n increases (Figure 3(a–f)). Overall, this work highlights the need to consider the interactions between the precursors and growth surfaces during the development of similar ALD supercycles for other metal phosphate families.

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AF-MoP-10 Non–Magnetizing Microwave PEALD Enabled via Magnetic Shielding for Highly Uniform Double-Sided Al_2O_3 Film Deposition*, Michel Marti, **Alejandra Vanessa**, Ramis Hertwig, Dominik Hartmann,* Evatec AG, Switzerland

Plasma enhanced atomic layer deposition (PEALD) is a key technique for the low temperature fabrication of conformal, high quality thin films used in semiconductor, photonic, and MEMS technologies. In microwave driven PEALD systems, magnetic fields are commonly employed to stabilize the plasma and tailor electron density. However, these fields may unintentionally magnetize magnetic or magnetically sensitive substrates, limiting the applicability of the process for advanced device architectures [1,2]. Recent reviews of ALD process engineering have emphasized the importance of reactor design, plasma configuration, and substrate specific constraints, including magnetic sensitivity, when targeting precision thin film properties in industrial ALD platforms [3].

In this work, a non-magnetizing microwave PEALD approach for Al_2O_3 thin films is demonstrated in a batch processing tool enabling simultaneous double-side wafer deposition with excellent conformality and coverage on both sides. A dedicated magnetic shielding concept was developed specifically for this batch architecture, where magnetic neutrality and highly uniform film properties across both wafer surfaces are critical. Three-dimensional magnetic field simulations were used to guide the design of a magnetic absorber, systematically evaluating the influence of shield size, aperture geometry, and distance to the substrate on the magnetic flux density at the sample position. The finalized shielding concept was implemented directly into the PEALD reactor without compromising plasma ignition or stability.

Magnetic field measurements confirmed that the shielding reduced the magnetic field at the substrate position below the magnetization threshold of sensitive materials, preventing permanent substrate magnetization during plasma exposure. Subsequently deposited films exhibited excellent thickness uniformity on each side of each substrate, stable refractive index, and strong wafer to wafer reproducibility.These results establish a viable route for non-magnetic PEALD processing in microwave plasma environments and provide a framework for integrating magnetic field mitigation strategies into industrial ALD systems for sensitive applications.

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AF-MoP-11 Amine Adducts of Cyclopentadienyl Magnesium as Precursors for Magnesium Containing Films Deposition*, **Anuththara Arachchige**, Hima Kumar Lingam, David Roberts,* Ereztech Labs LLC

Magnesium–containing thin films—including magnesium oxides, magnesium fluoride, magnesium nitrides, and magnesium–doped GaN/ZnO—are useful for energy storage, electrical insulation, and optical coatings. Cyclopentadienyl–magnesium precursors ($Mg(RCp)_2$) are widely used in deposition studies because they are highly volatile, thermally stable, and strongly reactive toward co–reagents. However, most of these manganocene compounds are pyrophoric, making them difficult to store and handle. The present study describes the synthesis of magnesium cyclopentadienyl amine adducts, which mitigate the pyrophoricity of the parent compounds while maintaining desirable precursor characteristics.

Here, we describe the synthesis of amine adduct of magnesium cyclopentadienyl complexes, Mg(MeCp)2TMEDA (1), Mg(MeCp)2TEEDA (2), Mg(MeCp)2TMPDA (3), Mg(MeCp)2TMBDA (4), Mg(EtCp)2TMEDA (5), Mg(MeCp)2TEEDA (6) (Fig. 1). Pure complexes 1-6 were obtained by sublimation at low vacuum. Purity and structures were confirmed by 1H NMR, 13C NMR, and X-ray crystallography. Thermal behavior and volatility of complexes was investigated by TG and DSC. Compound 1-6 showed clear evaporation with <0.5% residue after 200° C (Fig 2). Preliminary air-exposure testing indicated that none of the compounds exhibit spontaneous ignition when exposed to air. Overall, complexes 1–6 exhibit promising properties as precursors for magnesium–containing metal depositions, and their reduced pyrophoricity relative to the parent compounds offers clear advantages for safer storage, transfer, and handling.

Lingam, H. K.; Arachchige, A. A.; Roberts, D. A. Amine adduct of group 2 metallocene precursors for deposition of group 2 metal films for Ereztech Labs. US. Pat. Appl. US 2025/0353865 A1, 2025.

AF-MoP-12 Kinetics of the Atomic Layer Deposition Trimethyl Aluminum – Ozone Reaction Studied Through Variations of Surface Area and Temperature with *in-Situ* Quadrupole Mass Spectrometry*, **Eric Bissell**, Jacob Furst,* University of Central Florida*; Nicholas G. Rudawski,* University of Florida, Gainesville*; Fernando Uribe-Romo, Titel Jurca, Kathleen Richardson, Parag Banerjee,* University of Central Florida

Ozone (O_3) is investigated as a co-reactant with trimethylaluminum (TMA) for atomic layer deposition (ALD) of Al_2O_3 on ZnOnanopowders, producing core-shell powders subsequently densified into ceramics. O_3 is explored as an alternative to H_2O due to the propensity of moisture to form capillary bridges in nanoparticle beds, leading to strong interparticle cohesion, reactant retention, and non-ideal ALD behavior including parasitic chemical vapor deposition-like growth and powder agglomeration.1Minimizing agglomeration is critical because the Al_2O_3 coating is intended to act as a diffusion barrier that suppresses ZnOgrain growth during sintering for nanocrystalline ceramic fabrication.

Nanoparticle beds exhibit high specific surface areas (18 $m^2\ g^{-1}$ in this study), resulting in ALD processes that are transport-limited within the powder bed. Consequently, extended exposure and purge times are often required for half-reactions to approach saturation, presenting challenges for scalable powder coating.

In this work, the effects of reactor temperature and powder mass loading on O_3-based ALD kinetics are examined using a rotary powder ALD reactor. ZnO nanoparticle loadings of 0 g (empty reactor), 1 g (18 m2), 3 g (54 m2), and 6 g (18 m2) are studied at temperatures of 120 °C, 175 °C, and 250 °C. Reaction progress is monitored in situ using a quadrupole mass spectrometer (QMS) residual gas analyzer (RGA) to track gas-phase reactant consumption and reaction by-products during each half-cycle. Powder surface area before and after coating is measured using the Brunauer–Emmett–Teller (BET) method.

Across all temperatures and powder loadings examined, QMS-RGA signatures associated with the TMA half-reaction exhibit progressively shorter saturation times with increasing ALD cycle number. BET measurements indicate no appreciable change in total surface area following coating. Taken together, these observations suggest a progressive reduction in the density or accessibility of reactive surface sites during cycling, consistent with incomplete surface regeneration during the O_3 half-reaction under the conditions studied. These effects are attributed to transport limitations and/or rapid recombination of ozone-derived oxygen species within the nanoparticle bed, which may hinder full restoration of reactive sites between cycles.

This work demonstrates that while O_3 effectively mitigates moisture-induced agglomeration in nanoparticle ALD, its transport and reaction characteristics can limit surface renewal in highsurfacearea powder systems, thereby constraining its effectiveness as an oxidant for conformal coating of dense nanoparticle beds.

