ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF-MoA

ALD Precursor Design I

Moderators: Rick Chen, The Electronics business of Merck KGaA Darmstadt, **Atsushi Sakurai**, ADEKA CORPORATION

4:00pm **AF-MoA-11 Bridging Code and Chemistry: The Origin of Precursor Decomposition***, **Seungjin Song**, Ga Youn Lee, Dexter Dimova, Sean Barry,* Carleton University, Canada

Yttrium (Y) and scandium (Sc) play critical roles in high-k material by forming Y_2O_3 and Sc_2O_3 high-k dielectric oxides, so that they can suppress leakage current and improve thermal stability in advanced semiconductor devices. Conventional Cp- and β-diketonate-based precursors suffer from limitations such as high deposition temperatures, low surface reactivity, and carbon contamination. Therefore, the development of next-generation Y and Sc precursors with high volatility, strong reactivity, and low impurity incorporation is essential for future nanoscale device fabrication.

Our group uses a silicon-containing ligand to prepare the homoleptic Y and Sc precursors and investigates the origin of thermal decomposition in precursors containing highly basic ligands. We synthesized the homoleptic group 3 precursor using salt metathesis and acid-base reaction. Our product was characterized through nuclear magnetic resonance (NMR) spectroscopy and single-crystal X-ray diffraction (SC-XRD). We investigated the thermal properties of the complex by thermogravimetric analysis and, using flame-sealed samples in a glass tube, revealed the origin of the thermal decomposition mechanism by NMR spectroscopy and density functional theory (DFT) calculations with Eyring analysis.

Our DFT calculations and Eyring analysis allow us to identify the key structural point in the precursors to prevent thermal decomposition. This talk will focus on connecting the experimental observations and DFT calculations through the Eyring analysis. The presentation will show a detailed synthesis and characterization, and mechanistic thermal decomposition pathways for a representative methodology on how we connect the DFT calculations and experimental observations.

4:15pm **AF-MoA-12 Multi-Objective Discovery of New Precursors for ALD with Steerable Generative AI***, **Tristan Deleu**,* Entalpic, Canada*; Alexandre Duval,* Entalpic, France

Advances in atomic layer processes are often constrained by the limited availability of precursors that satisfy an increasingly complex set of requirements for the deposition of specific thin films. The development of novel precursors for ALD poses unique challenges in organometallic chemistry, where ideal candidates must balance multiple objectives simultaneously. For example, they must be stable at room temperature for safe storage in liquid form and possess a volatility range that matches the optimal ALD temperature window, all while guaranteeing proper reaction with the substrate to avoid contamination. While historically the design of new compounds has often relied on experience and chemical intuition, there is now an opportunity to leverage modern tools from artificial intelligence (AI) to navigate this massive chemical space at scale and accelerate discovery.

At Entalpic, we are building a platform that applies cutting-edge generative AI to find a wide range of new candidate precursors. Our approach integrates a collection of prediction models, each of them targeting desirable properties for ALD, to steer our generative models towards molecules of interest within a multi-objective optimization framework. We first train a general-purpose model capable of generating organometallic complexes, based on open-data available through initiatives such as LeMaterial. Depending on controllable settings, the model can either construct new molecules from an existing library of ligands available for purchase, or discover new ligands altogether while ensuring synthesizability of the final complexes.

Recognizing that ligands in transition metal complexes play an essential role in determining their properties, we train a variety of machine learning (ML) models, such as transformers, graph neural networks (GNNs), and machine learning interatomic potentials (MLIPs), to accurately predict vapor pressure and other critical parameters, while ensuring robust generalization to new ligands. These predictive models then provide a feedback signal to guide our pre-trained generative model with reinforcement learning (RL). Finally, these molecules suggested by the fine-tuned generative model undergo a series of thermodynamic screening steps to narrow down the set of promising candidates that can be submitted to the lab for evaluation.

4:30pm **AF-MoA-13 First-Principles Screening of Precursors and Inhibitors to Achieve Enlarged-Grain MoS_2 Through Area-Selective Deposition***, **Bram van der Linden**,* KU Leuven and Imec, Belgium*; Geoffrey Pourtois, Sergiu Clima,* IMEC, Belgium*; Ian Campbell,* IMEC*; Pierre Morin, César Javier Lockhart de la Rosa,* IMEC, Belgium*; Ageeth Bol,* University of Michigan, Ann Arbor*; Annelies Delabie,* KU Leuven and Imec, Belgium

MoS_2 is a promising channel material for field-effect transistors, owing to its superb intrinsic carrier mobility at nanoscale dimensions. While Atomic Layer Deposition (ALD) enables conformal deposition of MoS_2, it typically yields nanocrystalline layers with low mobility due to grain-boundary scattering. Enlarged MoS_2 grain sizes are essential to obtain the mobility needed for nano-electronic devices. This may be achieved through inhibitor molecules that passivate part of the reactive groups at the initial surface, thus reducing the number of sites available for nucleation. The vast number of possible precursor-inhibitor combinations makes experimental assessment too time-consuming and costly. We therefore use first-principles thermodynamic simulations to evaluate the two most important criteria for achieving large MoS_2 grain sizes using surface inhibitors: highly reactive molybdenum precursors and sulfur co-reactants, and effective surface inhibitors that block adsorption of the molybdenum precursors and sulfur co-reactants.

To enable efficient screening of precursors and inhibitors, we developed a three-step first-principles thermodynamic approach. Using this framework, we assess the reactivity of 14 molybdenum precursors reported for the growth of various molybdenum-based materials, with H_2S as the sulfur source. The precursor reactivity is evaluated in combination with 15 SiO_2 surface (passivation) chemistries under typical low–temperature ALD conditions (200°C, 0.1Torr). First, we evaluate the thermodynamic driving force for each precursor to form monolayer-thin MoS_2 crystals of various sizes. $Mo(NMe_2)_4$ is the only precursor that exhibits strong thermodynamic driving forces for forming all tested grain sizes, consistent with the low ALD growth temperature (60°C) reported for this precursor[1]. For all precursors, reactivity improves with increasing grain size. In addition, we could identify new promising precursors for MoS_2 ALD, such as $MoCl_4O$. Second, we use a SiO_2 cluster model to calculate the reaction energies of molybdenum precursors and H_2S with the reactive surface hydroxyl groups and candidate surface-passivation groups. -Si-F emerges as one of the most promising surface passivation groups, as precursor reactions yield largely endothermic reaction energies, suggesting strong inhibition of MoS_2 growth. Third, to verify the results of the SiO_2 cluster approach, we compute the reaction energies for selected precursor-inhibitor combinations using a periodic SiO_2 surface slab model. The combined use of cluster and slab models enables efficient screening of precursors and inhibitors, ultimately identifying promising ALD process conditions that yield films with enlarged MoS_2 grains.

(1) T. Jurca et al. Low-Temperature Atomic Layer Deposition of MoS_2 Films. *Angew Chem Int Ed* **2017**, *56* (18), 4991–4995.

4:45pm **AF-MoA-14 Molecular–Level Insight Into Thermal Stability and Substrate–Dependent Nucleation of DDAP for Platinum ALD***, **Tomohiro Tsugawa**, Hideaki Nakatsubo, Yohei Kotsugi, Ryosuke Harada,* TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd., Japan

Platinum (Pt) thin films are widely utilized in advanced semiconductor devices due to their low resistivity, high work function, catalytic activity, and excellent thermal stability. Atomic layer deposition (ALD) of Pt is essential for achieving film thicknesses below 20nm with superior conformality in high–aspect–ratio 3D structures. However, stable and uniform Pt–ALD remains difficult because conventional precursors exhibit limited thermal stability, insufficient volatility, and substrate–dependent nucleation behavior that is not yet fully understood.

In this work, we investigate the Pt precursor DDAP (Dimethyl-(3,4–*η*)-*N*,*N*–dimethyl–3–butene–1–amine–*N*)platinum(II), $C_8H_{19}NPt$), which has demonstrated high ALD growth rates and low–resistivity Pt films using O_2 as a reactant [1, 2]. Despite its promising performance, the molecular–level origins of its thermal stability and substrate–specific growth characteristics have remained unclear. We present a combined experimental and simulation study such as density functional theory (DFT) to clarify these mechanisms.