AF-MoP-13 Phase-engineered TiO_2–RuO_2 top interface for a High-k TiO_2 dielectric with bottom interfacial stabilization via a ZrO_2 layer in Tin-based DRAM capacitors*, **Kyungmo Yang**, Woojin Jeon, Chaeyeong Hwang,* Kyung Hee University, Republic of Korea

As DRAM devices continue to scale down, dielectric materials that can simultaneously provide a high dielectric constant and low leakage current are required to secure sufficient capacitance within a reduced cell area. In metal–insulator–metal (MIM) capacitor structures employing TiN bottom electrodes, oxygen scavenging by TiN induces interfacial degradation, leading to increased oxygen vacancy formation in adjacent oxide dielectrics and consequent degradation of electrical reliability. Although TiO_2 has been widely investigated as a high-k dielectric candidate, its relatively small band gap and unstable interface with TiN limit its applicability in single-layer configurations.

In this study, a ZrO_2/TiO_2 stacked dielectric structure incorporating a ZrO_2 buffer layer between the TiN bottom electrode and the TiO_2 dielectric is proposed to alleviate interfacial degradation and suppress leakage current. Electrical characterization revealed that TiO_2 single-layer capacitors exhibited pronounced DC nonlinearity and increased leakage current due to poor interfacial properties at the TiN/TiO_2 interface. In contrast, the introduction of a ZrO_2 buffer layer significantly reduced dielectric loss and leakage current, resulting in improved capacitance stability. Chemical analysis confirmed that the ZrO_2 buffer layer effectively suppressed oxygen scavenging from the TiN electrode, thereby reducing oxygen vacancy formation in the TiO_2 layer and enhancing interfacial stability.

Furthermore, recrystallization induced by the oxide top electrode was utilized to enhance the dielectric constant. When sufficient thickness was provided, the ZrO_2 and TiO_2 films were well crystallized into tetragonal-ZrO_2 and anatase-TiO_2 phases, respectively. As the TiO_2 thickness decreased, a localized phase transformation from anatase to rutile TiO_2 was induced at the interface with the oxide top electrode, contributing to an enhanced dielectric constant. Systematic variation of the ZrO_2/TiO_2 thickness ratio revealed a trade-off between dielectric constant and leakage current, with thicker ZrO_2 layers providing superior leakage suppression. In particular, a ZrO_2 buffer thickness of 7 nm or greater was found to be effective in achieving low leakage characteristics while maintaining an enhanced dielectric response.

These results demonstrate that the ZrO_2/TiO_2 stacked dielectric architecture, in which TiO_2 thickness is controlled to realize mixed anatase–rutile phases, is a promising dielectric design for next-generation TiN-based DRAM capacitor applications.

AF-MoP-14 Influence of Process Pressure on the Growth Kinetics and Electrical Properties of NbN Thin Films Prepared by PEALD using TBTDEN*, **Hae Yong Jeong**, Shin Keun Kim, Taek Kim,* Korea Advanced Nano-fab Center, Republic of Korea

Niobium nitride (NbN) is a pivotal material for superconducting electronics and advanced barrier layers due to its excellent thermal and chemical stability. Among various deposition methods, Plasma-Enhanced Atomic Layer Deposition (PEALD) provides the advantage of high-quality film growth at relatively low temperatures with precise thickness control. In this study, we investigated the influence of process pressure, precisely controlled via pumping valve modulation, on the growth kinetics and material properties of NbN films. The films were synthesized using tert-butylimido-tris-diethylamido-niobium (TBTDEN) as the Nb precursor and N2/H2 plasma as the reactant. The deposition was conducted at a substrate temperature of 350°C, with the process pressure varied by adjusting the pumping valve position from 18% to 11.5%. Experimental results indicate that variations in process pressure play a decisive role in modulating film characteristics. Specifically, the growth per cycle (GPC) exhibited a measurable response to pressure changes, shifting from 0.927 Å/cycle at an 18% valve opening to 0.872 Å/cycle at 11.5%. This shift suggests that the pressure environment significantly influences precursor residence time and the flux of reactive species, thereby affecting surface reaction efficiency. Furthermore, the electrical resistivity showed a notable improvement with increasing pressure (decreasing valve opening), dropping from 298 μΩ·cm at 18% to 229 μΩ·cm at 11.5%. This trend indicates that higher pressure conditions may promote film densification and optimize stoichiometric nitrogen incorporation. Preliminary structural observations suggest a strong correlation between these electrical improvements and enhanced crystallinity. Detailed X-ray Diffraction (XRD) analysis and X-ray photoelectron spectroscopy(XPS) depth profiling are currently underway to further elucidate the relationship between pressure-driven plasma chemistry and the microstructural evolution of the NbN films. This work demonstrates that process pressure is a critical parameter for tailoring PEALD-NbN properties, providing essential insights for optimizing NbN films in next-generation quantum applications.

AF-MoP-15 Oxide Film Properties Using OH Radicals Generated by Water Vapor Mixed Pure Ozone Gas as ALD Oxidant*, **Naoto Kameda**,* MEIDENSHA corp., Japan*; Kenichi Uehara, Shigeo Yasuhara,* Japan Advanced Chemicals Ltd., Japan*; Soichiro Motoda, Tetsuya Nishiguchi,* MEIDEN NANOPROCESS INNOVATIIONS Inc., Japan

The gate dielectric oxide film (e.g. HfO_2) for FET requires low impurity levels and excellent electrical properties. ALD enables the deposition of high-quality gate oxide films, and O_2 plasma, which generates highly reactive atomic oxygen (O radical), has been widely used. However, recent FET devices have become increasingly stacked (e.g., GAA), gate dielectric films must be deposited deep into nanometer-scale microfabricated trenches exceeding an aspect ratio of 100.O_2 plasma ALD cannot deposit the HfO_2 film inside trenches with aspect ratios over 50 due to the deactivation of O radical within trench diffusion[1]. We have reported the high quality of Al_2O_3 film properties by ALD using pure ozone gas (PO-ALD), which is high-concentration pure ozone gas (≥80 vol%) as the oxidizing source and reported the Al_2O_3 film can be formed in trenches with high aspect ratio(> 1500) [2], while cannot deposit with low aspect ratio (<100) using O_2 plasma[1]. Furthermore, it was reported that highly reactive OH radicals can generate by mixing water vapor with high-purity ozone gas at 250°C[3]. This presentation discusses the effect of using OH radicals as an ALD oxidation source on the film quality of HfO_2 films.

Figure 1 shows the schematic ALD chamber and gas piping systems. The distribution of the gas phase temperature inside the chamber by a hot wall method is controlled to under 100°C upstream of the substrate, and to substrate temperature (>150°C) of the downstream the substrate. These temperature distribution is the generation of atomic oxygen near the substrate through the thermal decomposition reaction of ozone ($O_3 \rightarrow O_2+O$).By supplying a mixed gas of ozone and water vapor under these temperature conditions, the ozone thermally decomposes near the substrate, generating O, which then reacts with H_2O to generate OH radicals, which can then be supplied to the substrate (see Fig. 2). Gas supply conditions for ozone and water vapor (flow rate mixture ratio, etc.) are determined by increasing ahing rate at the substrate position due to the supply of OH radicals. Precursor and carrier gases are TDMAH($((CH_3)_2)_4Hf$) and Ar, respectively. Figure 3 shows the relationship between the number of ALD cycles and HfO_2 film thickness at a substrate temperature of 200°C. The introduction of water vapor slightly increases the film thickness. The estimated GPC are 0.138 nm/cycle(with water vapor) and 0.126 nm/cycle (w/o water vapor), respectively. We will report on film quality, including a comparison of impurity levels in the film, using SIMS and XPS.