DFT analysis identifies intrinsic thermal decomposition pathways and activation barriers consistent with the experimentally observed onset of precursor decomposition near 275 ℃, providing mechanistic insight into the established ALD process window. Furthermore, adsorption energetics were evaluated on technologically relevant surfaces including Pt, Cu, TiN, and oxide substrates such as OH–terminated SiO_2, Al_2O_3, and ZrO_2. DDAP exhibits weaker adsorption on oxide surfaces compared to metals, correlating with delayed nucleation and non–uniform initial Pt growth observed experimentally on SiO_2.

By linking ALD behavior directly to DFT–derived energetics, this study provides a molecular–level explanation for DDAP's thermal properties and substrate–dependent nucleation phenomena. These insights offer guidance for designing next–generation Pt precursors optimized for highly conformal and substrate selective ALD processes.

References

[1] Se-Hun Kwon et. al*., Chem. Mater.* **2019**, *31*, 5056-5064.
[2] Soo-Hyun Kim et. al., *J. Vac. Sci. Technol. A* **2020**, *38*, 032404.

5:00pm **AF-MoA-15 Theoretical Analysis on Organic Sulfur Sources for Atomic Layer Deposition of MoS_2***, Myeong Kyun Nam,* Hongik University, Republic of Korea*; Bonggeun Shong,* Hanyang University, Republic of Korea

Molybdenum disulfide (MoS_2) is widely recognized as a promising two-dimensional semiconductor material. Atomic layer deposition (ALD) can provide a scalable route for the controlled synthesis of MoS_2. Conventional ALD processes of sulfides often employ H_2S as the sulfur source; however, its extreme toxicity has motivated development of benign alternative sulfur sources. Previous studies have reported MoS_2 ALD processes using organic sulfur precursors such as diethyl sulfide (DES) and diethyl disulfide (DEDS), in combination with $Mo(CO)_6$ as the molybdenum precursor [1]. Experimental results indicate that DEDS achieves higher growth rates and more efficient nucleation than DES [1]. In this work, density functional theory (DFT) and machine learning interatomic potential (MLIP) calculations are employed to elucidate the chemical reaction mechanisms and fundamental origins of the distinct reactivities of DES and DEDS during MoS_2 ALD. MoS_2 edge models with thermodynamically stable hydrogen coverages are constructed under appropriate temperature and pressure conditions. Adsorption of $Mo(CO)_6$ on these surfaces exhibits self-limiting behavior, consistent with the characteristics of ALD processes. Subsequent reactions with DES and DEDS are investigated with emphasis on the removal of residual CO ligands bound to surface Mo. Our results reveal that the cleavage of the S-S bond, present only in DEDS, is relatively facile in contrast to the cleavage of the C-S bonds. Current research could contribute to a deeper understanding of the chemistry behind sulfide ALD, and provides insights into utilization of organic reactants in ALD.

References [1] Adv. Mater. 29, 47, 1703031 (2017)

5:15pm **AF-MoA-16 A Data-Science Approach to the Analysis of Temperature-Dependent Alumina Atomic Layer Deposition Growth Per Cycle***, Raymond Adomaitis,* University of Maryland

Temperature-dependent alumina atomic layer deposition (ALD) growth per cycle (GPC) data were collected from nearly 40 studies of the trimethylaluminum (TMA)/water ALD process. The data were used in multiple regression approaches based on fitting the data to globally defined polynomials in temperature T, and two linear piecewise-continuous representations of the fitted data, each patterned after the hypothesized existence of an ALD window exhibiting constant or linear GPC(T) dependence. All three regression approaches identified a low-T region characterized by rising GPC with T, reaching a maximum of approximately 1.1 A/cycle slightly below 200 deg. C, followed by a slower decline in GPC with T after this point. The results indicate that a temperature-independent ALD window for the TMA/water system may be relatively small (with lower and upper limits of 177 and 208 deg. C, respectively), if it exists at all. Multiple approaches to statistical analysis of the validity of observed trends will be presented.

Reference

Adomaitis, R. A., "Regression analysis of temperature-dependent alumina atomic layer deposition growth per cycle using trimethylaluminum and water as precursors," J. Vac. Sci. Technol. A 43 062406 (2025) DOI: 10.1116/6.0004738

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.

This work was supported by the Israel Science Foundation (Grant No. ISF 1755/23) and by the Israel Ministry of Science and Technology (Grant for Proposal No. 0007465).
The work is the subject of a pending U.S. patent application (No. 63/844,832).

The first author gratefully acknowledges support from Ariel University through a Ph.D. scholarship.

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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.

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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 350ºC, 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 250ºC[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 100ºC upstream of the substrate, and to substrate temperature (>150ºC) 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)], IGZO[2)], IGO[3)], IWO[4)], and ITO[5)] 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™, for the ALD of high-quality Ta_2O_5 thin films.

2. EXPERIMENTAL

A novel liquid Ta precursor, RosiTa™ was synthesized and characterized. Its thermal properties and volatility were evaluated by thermogravimetric analysis (TGA). RosiTa™ 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™ 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™. 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™ has been successfully used for the ALD of high-quality Ta_2O_5 thin films. RosiTa™ 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™ 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 $R\text{depα}PAPB5/2$, and (2) self–etch, $2MoCl_5 + Mo \rightarrow MoCl_4 + Mo_2Cl_6$, with rate with rate $R\text{depα}PAPB5/2$. 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.

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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}.

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (grant No. RS-2025 25396489) and this work was supported by K-CHIPS(Korea Collaborative & High-tech Initiative for Prospective Semiconductor Research) (2410011219, RS-2023-00237030, 23027-15FC) funded by the Ministry of Trade, Industry & Energy(MOTIE, Korea).

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, $(Me_3Si)_2N$-SiH_2-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.

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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.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-TuM

ALD Precursor Design II

Moderators: Seán Barry, Carleton University, Canada, **Charles H. Winter**, Wayne State University

8:00am **AF1-TuM-1 Development in Thermal ALD Chemistry since 2010**, ***Markku Leskelä***, University of Helsinki, Finland; *Georgi Popov,* ASM Microchemistry Ltd., Finland; *Miika Mattinen, Mikko Ritala,* University of Helsinki, Finland

We recently published a review on the recent trends in thermal ALD chemistry (1). The review highlighted new ALD precursors and process chemistries based on the ALD database found in atomiclimits.com (2) until the end of 2023. The paper compared the processes published before 2010 (769 processes) to those published after 2010 (942 processes). The number of materials deposited by thermal ALD shows steady increase being 227 before 2010 and reaching 539 at the end of 2023. The most popular material group is oxides which are processed both as binary and ternary compounds.

The ALD process development can be divided to two categories: curiosity and application driven research. In the curiosity driven research the aim is to expand the portfolio of ALD processes by adding new elements and materials to the portfolio. From recent literature ALD processes for less common elements Be, Re, Os can be mentioned. However, the development of new ALD processes is clearly more application-driven and motivated by the most important application areas of ALD: microelectronics, energy technology, and catalysis. Need of new materials in these applications is seen in increased intensity of the development of ALD processes for metals, 2D transition metal dichalogenides, and halides

Metal halides, alkoxides, alkyl compounds, β-diketonates, and amides/imides are traditional ALD metal precursors. After 2010, amides/imides have increased their importance in new ALD processes. However, heteroleptic complexes containing two or more above mentioned ligands are the largest precursor type in new processes. Metal processes require the use of reducing agents and therefore research on novel reducing agents is vital.

In the presentation we summarize our most important findings from ALD literature between 2010 and 2023 and highlight the newest results from the last two years. The number of published new processes in 2024-2025 seems to stay at the level of the previous years.

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8:15am **AF1-TuM-2 Designing Stable Organosilane Precursors for High Quality Silicon Oxide**, ***Taylor Hayes***, *Anji Patel, Matthew MacDonald, Manchao Xiao, Haripin Chandra,* EMD Electronics, The Electronics business of Merck KGaA, Darmstadt, Germany

High-quality silicon oxide in a 3D NAND structure is an important material used as an electrical insulator and to form charge trap layers. Additionally, due to the nature of the 3D NAND structure, which achieves an extremely high aspect ratio with several hundred layers, atomic layer deposition (ALD) is critical for obtaining a conformal, high-quality SiO_2 film.