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AF-MoP-16 Expanding the Zinc Precursor Toolbox for Thermal ALD of ZnO*,* ***Jorit Obenlüneschloß,*** Leibniz Institute, IFW Dresden, Germany*; Jeffrey W. Elam,* Argonne National Laboratory*; Anjana Devi,* Leibniz Institute, IFW Dresden, Germany

Atomic layer deposition (ALD) of ZnO is most commonly based on the diethylzinc (DEZ)/H_2O process, which offers high reactivity and excellent film quality but is associated with significant safety risks due to DEZ's pyrophoric nature. In this work, we systematically evaluate three alternative zinc precursors—bis(3-(N,N-dimethylamino)propyl)zinc(II) (Zn(DMP)$_2$), bis(N-(2-ethoxyethyl)-2-penten-2-on-4-iminate)zinc(II) (Zn(EEKI)$_2$), and ethyl(di(trimethylsilyl)amido)zinc(II) (ZnEt(HMDS))—and benchmark their performance in thermal ALD against DEZ using water as the sole co-reactant.[1]

All four precursors exhibit self-limiting ALD behavior and facilitate the deposition of high-quality ZnO thin films at a common growth temperature of 200 °C. In-situ spectroscopic ellipsometry reveals distinct precursor-specific growth mechanisms, including variations in adsorption behavior, ligand desorption during purge steps, and ligand removal during the water half-cycle. While DEZ shows signatures of partial thermal decomposition, the other precursors retain more intact surface species with steric differences leading to variations in growth per cycle (0.8–2.3 Å) and surface morphology.

Comprehensive ex-situ characterization (XPS, RBS/NRA, AFM, TEM, XRD, and UV/Vis spectroscopy) confirms that all processes yield dense, polycrystalline, near-stoichiometric ZnO films with similar crystallinity and optical band gaps. However, notable differences in surface roughness and nucleation behavior are observed, especially for the bulkier ligand systems Zn(EEKI)$_2$ and ZnEt(HMDS). Importantly, ZnEt(HMDS) enables a previously unreported thermal ALD process with a growth rate comparable to DEZ, while avoiding its extreme pyrophoricity.

These results clearly demonstrate that alternative zinc precursors can deliver ZnO thin films of similar quality to DEZ while providing advantages in safety, growth chemistry, and process flexibility. Expanding the zinc precursor library is therefore an important step toward more robust ALD process design, especially for complex multicomponent oxides and advanced device architectures.

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AF-MoP-17 Comparative Study of Ga Precursors for Low-Temperature PEALD GaN: Trimethylgallium vs. Tris(dimethylamido)gallium*,* ***Taeyoon Kwon****, Jian Heo, Okhyeon Kim, Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

Gallium nitride (GaN) is essential for next-generation high-power electronics and optoelectronics. However, integrating high-quality GaN films onto temperature-sensitive substrates remains a significant challenge. Although plasma-enhanced atomic layer deposition (PEALD) allows lower processing temperatures than metal-organic chemical vapor deposition (MOCVD) or thermal ALD, selecting the appropriate Ga precursor is essential to optimize growth kinetics and film quality. Previous studies have used trimethylgallium (TMGa) and tris(dimethylamido)gallium (TDMAGa), yet there has been no direct, systematic comparison of their growth behavior and resulting film properties under identical plasma conditions. This study investigates low-temperature PEALD of GaN using alkyl-based TMGa and amido-based TDMAGa in an NH_3 plasma. We analyze the saturation behavior, growth rates, and physical and chemical properties of the deposited films to understand the effect of ligand chemistry. Our results demonstrate that the TDMAGa precursor is significantly more reactive than TMGa, achieving self-limiting growth with shorter exposure times and lower process temperatures. Consequently, films grown with TDMAGa displayed superior material quality, characterized by higher mass density, a higher refractive index, better stoichiometry, fewer carbon and oxygen impurities, and a smoother surface. Cross-sectional analysis of ALD-GaN on n-type GaN substrates revealed a homoepitaxial interface even at 125 °C when using TDMAGa. These results suggest that TDMAGa is the more advantageous precursor for producing high-quality, dense GaN films at low temperatures.Reference[1] S. Banerjee *et al.*, J. Phys. Chem. C 123 (2019) 23214.[2] C. Ozgit *et al.*, J. Vac. Sci. Technol. A 30 (2012) 01A124.

AF-MoP-18 Structural and Electrical Characteristics of Vanadium Oxide Thin Films Grown by ALD Using a Precursor with High Thermal Stability*,* ***Iksun Kwon****, Seungwoo Lee,* Kyung Hee University, Republic of Korea*; Hyunseok Oh, Donghun Shin, Yongjoo Park,* SK Trichem Co., Republic of Korea*; Woojin Jeon,* Kyung Hee University, Republic of Korea

Vanadium oxide (VO$_x$) exhibits structure and electrical properties that strongly depend on its oxidation state and crystal structure, making precise control over high-quality thin-film formation critically important. Atomic layer deposition (ALD) enables atomic-scale control of film thickness and composition, offering excellent compositional uniformity and process reproducibility. However, conventional vanadium precursors suffer from limited thermal stability, which restricts the maintenance of self-limiting deposition behavior at temperatures above 200 °C.

In this study, VO$_x$ thin films were deposited by an ALD process using a thermally stable vanadium precursor at deposition temperatures ranging from 150 to 320 °C, and their structural and electrical properties were systematically investigated. At 250 °C, the VO$_x$ films crystallized from an amorphous phase into polycrystalline V_2O_5, with the fraction of the high oxidation state V^{5+} increasing as the deposition temperature increased. In contrast, at 320 °C, partial reduction occurred due to oxygen deficiency induced by the high-temperature process, resulting in an increased contribution of the V^{4+} component. The resistivity of the VO$_x$ films grown on SiO_2 substrates was found to be within the bulk V_2O_5 values reported in the literature. These results demonstrate that a thermally stable precursor–based ALD process enables post-treatment-free control over the crystallinity and electrical conductivity of VO$_x$ thin films.

AF-MoP-19 Engineering Black TiOx: Kinetic Tuning of Ti^{3+} Defects and Polymorph Stability via ALD Pulse Control*,* ***Jan Leithäuser,*** Heinrich-Buff-Ring 16, Germany*; Jörg Schörmann, Martin Becker, Sangam Chatterjee,* Justus Liebig University Giessen, Germany

"Black" titanium dioxide (TiO$_{x<2}$) has attracted significant attention for photocatalytic and energy storage applications due to its reduced bandgap and high concentration of active Ti^{3+} surface defects. Conventionally, generating these specific defects requires harsh post-treatments like high-pressure hydrogenation. In this work, we improve on a direct, low-temperature Atomic Layer Deposition (ALD) route to synthesize and tune black TiO$_x$ films by exploiting the specific precursor kinetics of the TDMAT/H_2O process [1, 2, 3].

We hypothesize that the concentration of Ti^{3+} defects and consequently the resulting crystal phase can be precisely controlled by manipulating the precursor pulse duration. Using a process temperature of 200 °C, we show that variations in the pulse length allow for the targeted synthesis of specific defect environments.

Preliminary analysis reveals that this defect engineering directly dictates the polymorph stability upon annealing, enabling a tunable shift between anatase- and rutile-dominated modifications. To distinguish between self-limiting ALD growth and parasitic CVD-like decomposition as the origin of these defects, we correlate the structural evolution (GIXRD) with growth rates (GPC) and surface morphology (AFM).

Our results present a novel "kinetic knob" to tailor the stoichiometry and electronic properties of black TiO$_x$ without changing the thermal budget, offering new pathways for defect-enabled functional coatings.