In general, process temperature correlates with film quality; higher process temperatures yield higher quality films. However, in ALD depositions, higher process temperatures necessitate that the organosilane precursor remains stable and self-limiting.

In this paper, we will discuss methods to improve the thermal stability of common organosilane precursors, such as tris(dimethylamino)silane (3DMAS), and evaluate decomposition mechanisms using density functional theory (DFT) modeling.

The Si–H bond in 3DMAS is the weakest link and is prone to thermal decomposition. Replacing the Si–H bond with a Si–CH_3 bond, as seen in tris(dimethylamino)methylsilane (3DMAMS), enhances thermal stability by reducing the energetic feasibility of decomposition pathways. Furthermore, substituting the amino group with a CH_3 group, as in dimethylaminotrimethylsilane (DMATMS), also improves precursor thermal stability.

This paper will explore how higher deposition temperatures and molecular structure significantly influence the experimental film properties achieved using 3DMAS, 3DMAMS, and DMATMS.

8:30am **AF1-TuM-3 Development of Novel Liquid Zr Precursors with Excellent Thermal Stability for High-Temperature ALD Processes in Next-Generation DRAM Capacitors**, ***Taeyoung Lee***, *Sunyoung Baik, Sungjun Ji, Shinbeom Kim, Woongjin Choi, Kunhee Kim, Yiun Park, Sangbum Han,* EGTM Co., Ltd. R&D Center, Republic of Korea

With the continuous scaling of DRAM devices, dielectric materials that possess both excellent conformality in high aspect ratio structures and high dielectric constants (high-k) have become increasingly critical. Typically, high-temperature deposition processes are essential for the formation of the tetragonal phase of ZrO_2 thin films, which maximizes the dielectric constant. However, conventional cyclopentadienyl (Cp)-based Zr precursors suffer from limited thermal stability at high temperatures, leading to significant issues such as carbon impurity incorporation and particle generation. To address these challenges, we developed a novel liquid Zr precursor (EGTM Zr) with significantly improved thermal stability compared to conventional precursors. Thermal analysis (TGA and DSC) and visual thermal stability tests confirmed that EGTM Zr exhibited negligible discoloration or decomposition residues even after prolonged exposure to temperatures exceeding 200°C. Furthermore, its thermal decomposition temperature was 312°C, approximately 10°C higher than that of the conventional Cp-Zr precursor. Notably, ALD process evaluations demonstrated that the EGTM Zr precursor has a wider ALD process window of 280–380 °C, which is approximately 80°C wider than that of the reference precursor due to its enhanced thermal stability. This wider window allows for higher process temperatures, which promotes the formation of the high-k tetragonal crystalline phase instead of the lower-k amorphous phase, thereby enhancing device performance. Moreover, thanks to its excellent thermal stability, the EGTM Zr precursor can effectively eliminate issues related to carbon impurity incorporation and particle generation. Additionally, the precursor demonstrated superior step coverage compared to the reference, while the widened process window enables the deposition of high-quality, uniform thin films. Consequently, the EGTM Zr developed in this study is expected to be a promising candidate for next-generation high-performance DRAM capacitor applications.

8:45am **AF1-TuM-4 A New Zinc Amidinate Precursor for Thermal and Plasma-Enhanced ALD of ZnO**, ***Pierre-Alexandre Escarcega***, *Jean-Pierre Glauber, Lars Giebeler, Harish Parala, Anjana Devi,* IFW Dresden, Germany

As an n-type semiconductor with remarkable electronic and optical properties, zinc oxide (ZnO) is applicable for various applications. Its wide direct bandgap of 3.3 eV and large exciton binding energy of about 60 meV make it especially promising for use in optoelectronics.[1] Further attributes, including high electron mobility, optical transparency, piezoelectricity, and biocompatibility, render it a versatile material fordiverse technological applications, includingchannel layer in thin-film transistors (TFTs)[2,3] or sensing.[4] However, the integration and efficiency of ZnO in advanced technologies depend on overcoming fabrication challenges to reliably produce high-quality, high-purity thin films and nanostructures. In this regard, atomic layer deposition (ALD) and its variant, plasma-enhanced ALD (PEALD),[5] were shown to enable the deposition of high-quality, stoichiometric, and conformal films, with atomic-level control over film thickness, even at low temperatures. Despite the sophistication of such deposition techniques, developing advanced processes requires new precursors with optimized properties to broaden process windows and enhance film characteristics.

Our group recently reported a versatile Zn precursor, $[Zn(DMP)_2]$,[6] a non-pyrophoric alternative to the widely used DEZ, enabling the growth of high-purity ZnO thin films via ALD and PEALD over a broad temperature range. The ZnO thin films were mainly amorphous or of low crystallinity. In our recent attempts to identify new Zn precursors that can enable crystalline ZnO layers at low temperatures, we were successful in synthesizing bis(N,N'diisopropylacetamidinato)zinc, $[Zn(dpamd)_2]$. The target compound was successfully synthesized by stabilizing the central zinc atom through the delocalized π system of the amidinate ligand backbone.[7]While this ligand enhances the thermal stability, its all-nitrogen coordination guarantees sufficient reactivity.

$[Zn(dpamd)_2]$ is a volatile compound with physico-chemical properties suitable for both thermal and plasma ALD. Additionally, its synthesis can be scaled up, and it is non-pyrophoric, a significant advantage for safety and handling. The thermal properties of $[Zn(dpamd)_2]$ were examined using

thermogravimetric analysis (TGA) (Figure 1), which showed promising evaporation behavior. Based on these results, [Zn(dpamd)$_2$] was used in a thermal ALD process with water as the co-reactant, as well as in a PEALD process with O_2 plasma as the co-reactant. Both methods yielded stoichiometric, high-purity ZnO thin films on Si(100) substrates with self-limiting growth, confirming [Zn(dpamd)$_2$] as a promising and versatile new ALD precursor.

9:00am **AF1-TuM-5 Amidates and Dimethylaminopropyl Groups as Innovative Ligands: New Opportunities for Ru Precursors***, **Jorit Obenlüneschloß**,* Leibniz Institute, IFW Dresden, Germany*; Niklas Huster,* Ruhr University Bochum, Germany*; Harish Parala,* Leibniz Institute, IFW Dresden, Germany*; Michael Gock, Michael Unkrig-Bau, Detlef Gaiser,* Heraeus Precious Metals GmbH & Co. KG, Germany*; Anjana Devi,* Leibniz Institute, IFW Dresden, Germany

As the semiconductor industry moves to the 2 nm node and below, Cu as well-established interconnect material in integrated circuits (IC's), is reaching its limits due to diffusion and electromigration. Ru is the most promising replacement candidate in next-generation microchips as the interconnect metal.[1] Its resistivity is less dependent on thickness than that of Cu and Ru can be introduced without liner or diffusion barrier layers.[2] A reduction of up to 60% in resistance is expected when Ru vias are used with Cu wires.[3]

To deposit thin films uniformly on complex-structured substrates, such as those in next-generation gate-all-around field-effect transistors (GAAFETs), atomic layer deposition (ALD) is the preferred method. However, finding suitable Ru precursors that meet ALD requirements, such as high vapor pressure, thermal stability, and high reactivity, is a challenging task for researchers in both academia and industry.

Herein, we showcase and compare two Ru precursors with novel ligand concepts:**[η5-CpRu(CO)$_2$(DMP)]** or dicarbonyl(η5-cyclopentadienyl)(3-dimethylaminopropyl)ruthenium, trade name **HeRu31**,[4]and **[Ru(CO)$_2$(N-*s*BuiPrAD)$_2$]** or dicarbonyl bis(*sec*-butylisopropylamidate)ruthenium, trade name **HeRu43**.[5] The former combines the proven half-sandwich structure dominated by a Cp ring with an aminopropyl ligand, which enhances the compound's stability while maintaining excellent reactivity. The reactive Ru-C bonds of this precursor enable facile deposition of Ru metal. The latter precursor relies on the 1,3-N,O-chelating amidate ligand. Introducing mixed N,O-coordination is a promising approach to prevent carbon contamination in deposited thin films. This coordination should also enable facile deposition via the Ru-N bond.

Employing both concepts, complexes with promising thermal properties for ALD have been obtained, as evidenced by TGA (Fig. 1). Both classes are liquid at room temperature, a highly desirable trait for a precursor intended for large-scale implementation. The compounds were identified and thoroughly characterized by NMR, LIFDI-MS, FTIR, EA, and SC-XRD. An ALD process using **HeRu31** and O_2 was developed to deposit dense, homogeneous Ru metal thin films at 280 °C with low resistivities. These new precursors show great promise to advance the deposition abilities for Ru and enable the foreseen adaptation of Ru at the smallest levels of ICs.

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9:15am **AF1-TuM-6 Functional Precursor-Driven High-k Atomic Layer Deposition with Improved Throughput and Dielectric Performance***, **Min Chan Kim**, Seong A Shin, Hae Lin Yang, Jin-Seong Park,* Hanyang University, Korea

With rapid AI advancements intensifying semiconductor demands, interest in high-k dielectrics for logic and memory applications is increasing [1]. High-k materials enable strong gate control with reduced equivalent oxide thickness (EOT), overcoming scaling limitations. Their high dielectric constant primarily arises from strong ionic polarization associated with a narrow bandgap. However, this narrow bandgap lowers the energy barrier for carrier injection, making high-k dielectrics susceptible to increased leakage current. Elevated leakage leads to charge trapping, which degrades threshold voltage stability and overall device reliability [2]. Consequently, suppressing leakage current is essential for practical high-k integration.

In this study, we present a strategy to stabilize high-k dielectric thin films through the incorporation of a functional precursor during film growth. Density functional theory (DFT) calculations reveal that the functional precursor, introduced between the metal precursor and the reactant, induces a β-hydrogen elimination reaction that selectively removes residual bulky ligands, thereby exposing reactive surface sites and promoting a chemically stabilized growth surface. This ligand removal mechanism is experimentally confirmed by secondary ion mass spectrometry (SIMS), which shows a pronounced reduction in residual carbon and hydrogen species. Importantly, ligand elimination does not result in void formation but instead facilitates the formation of a denser and chemically more stable dielectric film. X-ray photoelectron spectroscopy (XPS) analysis further indicates a reduced oxygen vacancy concentration and an increased metal–oxygen (M–O) bonding ratio, accompanied by increased film density and reduced surface roughness. As a result of this combined chemical and structural stabilization, metal–insulator–metal (MIM) capacitor measurements exhibit a substantial suppression of leakage current and an increase in the dielectric constant. These results demonstrate that functional-precursor-assisted stabilization effectively mitigates leakage-induced reliability degradation while preserving the intrinsic advantages of high-k dielectrics.

Reference

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9:30am **AF1-TuM-7 From Facile Routes for Mid-Valent Molecular Synthons to Vapor Phase Growth of Molybdenum-Based Thin Films***, **Titel Jurca,*** University of Central Florida **INVITED**

ALD technology is established in semiconductor manufacturing and is emerging across broad areas of biotechnology to catalysis. The broad range of substrates, deposition temperatures, and other environmental factors governing the growth and fabrication of this myriad of materials and devices is underpinned by the availability of suitable molecular precursors. Thus, the understanding-based design of novel molecular precursors is pivotal to the continued development of ALD and related vapor phase thin film growth processes (area selective ALD, ALE, CVD). One can envision that a broad range of temperature windows, and ligand chemistries to enable nucleation and subsequent growth are necessary; as well as the design rules to tune those properties on the molecular scale. Currently, the scope of available molecular precursors across the majority of metals of interest is narrow, as is the understanding-based knowledge which governs their design.

For practical reasons, the majority of precursor synthesis often stems from a narrow pool of stable, commercially available, and often fiscally reasonable metal halide precursors. To broaden the pool of ALD precursors, we begin by broadening the pool of accessible metal halide salts; *the precursors to the precursors*. Using stoichiometric silanes, high-valent, mid d-block metal (e.g. Mo, W, Nb, Ta) halides can be controllably, stoichiometrically reduced to highly reactive mid-valent synthons (e.g. $MoCl_3$ from $MoCl_5$). The reactions are facile and produce only H_2 and recoverable and reusable chlorosilanes as byproduct. The resulting mid-valent metal chlorides form ideal starting points towards new precursors for ALD.

From this thrust, we leveraged an $MoCl_3$ synthon to generate the first homoleptic Mo(III)tris-amidinate and guanidinate species. These complexes expand the known scope of tris(amidinate) and tris(guanidinate)M(III) molecules to now include Mo, and add to the very limited knowledge of homoleptic mononuclear Mo(III) coordination complexes. We explore the impact of modifications to the ligand framework, and their implications on synthetic viability, volatility and applicability towards the growth of Mo-based materials by ALD.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-TuM

Powder ALD

Moderators: Arrelaine Dameron, Forge Nano, **Benjamin Greenberg**, Naval Research Laboratory

10:45am **AF2-TuM-12 ALD on Particulate Materials: Applications & Scale-Up*, J. Ruud van Ommen,*** Delft University of Technology, Netherlands **INVITED**

Atomic layer deposition (ALD) has been extensively investigated for a wide range of applications and is already used commercially in the semiconductor industry, which predominantly relies on planar substrates. However, the intrinsic ability of ALD to coat nearly any surface geometry with atomic-scale thickness control makes it highly appealing for the coating of particulate materials (particles) as well. Recently, we published a review paper with a quantitative analysis of 799 articles from this field, published from 1988 to 2023 [1]. The obtained dataset is the basis for abstractions regarding reactor types (specifically for particles), coating materials, reactants, supports, and processing conditions. Furthermore, the dataset enables direct access to specific processing conditions.

In this presentation, I will give some examples of ALD on particulate materials we have worked on in my group over the past years, such as pharmaceuticals, batteries, catalysts, and rubber tires. ALD can be used to give pharmaceutical particles delayed-release properties. Battery materials provided with an ALD-made, ultrathin coating have a longer lifetime. This approach of reducing degeneration can also be applied to catalysts, while the island-growth mode can be used to make catalysts in a very controlled way. Finally, replacing carbon black with nanosilica can improve the performance of rubber tires. Treating the nanosilica surface with molecular layer deposition can make it less polar, and enhance the mixing with the rubber during production.

For many of the above applications, it is important to process large amounts of particles, to be able to scale up. Scale-up of ALD on particles is quite different from that on wafers, due to the much larger surface area involved. Proper scale-up of ALD on particulate materials encompasses several aspects, including efficient use of reactants, consistent product quality, and safe operation. I will discuss these aspects, and show some different ways of achieving a large-scale process.

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11:15am **AF2-TuM-14 Temperature-Variation Atomic Layer Deposition: A Strategy for Tuning Particle Size and Dispersion toward High-Performance Catalysts*, Manh Duc Dang, Dieu Minh Nguyen,*** Phenikaa University, Viet Nam*; Sri Sharath Kulkarni, J. Ruud van Ommen,*** Delft University of Technology, Netherlands*; **Hao Van Bui,*** Phenikaa University, Viet Nam

Precise control over the metal nanoparticle size and dispersion is critical for the synthesis of high-performance catalysts, yet remains challenging due to particle migration and sintering on substrate surfaces. Here, we introduce a temperature-variation atomic layer deposition (TV-ALD) strategy to regulate nucleation and growth of noble metals, demonstrated for the deposition of sub-nanometer Pt on carbon nanopowders by ALD in fluidized bed reactors. By varying the deposition temperature within each ALD cycle, the interplay between the surface chemisorption and the metal species mobility can be manupulated. In particular, the precursor exposure at elevated temperatures ensures efficient chemisorption and nucleation, while the subsequent oxidant exposure at low temperatures suppresses surface diffusion and coalescence of Pt species. This temperature-variation approach enables the formation of highly dispersed Pt species with significantly narrower particle size distributions compared with conventional isothermal ALD processes. Transmission electron microscopy and surface analyses confirm the presence of sub-nanometer Pt clusters with enhanced dispersion across high-surface-area supports. The improved structural control translates directly into enhanced catalytic performance despite a substantially reduced Pt loading. The proposed TV-ALD strategy demonstrates a simple yet powerful process parameter for controlling the nucleation and growth in ALD, providing a scalable pathway toward the synthesis of size-selective noble metal nanoparticles and highly dispersed catalysts.