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AF-MoP-20 Studies of Pt ALD Film Conformality and Conductivity with Pillarhall Test Structures*, Jussi Kinnunen,* Chipmetrics Oy, Finland*; Anish Philip, Girish C. Tewari, Mahtab Salari Mehr,* Aalto University, Finland*; **Kalle Eskelinen,*** Chipmetrics Oy, Finland*; Thomas Werner,* Chipmetrics GmbH, Germany*; Ramin Ghiyasi,* Aalto University, Finland*; Stefan Polzin,* Chipmetrics GmbH, Germany*; Maarit Karppinen,* Aalto University, Finland

Atomic layer deposition (ALD) of noble metals such as platinum (Pt) is increasingly relevant for advanced device applications, yet remains challenging due to high precursor cost, narrow process windows, and limitations of conventional metrology for assessing conformality in high aspect ratio (HAR) features. In this work, we present the first demonstration of combined conformality and electrical characterization of Pt ALD films using the electrical test structure patterning enabled by PillarHall technology. The structure is based on pillar-stabilized large-area membrane that can be selectively removed by tape lift-off after the deposition. This membrane removal leaves controlled narrow line of thin film with probe/solder pads at each end, enabling direct electrical contacting without additional processing.

Pt thin films were deposited in a thermal ALD reactor (Picosun R100) using $MeCpPtMe_3$ and O_2 at 300 °C, based on a process previously optimized for planar substrates [1]. To enable reliable electrical probing while minimizing disturbance to the ALD process a thin dielectric precoating of 5 nm Al_2O_3 was introduced on top of the native oxide. Film thickness and conformality were evaluated optically using ellipsometry. For Pt thicknesses up to 25 nm, changes in optical parameters are sensitive to film growth, enabling thickness measurement along the lateral high aspect ratio (LHAR) channel. Beyond this range, ellipsometric response saturated, highlighting a fundamental limitation of optical metrology for thicker metallic films. In parallel, four-probe resistance measurements were performed on the same LHAR5 chips, enabling direct correlation between electrical properties and film thickness. The measured resistance followed the expected thickness dependence, increasing with decreasing Pt thickness, while temperature-dependent measurements showed metallic behavior, with resistance increasing with temperature in the range 100-400 K.

The current research demonstrates that the LHAR5 electrical test structure provides a controlled and robust platform for studying highly conductive films, enabling reliable measurements over wide temperature ranges and penetration depths. The methodology provides a practical route to study noble metal ALD processes in HAR structures and opens pathways for future work combining electrical, optical, and nanoscale characterization, including AFM-based conductivity mapping and SEM/EDS analysis.

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AF-MoP-21 Growth Rate of ALD Al_2O_3 on Nanocellulose – Quantification Technique and Analysis*, **Hugo Patureau,*** SIMAP, Grenoble-INP, CNRS, France*; Erwan Gicquel,* Cilkoa, France*; Frédéric Mercier, Elisabeth Blanquet, Arnaud Mantoux,* SIMAP, Grenoble-INP, CNRS, France

Cellulosic products have emerged as a solution to plastics in the packaging industry due to being recyclable and bio-degradable. Recent research has shown that functionalising cellulose substrates with Al_2O_3 deposited by atomic layer deposition (ALD) improves their barrier properties and grants hydrophobicity. While research on the topic is mainly focused on functional properties, relating these properties to film thickness is challenging, due to the fibrous nature of the substrate. Consequently, thickness on cellulosic substrates is often estimated from silicon wafers processed under identical conditions. ALD is known to be substrate dependent, making this approach unsatisfactory. This work demonstrates a strategy to quantify ALD Al_2O_3 on nanocellulose substrates. Quantification is achieved through acid digestion and inductively coupled plasma mass spectrometry (ICP-MS), and a calibration curve X-Ray fluorescence (XRF) is established (Figure 1). This allowed rapid, fully quantitative, and non-destructive measurements. This method was then used to investigate the Al_2O_3 ALD window on nanocellulose, saturation curves and insights on early stage ALD growth on the substrates. Findings indicate a substrate-enhanced growth rate on nanocellulose, with the steady state growth per cycle (GPC) significantly greater on nanocellulose, than on silicon wafers processed under identical conditions (Figure 2). These results highlight the importance of quantifying growth directly on the cellulosic substrates.

AF-MoP-22 Self-Assembled Monolayers of Phosphorus–Nitrogen Cages*, Justin Lomax,* Western University, Canada*; Michael-John Treanor,* St. Andrews, UK*; Michael Land,* Dalhousie University, Canada*; Wai-Tung Shiu, Bentley Jordan,* Western University, Canada*; Saurabh Chitnis,* University of Victoria, Canada*; Christopher Baddeley,* University of St. Andrews, UK*; **Paul Ragogna,*** Western University, Canada

Self-assembled monolayers (SAMs) are organized films that spontaneously form when molecules attach to a surface and arrange into ordered structures. SAM assembles and the modification of the surface are determined by the nature of the surface-binding group, the architecture of the backbone, and the terminal functionality. The molecule-surface interaction has a profound impact in areas such as molecular electronics and protective coatings. Carboxylic acids, thiols, silanes, phosphonic acids, and carbenes have been widely used for SAM coatings, while limited effort has been directed toward exploring alternative surface ligands, especially those based on inorganic scaffolds. The phosphaza-bicyclo[2.2.2]octane core is symmetrical and contains P(III) centers at axial positions within a rigid three-dimensional architecture. Its modular synthesis enables control over volatility and reactivity while preserving a chemically robust framework. We have establishedP_2N_6 as a new molecular platform for SAMs. By demonstrating deposition and selective adsorption on metals, we reveal the ability for monolayer formation that expands the precursor design space for deposition processes. This represents the first time that resilient, P-based SAM has been identified. Details of careful quartz crystal microbalance (QCM) experiments, molecular layer deposition (MLD) processes and scanning tunneling microscopy results will be presented.

AF-MoP-23 Mophological Analysis of ALD HZO Thin Films Using Cp-Based Hf/Zr Precursors*, **Chang Ho Lee,*** CN1 Co., Ltd, Republic of Korea

In recent years, extensive research has been conducted on application of doped-HfO_2 as high-k dielectric materials in advanced electronic devices such as dynamic random-access memory (DRAM), ferroelectric field-effect transistors (Fe-FETs), and ferroelectric junction transistors (FJTs). Among these materials, ZrO_2-doped HfO_2, specifically $Hf_{0.5}Zr_{0.5}O_2$ (HZO), has attracted significant attention as a promising alternative dielectric for DRAM capacitor applications. HZO exhibits various crystalline phases depending on dopant concentration and thermal conditions, including the tetragonal phase with a high dielectric constant and the non-centrosymmetric orthorhombic phase, which is associated with ferroelectric behavior. In this study, HZO thin films were deposited using an atomic layer deposition (ALD) process with Cp-based Hf and Zr precursors at low temperatures ranging from 250 to 350 °C. The morphological characteristics and thickness uniformity of the deposited HZO films were evaluated using atomic force microscopy (AFM) and X-ray reflectivity (XRR). The crystalline structure and phase distribution were analyzed by X-ray diffraction (XRD), while the microstructural features and interfacial properties were further investigated using transmission electron microscopy (TEM). This systematic analysis provides insight into the effects of deposition temperature on the morphological and structural properties of low-temperature ALD-grown HZO thin films, offering a fundamental understanding for process optimization in high-k dielectric applications.