11:30am **AF2-TuM-15 Achieving Conformality in Fluidized Bed Atomic Layer Deposition on Ultrafine Cohesive Nanopowders*, Austin Cendejas,*** *Benjamin Greenberg, Kevin Anderson, James Wollmershauser, Boris Feygelson,* Naval Research Laboratory

Nanoparticles with thin, conformal coatings are of significant interest in a growing number of applications including catalysis, battery technologies, and optoelectronics.[1] Fluidized bed atomic layer deposition (FB-ALD) is a promising technique towards scaling up the batch sizes of these coating processes to industrially relevant scales.[2] A significant challenge emerges as substrate particle size decreases and powders become increasingly “sticky”, or cohesive, and persistent agglomeration directly affects the conformality of coatings. In this work we explore several techniques to improve fluidization behavior and ultimately coating conformality of 35 nm diameter Y_2O_3 nanoparticles. Two modes of agitation are explored including vibration and mechanical stirring. Additionally, two coating materials are employed, Al_2O_3 and MgO, providing insight into contributions from precursor molecule size, sticking coefficient, and partial pressure. Each half-cycle of the FB-ALD process is analyzed not only on the reactor scale, but simultaneously on the microscale as persistent porous agglomerates undergo an infiltration-like ALD diffusion-reaction process on the time scale of precursor pulses.[3,4] Quadrupole mass spectrometry is used for in situ diagnostics of reaction progress and both scanning and transmission electron microscopy accompanied by energy dispersive X-ray spectroscopy are used to assess uniformity and conformality of the ALD coatings.

Funding source: NRL base funds, NRC Postdoctoral Fellowship Program

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11:45am **AF2-TuM-16 Atomic Layer DepositionEnabled Control of Densification and Grain Size in ZnO Ceramics*, Eric Bissell,*** *Anna Zachariou, Jacob Furst, Steve Lass,* University of Central Florida*; Nicholas G. Rudawski,* University of Florida, Gainesville*; Fernando Uribe-Romo, Titel Jurca, Kathleen Richardson, Romain Gaume, Parag Banerjee,* University of Central Florida

Atomic layer deposition (ALD) provides a versatile approach for applying conformal, nanometer-scale coatings to ceramic nanopowders, offering a means to influence grain-boundary chemistry during sintering. In prior work, ALD Al_2O_3 coatings on ZnO nanoparticles were shown to suppress grain growth;1 however, when consolidated under hot-pressing conditions, this grain growth suppression was accompanied by incomplete densification. These observations motivate a more systematic investigation of how sintering parameters affect densification behavior in ALD-modified powder systems.

In this study, ZnO nanoparticles with an average diameter of 60 nm were coated with 10 cycles of ALD Al_2O_3, corresponding to a nominal coating thickness of ~1 nm, and consolidated by hot pressing using a design of experiments (DOE) approach. The effects of maximum hold temperature (850–1000 °C), applied pressure (25–50 MPa), and hold time at peak temperature (1–120 min) were examined while maintaining identical heating ramps, cooling, and tooling conditions. Eight ceramic samples were produced, spanning a representative subset of the processing space.

The resulting ceramics exhibit systematic variations in relative density and average grain size, indicating that densification behavior remains sensitive to processing conditions despite strong ALD-induced grain growth suppression. This behavior is particularly relevant for transparent ceramic systems, where achieving high density while maintaining sub-wavelength grain sizes is necessary to reduce birefringence- and grain-boundary-related optical scattering. Taken together, these results provide an empirical basis for relating sintering parameters to final microstructure in ALD-coated ZnO systems and illustrate how DOE-based process exploration can inform the development of ALD-enabled ceramics with tunable density and grain size.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-TuA

ALD Metrology/Characterization I

Moderators: Dennis Hausmann, Lam Research, **Ruud van Ommen**, Delft University of Technology

1:30pm **AF1-TuA-1 Low Energy Ion Scattering Surface Analysis of ALD Coated Ti-Based Porous Transport Layers*, Philipp Brüner,*** *Thomas Grehl,* IONTOF GmbH, Germany*; Athina Tzavara-Roussi, Rens Kamphorst, Ruud van Ommen,* TU Delft, Netherlands **INVITED**

Porous transport layers (PTLs) play a crucial role in enabling efficient electrochemical reactions in water electrolyzers. Positioned between the electrodes and the current collectors, PTLs provide structural support, help transport reactants by allowing gas diffusion and moving water from the reaction sites, provide electrical conductivity between electrode and current collector, and aid in heat dissipation for thermal management.

Titanium-based PTLs are a common choice due to good conductivity, corrosion resistance, and mechanical strength, but long-term degradation effects occur under the harsh chemical conditions encountered in an electrolyzer cell. Protective coatings help mitigate these effects and improve PTL performance by improving the chemical stability of the PTL surface and modifying surface properties.

Atomic layer deposition (ALD) is an attractive method for applying the protective coating, as it is ideally suited to porous substrates, and its conformality and precision allows fine-tuning of the thin film properties. Here, we report on low energy ion scattering (LEIS) analyses of ALD-coated Ti-based PTLs, using various coating materials.

The extreme surface sensitivity of LEIS allows quantification of the surface coverage of the ALD film, providing crucial information about film growth and layer closure. At the same time, the film thickness is evaluated to provide insight into the ALD growth mode and growth per cycle. We discuss analytical challenges associated with the highly three-dimensional nature of the deposition substrate, which affect surface quantification and film thickness measurements.

2:00pm **AF1-TuA-3 In vacuo LEIS studies on cleaning and functionalizing substrate surfaces for ALD***, Heta-Elisa Nieminen, Johanna Majlund, Marko Vehkamäki, Mykhailo Chundak, Sakari Kettunen, Matti Putkonen,* ***Mikko Ritala,*** University of Helsinki, Finland

Starting surfaces play a critical role for the success of ALD processes. When loaded from air to the ALD reactor, substrate surfaces have adsorbed airborne hydrocarbon molecules. While some ALD processes may be robust little affected, some others may be blocked by the hydrocarbons or products from their reactions with precursors. For example, we showed that the $Ir(acac)_3 – O_2$ ALD process deposits Ir on fresh, *in situ* deposited Al_2O_3 but not on air exposed *ex situ* Al_2O_3. On air exposed SiO_2 the Ir was deposited, however [1].

While cleaning the surfaces before loading to the ALD reactor may decrease the amount of hydrocarbons on the surface, they may be hard to completely avoid this way. Therefore, it is important to clean the surfaces in the ALD reactor and study the cleaning processes *in situ* or *in vacuo*. In this work we have used the unique ALD cluster tool where a genuine flow type ALD reactor is connected in vacuo to low energy ion scattering (LEIS), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). With LEIS and TPD we studied Al_2O_3 and SiO_2 surfaces (i) directly after loading (*ex situ*), (ii) after heating at 300 °C, (iii) after exposing to ozone for 500 s in the ALD reactor at 300 °C, and (iv) after exposing to atomic oxygen at room temperature. *In situ* deposited Al_2O_3 served as a reference. Upon only heating to 300 °C, the hydrocarbons stay better bonded to Al_2O_3 than to SiO_2, but both the ozone and oxygen treatment clean the surfaces to a level comparable to the *in situ* Al_2O_3. We also used time-of-flight secondary ion mass spectrometry (TOF-SIMS) option of the LEIS instrument to compare hydrogen amounts on the Al_2O_3 surfaces.

SiN_x surface was studied directly after loading and after heating at 300 °C. This surface was found to have much less hydrocarbons than the two oxide surfaces. We also studied the SiO_2 and SiN_x surfaces after treatment with dilute 0.05 % HF and benzaldehyde vapor, aiming for passivation of the surfaces for area-selective deposition.

1. H.-E. Nieminen, M. Putkonen and M. Ritala, Chem. Mater. 2025, 37, 7251

2:15pm **AF1-TuA-4 ALD Outstanding Presentation Award Finalist: Operando Studies of Nitride ALD Using Ambient Pressure XPS*, Henrik Pedersen,*** Linköpings Universitet, Sweden*; Pamburayi Mpofu, Alaa Malekshahineia, Peggy Bagherzadeh Tabrizi,* Linköping University, Sweden*; Esko Kokkonen,* Max IV Laboratory, Sweden*; Joachim Schnadt,* Lund University, Sweden

Studies of the surface chemistry of the first few cycles of ALD using *in situ* and time-resolved *operando* techniques are attractive for realizing, understanding and obtaining mechanistic information during the deposition. We will present surface-chemistry investigations through time-resolved ambient pressure X-ray photoelectron spectroscopy (APXPS) using a dedicated ALD cell[1] at the MAX IV Laboratory to study of the initial growth of TiN, AlN and GaN. While this setup has been used for oxides[2,3] and metals[4], we can here show the first results on nitrides using TDMAT, TMA and TMG/TEG with NH_3 in thermal ALD processes.

Operando APXPS is conducted concurrently with the dosing of the precursor, *i.e.*, monitoring the chemical environment of the substrate and film surface while pulsing the ALD precursors.[5] As opposed to the more common *in situ* XPS experiments that are performed after ALD half-cycles and at times under non-realistic conditions (*e.g.*, high vacuum), *operando* APXPS closely mimics or replicates actual processing environments, such as atmospheric or near-pressurized conditions.

Deposition of nitrides is a thermodynamical uphill battle as metals have a stronger driving force to form and oxide than a nitride. This is reflected in our results as an initial formation of the metal oxide, followed by slow nitridation by the ammonia. We speculate that the native oxide on silicon is acting as a source of oxygen for the initial oxidation. We also propose that this initial metal oxide formation explain long nucleation delays seen in thermal ALD of nitrides, *e.g.*, approximately 120 ALD cycles in thermal ALD of AlN.[6]

A delay in nucleation on the TDMAT-terminated surface was also observed during the NH_3 pulse. The intensity of the Ti 2p and N 1s core levels began to increase after four ALD cycles, showing that the surface was coated with Ti and N atoms and no Si signals were observed with time. The results show that ligand exchange reactions take place before transamination reactions. This was verified using the periodic changes in the intensity and peak positions of the above-mentioned spectra and complemented by residual gas analysis using mass spectrometry.

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(3) Jones et al. *J. Vac. Sci. Technol. A* **2024**, *42*.

(4) Kokkonen, et al. *J. Vac. Sci. Technol. A* **2024**, *42*.

(5) Jones et al. *Surf. Sci.* **2025**, *753*.

(6) Mpofu et al. *J. Mater. Chem. C* **2024**, *12*, 12818–12824.

2:45pm **AF1-TuA-6 In-situ XPS Study of Ozone Oxidation of Aminosilane Adsorption Layers on Alumina*, Yuki Tsuchiizu,*** Institute of Fluid Science, Tohoku university, Japan*; Daisuke Ohori,* Institute of Fluid Science, Tohoku University, Japan*; Teruhisa Ohtsuka, Masashi Yamazaki, Hiroshi Arimoto,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; Kazuhiko Endo,* Institute of Fluid Science, Tohoku university, Japan

We have determined the post-oxidation surface termination of tris(dimethylamino)silane (TDMASi) on alumina under ozone exposure using in situ XPS. Alumina was used as a reproducible hydroxylated oxide model surface for first-cycle adsorption and oxidant-half-cycle studies. A TDMASi adsorption layer on alumina was exposed to ozone for 2-20 s at 200°C. C 1s deconvolution shows that the C-N component decreases, while a high-binding-energy component at 289-290 eV increases up to 5 s. In contrast, the Al 2p-normalized N 1s signal shows no large change over 2–20 s. These results indicate that ozone cleaves C-N bonds and promotes formation of oxidized carbon species, while nitrogen-containing fragments remain on the surface. Overall, the oxidant half-cycle approaches a saturated post-oxidation surface state.

SiO_2 spacers in back-end-of-line integration require conformal deposition below 400°C with atomic-layer thickness control on 3D devices. Aminosilane precursors enable low-temperature SiO_2 ALD, and ligand variants have been developed to tune growth per cycle (GPC) and impurity behavior. This trend implies that ligand identity governs ligand-fragment incorporation during growth, so the oxidant half-cycle may yield ligand-dependent surface terminations. Because ligand-fragment retention during

early cycles can affect dielectric properties (reliability/leakage) and spacer etch response, the termination chemistry is directly relevant to BEOL SiO_2 process design. We previously used in-situ XPS to show that both the ease of initial adsorption and the adsorption structure of aminosilanes on alumina depend on ligand architecture. In this study, we use TDMASi as a case study to identify post-oxidation termination motifs under ozone.

An alumina film was deposited on a Si substrate by ALD using trimethylaluminum and O2 plasma. TDMASi was adsorbed as an initial adsorption layer, followed by exposure to ozone (≧90%) for 2-20 s at 200℃. Samples were loadlock transferred under high vacuum to in situ XPS, where Al 2p, C 1s, and N 1s spectra were acquired.

Figure 1 shows the C 1s spectra of (a) alumina, (b) before ozone exposure, and (c) after 20 s ozone exposure. The C 1s envelope was deconvoluted into C-C/C-H, C-N, C=O, and carbonate (OCOO) components. Carbonate is already present on alumina (a). Compared with (b), the C-N component decreases in (c), indicating loss of C-N bonds in amino-derived species on alumina. Figure 2 shows Al 2p normalized ozone dose time dependences of the C 1s components and N 1s. C-C/C-H, C=O, and N remain nearly constant, whereas C-N decreases and carbonate increases up to 5 s. Thus, ligand-derived N does not desorb, while ozone cleaves C-N bonds and forms carbonate species, and the reaction approaches saturation with carbonate termination.

This work was partially supported by JSPS KAKENHI 24K0786 and MEXT ARIM (JPMXP1225AT0193).

3:00pm **AF1-TuA-7 In situ and Operando investigation of MLD of Hafnicone Using Ambient Pressure-XPS**, ***Hariprasad Parayil Kalappurackal,*** Lund University, Sweden

Molecular Layer Deposition (MLD) extends Atomic Layer Deposition (ALD) by enabling the growth of hybrid organic–inorganic thin films through sequential, self-limiting surface reactions. By incorporating organic precursors into ALD-type processes, MLD (cf. Fig. 1) provides access to materials with tunable chemical functionality while maintaining the precise thickness control, conformality, and scalability of conventional ALD. Such hybrid materials are of growing interest for applications requiring tailored mechanical, electronic, or chemical properties.

Understanding MLD surface chemistry, particularly during nucleation and low-temperature growth, remains a key challenge. Here, MLD processes are studied using a dedicated ALD/MLD reactor cell integrated with ambient pressure x-ray photoelectron spectroscopy (APXPS) at the SPECIES beamline of the MAX IV Laboratory,[1A] Lund, Sweden. The setup mimics ALD reactor conditions and enables time-resolved in situ observation of surface reactions under realistic growth environments.

As a model hybrid system, we demonstrate the MLD of hafnicone[2] on silicon substrates using a deposition sequence in which the inorganic precursor TDMAHf is pulsed before the organic precursor ethylene glycol. The deposition process took place at a substrate temperature of 100℃ and the steps consists of precursor adsorption, nucleation, and saturation, which together define the deposition cycle and can be followed in real time using APXPS. As shown in Fig. 2, presence of the N 1s and Hf 4f signals from the very beginning of the measurement are due to preceding ALD experiments in the same cell: the surface is saturated by adsorbed TDMAHf already before the metal precursor pulse. Following introduction of the organic precursor, the N 1s signal completely disappears, consistent with the expected complete removal of the -NMe_2 ligands by ethylene glycol and their replacement by oxygen containing groups from the organic precursor, leading to the formation of Hf-O-C bonds characteristic of hafnicone. The shifts of the Hf 4f and C 1s core levels toward higher binding energy indicate a decrease of electron density on these atoms. The O 1s shifts towards lower binding energy. Both observations are in agreement with the formation of new oxygen bonding environments, consistent with metal organic Hf-O-C film formation. The C 1s binding energy is in line with presence of an intact ethylene linker, as expected for the present MLD process.