AF-MoP-24 Indium Precursor Development for High Quality InOx-based Film for Future Oxide Semiconductor Applications*, **Nana Okada,** Atsushi Sakurai, Ryota Fukushima, Keisuke Takeda, Masaki Enzu,* ADEKA CORPORATION, Japan*; Tomoharu Yoshino,* ADEKA KOREA CORPORATION, Korea (Democratic People's Republic of)*; Atsushi Yamashita, Yoshiki Oe, Yutaro Aoki,* ADEKA CORPORATION, Japan*; Akihiro Nishida,* a.nishida@adeka.co.jp

Indium-based oxide semiconductors (OS) such as $In_2O_3$1), IGZO2), IGO3), IWO4), and ITO5) have garnered significant attention for future logic and memory applications due to low leakage, high mobility, and BEOL compatibility as channel materials. As the OS film is expected to be grown on a 3D architecture different from a Si crystal, there is a strong demand for ALD indium precursors which enable conformal deposition, precise thickness and compositional control. As a result, we have focused on indium precursor development for high temperature ALD processing to produce high quality InOx-based thin films with a very small amount of organic impurities.

Here we present DKI-6 which is a heteroleptic indium precursor with bulky β-diketimine and methyl ligands (Fig.1). It is a liquid at room temperature, has a 1 torr vapor pressure at 105°C, and decomposed at 328°C (onset, DSC). DKI-6 successfully produced smooth and high quality In_2O_3 films with a GPC of 0.54 Å/cycle on an SiO_2 substrate using O_3 ALD processing at 300°C (Fig.2 and Fig.3). Interestingly, we found Si diffusion into the In_2O_3 film from the SiO_2 underlayer using H_2O ALD at 300°C, which could imply lower density In_2O_3 film growth with lower GPC of 0.40Å/cycle (Fig.4).

In conclusion, we successfully obtained ALD In_2O_3 films using DKI-6 and O_3 or H_2O coreactants at 300°C with the reasonable GPC. This result will extend into further development of various kinds of InOx-based OS thin films.

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AF-MoP-25 Novel Tantalum Precursor for High-Quality Ta_2O_5 Thin Films by Atomic Layer Deposition*, **Luis Misal**, Sunao Kamimura,* Air Liquide Laboratories, Japan*; Nicolas Blasco,* Air Liquide, France

1. INTRODUCTION

Tantalum(V) oxide (Ta_2O_5) is a critical material for advanced optical coatings and next-generation DRAM capacitors due to its high refractive index, low optical absorption, and high dielectric constant [1]. Atomic Layer Deposition (ALD) is the preferred method for depositing highly uniform and conformal films required for these applications, especially on curved substrates. However, common tantalum precursors (e.g. TBTDET, TBTEMT) often lead to films with high carbon and nitrogen contamination [2,3], which is detrimental to thin film performance. This work introduces a novel tantalum precursor, RosiTa^{TM}, for the ALD of high-quality Ta_2O_5 thin films.

2. EXPERIMENTAL

A novel liquid Ta precursor, RosiTa^{TM} was synthesized and characterized. Its thermal properties and volatility were evaluated by thermogravimetric analysis (TGA). RosiTa^{TM} has good volatility (1 Torr at 106 °C, Fig. 1), and presents long-term thermal stability with no decomposition detected after 12 weeks at 110°C, making it suitable for ALD applications. Ta_2O_5 thin films were deposited by thermal ALD on silicon substrates using RosiTaTM as tantalum source and ozone (O_3) as the oxygen source. The deposition was carried out in a temperature range of 200-350 °C, with a GPC ~0.48 Å/cycle (ALD window 275-300 oC). The resulting films were analyzed by X-ray photoelectron spectroscopy (XPS) (Fig. 2) to determine their composition and purity. The ALD process using RosiTa^{TM} and O_3 yielded highly conformal Ta_2O_5 thin films with excellent step coverage on high-aspect-ratio structures (Fig. 3).

A key finding of this work is the exceptionally low nitrogen and carbon contamination in the Ta_2O_5 films grown with RosiTa^{TM}. This is a significant improvement over other precursors (e.g. TBTDET, TBTEMT) and is a critical advantage for different applications.

3. SUMMARY

The novel volatile tantalum precursor, RosiTa^{TM} has been successfully used for the ALD of high-quality Ta_2O_5 thin films. RosiTa^{TM} stands out due to its excellent thermal stability and the ability to produce highly conformal Ta_2O_5 films with nitrogen and carbon contamination below the detection limit for XPS. These features make RosiTa^{TM} a very promising precursor for demanding ALD thin film applications.

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AF-MoP-26 Growth and Characterization of Bi_2O_3 Thin Films Prepared by Atomic Layer Deposition from $Bi(O^tBu)_3$*, **Hyo Jin Park**,* Sookmyung Women's University, Republic of Korea*; Injeong Ryu, Gwon Deok Han,* Sookmyung Women's University, Republic of Korea

High-bandwidth memory (HBM) is essential for AI-based computing, necessitating the development of high-performance dynamic random access memory (DRAM). DRAM devices are evolving toward higher efficiency through higher integration, which inevitably requires reducing the physical size of DRAM capacitors. Therefore, the development of next-generation high-k dielectric materials that maintain sufficient capacitance without compromising leakage current levels is crucial. In this study, we investigated bismuth oxide (Bi_2O_3) films deposited by atomic layer deposition (ALD) as a promising high-k candidate material for future DRAM capacitors. We explored the applicability of bismuth tertiary-butoxide ($Bi(O^tBu)_3$), a precursor with limited research experience in ALD processes. Furthermore, we compared the structural and electrical properties of films deposited using different reactants (O_2 and O_3). The comparative analysis revealed significant differences in growth behavior, crystallinity, and interface quality depending on the choice of reactants. Additionally, the energy bandgap and dielectric constant were evaluated to determine the material's suitability for scaled capacitor nodes. This presentation explores the potential of ALD-grown Bi_2O_3 as a viable dielectric solution for next-generation DRAM technology.

AF-MoP-27 Effect of Temperature and Oxidant on Structural, Chemical, Optical and Morphological Properties of ALD Grown Cobalt Oxide*, Swapnil Nalawade, Ahmed Wasif Mustakim, **Shyam Aravamudhan**,* North Carolina A&T State University

Cobalt oxide thin films are of significant interest for applications in electrochemical energy storage, catalysis, gas sensing, and emerging electronic and neuromorphic devices, where precise control over phase, stoichiometry, and surface morphology is critical. In this work, we report a comprehensive study of the growth behavior and property evolution of cobalt oxide thin films deposited by atomic layer deposition (ALD) using cobalt(II) ethylpropanimidamidato as the metal precursor and ozone or water vapor as the oxidant, with particular emphasis on the role of deposition temperature. Saturated ALD growth was achieved within a temperature window of 180–260 °C. Film composition and oxidation states were analyzed using X-ray photoelectron spectroscopy (XPS), while crystallographic structure was examined by X-ray diffraction (XRD). Atomic force microscopy (AFM) revealed a strong dependence of surface morphology on deposition temperature. Raman spectroscopy confirmed that films deposited at lower temperatures exhibit a mixed-phase composition consisting of Co_3O_4 and CoO, whereas higher temperatures promote phase purity. Spectroscopic ellipsometry was employed to determine film thickness and extract temperature-dependent optical constants. This work demonstrates ALD as a highly repeatable and scalable pathway for depositing uniform cobalt oxide thin films with tunable phase composition and optical properties, enabling materials optimization for application-specific integration.