Hafnicone type materials are of interest due to their potential functionality, including enhanced mechanical flexibility and tunable dielectric or chemical properties resulting from the incorporation of organic linkers into a hafnium based inorganic framework.

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[2] Lee, B. H. et al. ACS Appl. Mater. Interfaces 6, 16880–16887 (2014).

3:15pm **AF1-TuA-8 Pyroelectric Calorimetry of MgO and ZrO_2: Untangling Thermodynamics, Kinetics, and Precursor Transport**, ***Ashley Bielinski,*** *Cong Liu, Alex Martinson,* Argonne National Laboratory

A detailed understanding of ALD surface reaction mechanisms, thermodynamics, and kinetics is essential for the development of new processes, particularly those that rely on chemical selectivity between different surface sites.While computational modeling, such as DFT can provide valuable insight on the thermodynamically favorable reactions of ALD precursor molecules, this approach is limited to simplified and idealized substrate surfaces and reaction conditions. In situ and operando studies of ALD surface reactions provide necessary information on how ALD reactions proceed on realistic substrates and under typical deposition conditions. ALD pyroelectric calorimetry provides quantitative measurements of reaction heat generation and heat transfer from surface reactions as well as precursor and byproduct flow with sufficient time resolution to measure the dynamics of these processes.

We have investigated ALD processes including the reaction between tetrakis(dimethylamido)zirconium(IV) (TDMAZr) and water to form ZrO_2 and the reaction between bis(ethylcyclopentadienyl)magnesium ($Mg(CpEt)_2$) and H_2O to form MgO using pyroelectric calorimetry.These experimental results show how practical processes both agree with and contrast computationally proposed reaction mechanisms.Additionally, we present the design of an ALD reactor customized for pyroelectric calorimetry measurements with improved timing across and array of calorimeters. Combined with reactor-scale modeling, this enhanced experimental platform gives new insight into the interplay between precursor delivery, reaction kinetics, and the role of reaction byproducts.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-TuA
ALD Metrology/Characterization II

Moderators: Henrik Pedersen, Linköping University, Sweden, **Angel Yanguas-Gil**, Argonne National Lab

4:00pm **AF2-TuA-11 ALD Outstanding Presentation Award Finalist: Where Does the Reaction Happen? Concurrently Monitoring Ultrafast Surface and Gas-Phase Dynamics in Solid–Gas Interfacial Reactions**, *Keith Blackman, Eric Segrest, Aakash Gupta, S. Novia Berriel, Parag Banerjee,* ***Mihai E. Vaida,*** University of Central Florida

Understanding and controlling surface-limited reactions while minimizing parasitic gas-phase chemistry remains a central challenge in atomic layer deposition (ALD). Conventional in situ ALD diagnostics typically infer surface and gas-phase processes indirectly, making it difficult to disentangle their contributions. To address this, we present an experimental technique that directly distinguishes reaction products originating from the surface and the near-surface gas phase while simultaneously resolving their ultrafast dynamics, enabling detailed mechanistic insight into the underlying chemical processes. This method allows simultaneous, real-time monitoring of ultrafast reaction dynamics at the surface and above the surface during photoinduced heterogeneous reactions.

The technique combines femtosecond pump-probe spectroscopy with mass spectrometric detection, allowing concurrent observation of reaction intermediates and products formed at the solid-gas interface and within the adjacent gas phase. As a model system, we investigate the photoinduced reaction of methyl iodide on a cerium oxide surface. Species detected simultaneously from the surface and gas phase exhibit distinct signatures in the mass spectra, characterized by a sharp peak followed by a broader shoulder. Time-resolved analysis assigns the sharp peak to species emitted directly from the surface, while the broader shoulder originates from species formed in the gas phase above the surface.

By tracking the evolution of these spectral features as a function of pump-probe delay, we resolve the ultrafast dynamics governing surface-confined reactions and gas-phase processes on femtosecond to picosecond timescales. SimION simulations further corroborate the spatial origins of the detected ions. This approach enables real-time differentiation of surface and gas-phase reaction pathways, opening new possibilities for investigating precursor activation, reaction selectivity, and parasitic chemistry relevant to ALD and related thin-film deposition processes.

4:30pm **AF2-TuA-13 Dual-Box Model for In-Situ Spectroscopic Ellipsometry Data Analysis in Plasma Enhanced ALD Growth Processes**, *Ufuk Kilic, Yousra Traouli, Mathias Schubert,* ***Eva Schubert,*** University of Nebraska - Lincoln

We employ in-situ spectroscopic ellipsometry (SE) to investigate the growth dynamics of ultrathin transition metal oxide films (ZnO, WO_3, TiO_2, Ga_2O_3) during plasma-enhanced atomic layer deposition (PE-ALD). To analyze the dynamic optical response, we introduce a dual-box regression model: the first box represents surface roughness using an effective medium approximation (EMA), while the second box captures cyclic variations in the subsurface layer thickness arising from molecular rearrangements during each ALD cycle. This approach provides a time-resolved, quantitative view of both surface roughness and subsurface film growth dynamics, enabling accurate characterization of layer-by-layer deposition.

The accurate extraction of film thickness, density, and roughness at elevated substrate temperatures requires knowledge of the temperature-dependent dielectric function (TDF) of the transition metal oxides, which can significantly vary from room-temperature values. In this work, the TDF was determined via a multi-sample analysis, using optical data from films of varying thickness measured at different stages during the growth process. The incorporation of experimentally verified dielectric functions ensures that the dual-box model reliably describes the evolving optical response during high-temperature deposition, enabling detailed monitoring of sub-monolayer coverage, interface formation, and roughness evolution throughout the ALD process.

The ALD processes employ organometallic precursors with remote oxygen plasma and water co-reactants, providing controlled stoichiometry, high uniformity, and optimized interface quality. Temperature-dependent studies further elucidate the influence of surface kinetics on nucleation, growth rate, and steady-state dynamics, linking chemical reactions and surface rearrangements.

Post-deposition structural and chemical characterization, including scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), corroborates the in-situ optical measurements and provides complementary insight into film crystallinity, morphology, and composition.

[1]U. Kilic, A. Mock, D. Sekora, S. Gilbert, S. Valloppilly, G. Melendez, N. Ianno, M. Langell, E. Schubert, M. Schubert, Precursor-surface interactions revealed during plasma-enhanced atomic layer deposition of metal oxide thin films by in-situ spectroscopic ellipsometry [https://scholar.google.com/citations?view_op=view_citation&hl=en&user=pAVudUUAAAAJ&cstart=20&pagesize=80&citation_for_view=pAVudUUAAAAJ:vV6vV6tmYwMC], Scientific reports 10 (1) 10392 (2020).

[2]Y. Traouli, U. Kilic, S. G Kilic, M. Hilfiker, D. Schmidt, S. Schoeche, E. Schubert, M. Schubert, In-cycle evolution of thickness and roughness parameters during oxygen plasma enhanced ZnO atomic layer deposition using in situ spectroscopic ellipsometry [https://pubs.aip.org/avs/jva/article/42/5/052403/3311662], J. Vac. Sci & Technol. A 42 (5) (2024).

4:45pm **AF2-TuA-14 Imaging Ellipsometry with LHAR Test Structure for Characterizing ALD Conformality**, ***Hiroshi Nishizato,*** Kumamoto University, Japan*; Yugo Nakaya,* HORIBA STEC, Co., Ltd., Japan*; Lianhua Jin,* University of Yamanashi, Japan*; Takeshi Momose,* Kumamoto University, Japan

We developed a novel methodology to quantitatively evaluate the penetration depth (PD) of films in three-dimensional (3D) features deposited by atomic layer deposition (ALD), combining our developed imaging ellipsometry with an in-house lateral high-aspect-ratio (LHAR) test structure. The effectiveness of this methodology was confirmed using ALD Al_2O_3 from trimethylaluminum (TMA) and H_2O.