AF-MoP-28 Hybrid 1D/3D Analytical Step–Coverage Modeling for Inhibitor-Free Superconformal Molybdenum Gap-Fill*, **David Mandia**, Lee Brogan, Matthew Griffiths, Jennifer O'Loughlin Petraglia,* Lam Research Corporation

Void–free metallization in sub–20 nm features requires predictive control of conformality while avoiding etch–dominated failure. Depending on the application, a conformal, bottom-up (selective), or superconformal step coverage is required.[1] Herein, an analytical step coverage (SC) function is derived using 1D trench-filling kinetics and employed in conjunction with Lam's SEMulator3D® to understand and predict the regimes of subconformality, conformality, and superconformality for Mo gap-fill. Our model system is the $MoCl_5/H_2$ ALD process, which also contains self-etching pathways that need to be considered. The $MoCl_5/H_2$ chemistry is described using two competing surface pathways: (1) deposition,$MoCl_5 + 5/2\ H_2 \rightarrow Mo + 5HCl$, with rate with rate Rdepα$PAPB$5/2, and (2) self–etch, $2MoCl_5 + Mo \rightarrow MoCl_4 + Mo_2Cl_6$, with rate with rate Rdepα$PAPB$5/2. The stoichiometric flux terms for 1D Knudsen trench filling are mapped onto the 2D/3D SEMulator3D model to understand $MoCl_5/H_2$ flux regimes that lead to a SC function which is <1 (subconformal), ≈1 (conformal), ≤0 (stalled/over-etch), or >1 (superconformal). In this feature-scale growth physics modeling approach, we present the transition between these regimes using experimental results obtained from internal high-aspect-ratio structure data. The 1D model provides fast, physics–transparent process boundaries, while SEMulator3D® modeling propagates these conditions into realistic 2D/3D profiles, enabling accelerated and robust process development for Mo interconnects.

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AF-MoP-29 Low Temperature ALD Vanadium Nitride Using Anhydrous Hydrazine*, Dan Le, Austen Adams, **Lorenzo Diaz**,* RASIRC*; Dushyant Narayan, Minjong Lee, Thi Thu Huong Chu,* University of Texas at Dallas*; Adrian Alvarez,* RASIRC*; Jiyoung Kim,* University of Texas at Dallas

As device dimensions continue to shrink, TiN as the electrode material for advanced devices faces critical limitations, including high resistivity and increased leakage current density arising from its relatively low work function (~4.2 eV) [1,2]. These constraints drive the need for improved electrode materials for the next scaled technological node. Vanadium nitride (VN) is a promising candidate owing to its favorable characteristics, including a high work function (up to ~5.5 eV), low resistivity, and notable mechanical properties [3].

In this work, we focus on the development of a BEOL-compatible, low-temperature thermal ALD process for vanadium nitride (VN) thin films, employing BRUTE® anhydrous hydrazine (N_2H_4) as the nitrogen source to enable integration as a potential electrode material for next-generation devices. Using the anhydrous N_2H_4 source, uniform VN thin films were successfully deposited at temperatures as low as 250 °C, achieving a growth rate of ~0.05 nm per cycle and a film density of ~5.40 g/cm^3. XPS analysis of a 10 nm VN film deposited at 250 °C confirmed successful nitride formation at this reduced temperature, although ~15 at. % oxygen contamination was detected within the film. The as-deposited VN films exhibited a resistivity as low as ~600 μΩ·cm, with less than 5% variation across the test wafer, indicating good film uniformity and electrical consistency. MOS capacitors will be fabricated to further evaluate the electrical properties of the deposited films. Detailed experimental procedures and comprehensive characterization results will be discussed.

References

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AF-MoP-30 Non-Destructive Characterization of Alumina Film Thickness and Fractional Coverage Utilizing XPS and StrataPHI for Metrological Analysis

Amy Ferryman, *Norb Biderman, Kateryna Artyushkova,* Physical Electronics

Atomic layer deposition (ALD) is widely used due to its precise deposition capabilities, allowing for the creation of very thin, conformal, and high-quality films on the nanometer scale. These films are ideal for applications requiring precise barrier layers, passivation layers, or protective coatings in complex geometries, particularly in microelectronics, sensors, and medical devices. ALD deposition of alumina offers several advantages, including uniform coating on complex 3D structures, precise thickness control, high purity, and suitability for sensitive substrates due to its low deposition temperature. The self-limiting behavior of ALD cycles allows for controllable film growth in which a homogenous film can be achieved at the lowest film thickness. To control the thickness in a range of few nanometers, it is important to understand the interaction between the reactants and substrate during the nucleation period, or the first few cycles. X-ray photoelectron spectroscopy (XPS) is a well-established technique for non-destructive analysis of the chemical composition of thin layers and interfaces. By analyzing a material at varying takeoff angles between the sample and analyzer, angle dependent XPS (ADXPS) can be utilized to probe the thickness and chemical composition of thin films without creating ion beam-induced damage associated with destructive sputter profiling. The spectral results obtained by ADXPS can be furthered evaluated by *Strata*PHI, a software product designed by Physical Electronics, to calculate not only the thickness of thin films but also provide an estimate of fractional coverage, which is of great importance for high-throughput metrology of thin-film structures. This presentation will highlight the benefits of utilizing angle dependent XPS in combination with StrataPHI modeling software to non-destructively characterize and simultaneously calculate the layer thickness and fractional coverage of a series of aluminum oxide films deposited on glass substrates throughout the nucleation period by the ALD process.

AF-MoP-31 Effect of Pnictogen Hydrides XH_3 (X=P, As, Sb) Doping on Silicon Deposition: A First-Principles Study

Rabi Khanal, *Raymond Joe, Anthony Dip,* Tokyo Electron America, Inc.

Pnictogen hydrides, such as PH3, have been used to dope silicon (Si) surfaces during the fabrication of quantum electronic devices with atomic-scale precision. Additionally, dissociative adsorption of XH3 is believed to effectively alter surface energetics and morphology during film growth, enabling control over dopant concentration and spatial distribution within the film. Once the dopant is incorporated into the surface, the growth of silicon can be affected by the dopant's concentration as well as its chemical and physical properties. Developing a fundamental understanding of dopant characteristics and growth processes is essential to ensure and improve a priori prediction of suppressed or enhanced growth rates and uniformity in critical Si film deposition for many applications, including logic, NAND, and DRAM devices.

In this study, we first performed ab initio molecular dynamics (AIMD) simulations of SiH4 (a Si precursor) deposition on the Si(001) surface at various dopant concentrations. Our simulations show that dilute dopant concentrations at the surface, in the absence of hydrogen, do not significantly affect SiH4 deposition. To have a meaningful impact on Si film growth, an adequate amount of dopants must be present on the surface. We also analyzed the detailed reaction mechanism of SiH4 deposition on a surface using a dimer model at the density functional theory level with dissociatively adsorbed XH3. For the XH3-incorporated Si(001) surface, we considered the most widely used dissociative adsorption states: XH2+H, XH+2H, and X+3H. Our results indicate that the energy barrier for silane (SiH4) deposition increases in the presence of XH3 compared to a surface without dopants, implying slower film growth. The magnitude of the energy barrier—and its effectiveness in limiting film growth—strongly depends on the state of adsorbed XH3 (XH+2SiH versus X+3SiH) on the Si surface. Furthermore, we will discuss how surface-site dependence influences Si adsorption relative to dopant location and chemistry (e.g., As, Sb, P), aiming to link these effects to intrinsic dopant properties, such as electronegativity and atomic radius.

AF-MoP-32 Rutile TiO_2 Thin Films Grown by Remote Plasma ALD on RuO_2 Seed Layers for Advanced Capacitor Structures

Yongwoon Jang, *Jiwon Kim, Byungwook Kim, Minkyun Kang, Hyeonwu Nam, Changbun Yoon,* Tech University of Korea

As DRAM capacitor structures continue to scale down, achieving ultrathin dielectric films with high capacitance density and low leakage current has become increasingly important. Rutile-phase TiO_2 is a promising high-k dielectric material due to its intrinsically high dielectric constant; however, stabilizing the rutile phase in ultrathin films remains challenging because of phase instability and interfacial degradation.

In this study, RuO_2 bottom electrodes were fabricated by reactive RF sputtering using a metallic Ru target, with oxygen flow ratios of 20%, 30%, and 40% and substrate temperatures ranging from 300 to 500 °C. These parameters significantly influenced the oxidation state and crystallinity of the RuO_2 films, which in turn affected the subsequent growth behavior of TiO_2. TiO_2 thin films were deposited on the RuO_2 electrodes using remote plasma plasma-enhanced atomic layer deposition (PEALD), and the impact of RuO_2 seed layer crystallinity on TiO_2 phase evolution was systematically investigated. Post-deposition oxygen annealing was additionally employed to enhance rutile phase stability.

As a result, highly crystalline rutile-phase TiO_2 thin films were successfully obtained, exhibiting an equivalent oxide thickness below 1 nm and leakage current densities lower than 10^{-5} A cm^{-2}.

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AF-MoP-33 2.5 Å/cycle PEALD of SiO_2 Using a Tri-Silyl Precursor for Advanced Gap-Fill Applications

Wonyong Koh, *Byung-Kwan Kim, Won-Jeong Hwang, Su-Yeon Lee, Seung-Gyun Hong, Jin-Sik Kim, Hyun-Kyu Ryu,* UP Chemical Co., Ltd., Republic of Korea

High-quality SiO_2 films were deposited by plasma-enhanced atomic layer deposition (PEALD) using hexamethyldisilylaminodimethylaminosilane (HMDMS, $(Me_3Si)_2N\text{-}SiH_2\text{-}NMe_2$) and O_2 plasma at 550°C, achieving growth per cycle (GPC) of 2.5 Å/cycle. For comparison, thermal ALD process using the same precursor with O_3 at 700°C reported GPC of 3.0 Å/cycle, excellent electrical properties and good conformity [1]. Secondary ion mass spectrometry (SIMS) analysis revealed that PEALD SiO_2 films exhibit comparable C and N impurity levels to a thermally grown oxide film, with only 30% higher H content. The wet etch rate in 100:1 diluted HF was 1.5 Å/s, approximately twice that of thermal oxide (0.8 Å/s), indicating excellent film density. Transmission electron microscopy demonstrated outstanding conformality, with 98.6% step coverage for 10-nm-thick films on 20:1 aspect ratio hole patterns. Electrical characterization of 20-nm-thick PEALD SiO_2 films showed low leakage current density (0.7 nA/cm^2 at -2 MV/cm) and Fowler-Nordheim tunneling behavior at high electric fields, confirming high-purity, defect-free dielectric properties comparable to thermal SiO_2 ALD at 600-700°C [1]. The combination of high GPC, excellent conformality, and superior electrical properties makes this PEALD process promising for dielectric gap-fill applications in advanced semiconductor devices, particularly 3D NAND memory.

[1] C. Kim et al. "High-temperature high-growth-rate atomic layer deposition of SiO_2 using hexamethyldisilylamino-dimethylamino-silane," Appl. Surf. Sci. 723 (2026) 165606. https://doi.org/10.1016/j.apsusc.2025.165606

AF-MoP-34 Non-Pyrophoric Zinc Precursor AP–MDS™131: Extended ALD Window and Benchmarking Against Diethylzinc*, **Lukas Mai, Jan-Lucas Wree,* EMD Electronics, Germany*; Bhushan Zope, Randall Higuchi, Khang Ngo,* EMD Electronics*; Holger Heil,* EMD Electronics, Germany*; Sergei Ivanov,* EMD Electronics

Atomic layer deposition (ALD) of ZnO is a key enabling technology in advanced electronic and optoelectronic devices, but the benchmark precursor diethylzinc (DEZ) shows limited thermal stability in the higher temperature regimes required for next–generation processes. In this work, we evaluate a new zinc precursor, AP–MDS™ 131, with the dual objectives of improving high–temperature process robustness relative to DEZ (>150 °C for H_2O and >250 °C for O_3) and achieving lower, more controllable growth rates within well–defined ALD windows. Thermogravimetric and calorimetric data indicate that AP–MDS™ 131 combines usable volatility with enhanced thermal stability, supporting operation at elevated temperatures without precursor decomposition under ALD conditions; moreover, AP–MDS™ 131 is non–pyrophoric, in contrast to pyrophoric DEZ, which has clear handling and safety advantages.

Process studies show that both DEZ and AP–MDS™ 131 exhibit no detectable decomposition on SiO_2 under the tested high–temperature conditions, but they differ in desorption behavior and process windows. For O_3–based ZnO ALD, literature and internal data indicate that DEZ lacks a clear high–temperature ALD window due to strong desorption, whereas AP–MDS™ 131 provides a distinct high–temperature ALD window with only limited desorption at even higher temperatures. At representative conditions, both precursors display saturation behavior consistent with self–limiting ALD growth.

With H_2O as co–reactant, AP–MDS™ 131 enables an additional ALD window at intermediate temperatures, with well–defined saturation of both precursor and reactant and no evidence of decomposition on SiO_2. In comparison, DEZ/H_2O operates at lower temperatures and yields higher growth per cycle, whereas AP–MDS™ 131/H_2O provides substantially reduced growth rates within its window—a central development target to enable highly controlled, thickness–tunable processes. Across all investigated conditions, ZnO films from both precursors exhibit carbon below detection, near–stoichiometric O/Zn ratios, and high densities, demonstrating that the improved high–temperature capability and reduced growth rate of AP–MDS™ 131 are achieved without compromising film quality.

Overall, AP–MDS™ 131 expands the usable ALD window for ZnO toward higher temperatures for both O_3 and H_2O processes compared to DEZ, while offering lower, more manageable growth rates, non–pyrophoric handling, and maintaining high film purity and near–ideal stoichiometry—making it a strong candidate for tightly controlled ZnO ALD in microelectronics and display technologies.

AF-MoP-35 Indium Precursors Targeting ALD of Indium Films*, **David Ermert,* Entegris, Inc.

Multicomponent metal-oxide thin-film transistors (TFTs) are promising candidates for next-generation memory components owing to their high electron mobility and low-leakage properties. For example, Indium-Gallium-Zinc-Oxide (IGZO) films are candidates for channel materials in 3D DRAM. Given the aggressive features of proposed device architectures, ALD of IGZO type films will be required for vertical scaling. The incumbent precursor for many indium-containing films is $InMe_3$, a pyrophoric solid which presents physical challenges and limitations to widespread adoption and underscores the need for novel, safe, and suitable precursor chemistry to accommodate ALD growth.

We report, herein, on physical properties and thermal analysis of a structurally diverse collection of indium compounds, including known and novel compositions. We also present varied synthetic approaches to organometallic indium compounds with an emphasis on non-pyrophoric routes and reagents. In addition, we discuss In_2O_3 film growth from a newly developed non-pyrophoric organometallic indium precursor.

AF-MoP-36 Imaging Spectroscopic Ellipsometry as a Wafer-Scale Metrology Tool 2D TMDs*, **Mangesh Diware,* Park Systems Inc*; Michael Curtis,* Micron School of Materials Science and Engineering, Boise State University*; Ashton Enrriques,* Park Systems Inc*; David Estrada,* Micron School of Materials Science and Engineering, Boise State University

Imaging spectroscopic ellipsometry (ISE) combines spectroscopic sensitivity with spatially resolved measurements, providing a powerful, non-destructive approach for characterization of ultra-thin materials. In this work, ISE is applied to wafer-scale MoS_2 and WS_2 films deposited by atomic layer deposition, enabling simultaneous mapping of thickness and optical properties with micrometer-scale spatial resolution. This capability is well suited for deposition process development and uniformity assessment.

ISE measurements were performed over a broad energy range to capture excitonic and interband transition features characteristic of monolayer and few-layer transition metal dichalcogenides. The extracted dielectric functions exhibit well-defined excitonic resonances consistent with reported literature values, while wafer-scale thickness maps reveal both uniform regions and localized deviations. These results demonstrate the capability of ISE as a quantitative, high-throughput optical metrology technique for ultrathin films. The demonstrated approach is applicable to both research and manufacturing environments, providing scalable characterization of ultra-thin semiconductors.

AF-MoP-37 Developments in low growth rate aluminum oxide ALD with AP-MDS™ 026 and AP-MDS™ 027*, **Jan-Lucas Wree, Lukas Mai,* EMD Electronics, Germany*; Bhushan Zope,* EMD Electronics, USA*; Randall Higuchi,* EMD Electronics*; Khang Ngo,* EMD Electronics, USA*; Holger Heil,* EMD Electronics, Germany*; Sergei Ivanov,* EMD Electronics, USA

Precise thickness control in multilayer stacks motivates the development of aluminum oxide (Al_2O_3) atomic layer deposition (ALD) processes with intrinsically low growth-per-cycle (GPC). We evaluated new organoaluminum precursors—AP-MDS™ 026 and AP-MDS™ 027—against conventional chemistries (e.g., TMA, TDMAA, aluminum sec-butoxide, $Al(mmp)_3$) to identify process windows that reliably deliver low GPC while maintaining surface saturation, film uniformity and high conformality.

Across co-reactants, both H_2O- and O_3-based processes exhibited clear precursor saturation behavior, with O_3 generally yielding lower deposition rates than H_2O under otherwise comparable process conditions.

Benchmark GPCs spanned approximately 1.0–1.2 Å/cycle for TMA/O_3 and 0.8–1.0 Å/cycle for TDMAA/H_2O or O_3, decreasing to 0.4–0.5 Å/cycle for aluminum sec-butoxide/O_3 (<250 °C) while water processes always yield growth rates above 0.6 Å/cycle. Notably, AP-MDS™ 027 paired with O_3 enabled the lowest GPC regime observed, ~0.19–0.26 Å/cycle at 250–300 °C, while AP-MDS™ 026/H_2O and AP-MDS™ 027/H_2O both yielded ~0.6 Å/cycle under the measured conditions rendering them as suitable candidates for lowering the growth rate of aluminum oxide ALD with both ozone and water as co-reactants.

Early-cycle behavior (i.e. growth delay) was strongly precursor- and co-reactant-dependent and substrate effects on growth were more pronounced for AP-MDS™ 026 and AP-MDS™ 027 compared to conventional precursors. Moreover, process optimization emphasized the benefits of a less reactive, sterically bulkier yet volatile and thermally stable precursor for controllable Al_2O_3 ALD.

Collectively, these results establish O_3-driven and H_2O-driven AP-MDS™ 026 and AP-MDS™ 027 as a robust route to sub-0.3 Å/cycle and ~0.6 Å/cycle Al_2O_3 ALD, respectively. Our processes demonstrate that precursor selection, co-reactant and substrate choice provide orthogonal controls to tune nucleation and growth for angstrom-level thickness control in complex multilayer architectures.

AF-MoP-38 Inline XPS and Raman Metrology for Evaluating Integrity of Selectively Deposited Graphene During Thin Film Deposition*, Dominic Esan, Kitty Kumar, Ahmad Al-Kukhun, Wing-Shun Lam, Sisi Cao,* Intel Corp.*; **Ganesh Vanamu**,* Nova Ltd.*; Yinon Katz, Haim Prigozin, Lior Neeman, Tamar Hess,* Nova Ltd., Israel*; Sumegha Godara, Roland Barbosa,* Nova Ltd.

As semiconductor devices shrink below 2-nm, copper (Cu) interconnect reliability is increasingly constrained by electromigration and diffusion into surrounding dielectrics. Traditional capping layers such as Cobalt provide protection but add unwanted parasitic resistance and limit further scaling. Graphene offers a promising alternative due to its atomic thickness and high electrical conductivity [1-2]. However, integration of graphene in the back-end-of-line stack requires protection of graphene structure and properties from the downstream processing steps such as thin film deposition, etching, etc. This work investigates the impact of plasma assisted (DL1) and thermally grown (DL2) dielectric thin films on the graphene composition, thickness, and hybridization states using VeraFlex (XPS) and Elipson (Raman) metrology tools, developed by Nova Ltd. The study identifies key process–structure correlations and strategies to enable reliable graphene–dielectric integration in advanced interconnects.

Sensitivity of many graphene attributes, like layer-number identification, structural quality and defects, makes Raman spectroscopy a promising tool for process development [3-4]. Plasma deposition, which uses ions bombardment of the surface, can lead to significant damage to the substrate layers [5]. Here, we examine the extent of this effect in multiple scenarios. The Raman spectra reveals that the thermal DL2 layer deposited directly over Graphene had minimal impact on the Graphene's spectrum, while a plasma DL1 layer changed significantly. The significant change in graphene quality by DL1 is evident from the drop of the 2D peak intensity, indicating reduction in the quality of the graphene film as compared to pristine graphene and graphene_DL2 sample (Fig.1). On patterned wafers, the graphene quality deteriorates when exposed to the plasma deposition even when protected by one or few thermal layers. This damage is reflected in the reduction of the 2D peak amplitude and peak broadening. However, as the number of thermal layers increases, the extent of this damage diminishes (Fig.2), indicating DL2 can offer partial protection against plasma-induced damage. Complementary XPS analysis confirmed uniform deposition of both DL1 and DL2. Compared to the sp^2/sp^3 ratio derived from the C1s spectra of pristine graphene (Fig.3a), DL1 processing leads to a reduction in the sp^2/sp^3 ratio, indicating increased disorder, whereas optimized DL2 layers restore a higher sp^2 fraction, consistent with reduced damage (Fig.3b). Further, the results demonstrate uniform thermal DL2 growth and a clear correlation between DL2 thickness and graphene protection (Fig.4). These findings provide process-level insight into dielectric–graphene interactions and establish guidelines for integrating graphene with dielectric thin films in advanced interconnects.

AF-MoP-39 Design of Experiments Approach to Controlling ALD-Grown Hafnium Oxide Film Properties

Emily Wang, Tarun Maredla, Iryna Golovina, David Barth, ***Lucas Barreto,*** University of Pennsylvania

Hafnium oxide (HfO_x) is a versatile material with applications across multiple technological fields. Its compatibility with CMOS processes enables integration into microelectronic devices, where its high dielectric constant makes it an attractive alternative to silicon dioxide. In addition, hafnia exhibits a high refractive index, which is advantageous for optical and protective coating applications, while its excellent thermal stability supports use in high-temperature environments.

Atomic layer deposition (ALD) provides precise control over the growth of HfO_x thin films, with process parameters strongly influencing the deposition rate and resulting film properties. In this work, we investigate the effects of deposition temperature, precursor pulse time, and purge time on the properties of thermal ALD-grown HfO_x films. A full-factorial design of experiments is employed to systematically evaluate how these parameters affect growth per cycle, refractive index, and film density.

We use tetrakis(dimethylamido)hafnium (TDMAH) as the metal precursor, and H_2O as the oxygen source. We measure the film refractive index using spectroscopic ellipsometry and the film density using X-ray reflectivity. The analysis enables identification of the statistically relevant factors and how factor interactions influence each response, providing optimal ALD process conditions to tune HfOx deposition.

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