ALD is widely used in the fabrication of 3D semiconductor devices that require high conformality. The PD is a consequence of ALD kinetics, including adsorption, desorption, and surface reactions; therefore, it is a critical parameter for assessing conformality in such complex 3D architecture. PD was thus evaluated using the LHAR structure comprising a Si substrate with a shallow, wide groove at the edge, capped with a quartz plate. The LHAR structure has an aperture of 20 μm × 4 mm and a depth of 6 mm. Sample imaging was enabled by installing an Offner optical system on our custom-built ellipsometer, allowing the PD formed in a groove on the Si substrate to be determined. To enhance imaging contrast, the retarders were set to 150° on the light-source side and 30° on the camera side, while both polarizers were set to 0°. The ALD Al_2O_3 film, with a thickness of 6-60 nm, was captured under these settings. Experimental results showed that the growth per cycle (GPC) measured on planar Si substrates with a 3 nm thermal SiO_2 underlayer was independent of the TMA dosing, while the PD in the LHAR structure increased with increasing TMA dosing. In this manner, we established a methodology to evaluate PD using imaging ellipsometry with the LHAR test structures. As it is in an offline setting, we plan to install them in an ALD chamber for real-time PD monitoring. On such occasions, precise control of the concentration and supply duration of both the precursor and the reactant is essential for accurately determining time-dependent PD evolution. Therefore, a piezoelectrically controlled vapor delivery system has already been installed on our ALD equipment for both TMA and H_2O, enabling precise, rapid dose control by adjusting the valve opening ratio and duration.

References

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5:00pm **AF2-TuA-15 Surface Chemistry Investigation for ALD of SiOCH Using in-Situ Reflection Absorption Infrared Spectroscopy (RAIRS)**, ***Sjoerd van der Werf,*** Eindhoven University of Technology, Netherlands

There is a need to replace silicon nitride inner spacers in gate-all-around field-effect transistors by low-k materials to reduce parasitic capacitance in these 3D architectures. Atomic layer deposition (ALD) is the method of choice for the fabrication of this material, due to the need for good conformality for this application. For this work the specific interest is in the surface chemistry that occurs throughout potential half-cycles to establish successful ALD cycles for carbon-containing SiO2.

The study focused on the adsorption of the silicon-carbon precursor BTDMASM (composed of two silicon atoms bridged by a CH2 group and six ligands), by identifying relevant surface groups and looking into the reaction of the surface groups with different reactants. These reactants include water, ethylene glycol, and an organic acid. In addition, more complex chemistries were considered, including ABC-type approaches, for example to activate surface groups or more efficient ligand removal.

The surface reactions were studied using in-situ RAIRS measurements, which resulted in a clear understanding of the surface reactions during an ALD cycle. For example, the organic acid was shown to react with the ligands of BTDMASM very efficiently, where all ligands are removed upon exposure to the acid. The adsorption of the organic acid on the surface leads to the removal of surface attached ligands from the precursor, which is observed in the CH stretch region as well as based on C=O and C-O bonds.

The data on the adsorption of BTDMASM on SiO2 suggests that the precursor is susceptible for adsorbing on hydroxyl groups. The organic acid does not result in the replenishment of reactive adsorption sites. Therefore, water was introduced as a second co-reactant to remove the acid and replenish hydroxyl groups, which is observed by the removal of groups related to the adsorbed acid. The removal of the organic acid is temperature dependent where for a temperature of 350 C degrees the C=O and C-O bonds are no longer present at the surface. The surface chemistry of water and the acid in combination with BTDMASM was investigated for different conditions, where temperature series have shown that the surface groups are temperature dependent, as is subsequent precursor adsorption. Overall, a better understanding is achieved regarding the surface chemistry for the thermal ALD of SiOCH with the use of RAIRS.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-WeM

Plasma Enhanced and Low Temperature ALD

Moderators: Jolien Dendooven, Ghent University, Belgium, **Mikko Ritala**, University of Helsinki

8:00am **AF1-WeM-1 Understanding Temporal Behavior of Adsorption and Desorption in ALD via Multiple Injections of Precursor**, ***Yu-Sen Jiang***, Stanford University; *Miso Kim,* Standford University; *Yukio Cho,* Stanford University; *Stacey Bent,* Standford University

Atomic layer deposition (ALD) is renowned for its self-limiting characteristics, enabling precise atomic-level control and high conformality. During an ALD half-cycle, precursors may adsorb onto the substrate as physisorbed species before reacting with surface ligands to chemisorb. However, even under nominally saturated conditions, full surface coverage may not be achieved due to phenomena such as steric hindrance or retention of excess physisorbed precursors. To address this limitation, multiple precursor injections within a single half-cycle are employed to increase the amount of chemisorbed precursor. The observation that ALD growth differs when performed with discrete injections compared to a single injection suggests that adsorbed precursors undergo dynamic behavior on the timescale of a pulse. The temporal effects of precursor adsorption, rearrangement and desorption have received less attention in ALD, for which a single precursor pulse is typically assumed to be fully saturating.

In this work, ALD of HfO_2 with multiple-pulse sequencing was used to elucidate fundamental ALD mechanisms. A single long pulse of Hf precursor (tetrakis(dimethylamido)hafnium, TDMAH) was divided into several shorter sub-pulses to enable a direct comparison between single and multiple pulses during ALD with water as the counteractant at 200°C. The HfO_2 films grown by multiple pulse injection show a 26 % higher growth per cycle, as well as increased grain size, film density, and crystallinity. The improvement is attributed to a denser surface arrangement enabled by staggered precursor exposure. *In situ* infrared spectroscopy reveals differences in the types of hydroxyl groups consumed by precursors between single and multiple pulse modes. Hydroxyl species that were difficult to react in a single pulse (e. g. hydrogen-bonded OH) became more accessible through the multiple feeding of precursors.

To isolate the contribution from each pulse, the Zr precursor (tetrakis(dimethylamido)zirconium, TDMAZ) was introduced into the TDMAH pulse sequence as a “chemical tag” in HfO_2 ALD for defining the specific pulse. This approach enables direct observation of the fractional growth contribution from individual pulses under different pulse-time and pulse-sequence combinations. The results of X-ray photoelectron spectroscopy and *in situ* ellipsometry measurements between 150°C to 220°C indicate that during short pulses, only ~50% of the total growth occurs during the first pulse, resulting in a more sparsely populated surface that allows additional precursors to react in later pulses. Our results reveal that precursor residence time scales with precursor population, implying a coverage-dependent desorption mechanism. Low precursor loading, especially in the unsaturated regime, facilitates desorption and surface rearrangement, thereby enhancing the benefits from multiple-pulse strategy. Further mechanistic analysis of the single versus multiple pulse ALD schemes will be discussed.

8:15am **AF1-WeM-2 Improved Atomic Layer Deposition of Ultra-Thin HfO_2 Dielectrics on Transition Metal Dichalcogenide Surfaces via Low Impact Plasma Pretreatments**, ***Rebecca Dawley,*** University of Michigan; *Sudarat Lee, Wouter Mortelmans, Scott Clendenning,* Intel Corporation; *Ageeth Bol,* University of Michigan

2D transition metal dichalcogenides (TMDs) have shown to be promising candidates as alternative channel materials within scaled transistors in next generation electronics. As transistor dimensions continue to shrink and advanced device architectures evolve, there exists a need for the deposition of high quality, ultra-thin dielectrics onto semiconducting channels, typically via atomic layer deposition (ALD). However, deposition on pristine TMD basal planes is challenging due to the lack of dangling bonds and defect sites typically acting as ALD nucleation sites, thus resulting in nonuniform dielectric coverage.

In this work, we explore the effect of mild (low power, high pressure) H_2S plasma pretreatments to improve HfO_2 ALD on mono and few layer TMDs. First, we evaluate the effect of various plasma exposure duration times on monolayer WSe_2 at 250 °C. Minimal impact to WSe_2 following plasma exposure was confirmed via Raman, X-ray photoelectron, and photoluminescence spectroscopy. These plasma exposures were then applied to WSe_2 prior to ~ 3nm HfO_2 atomic layer deposition resulting in a significant improvement in dielectric nucleation and coverage on WSe_2 basal planes as compared to untreated control samples. To better understand the interplay between the plasma-pretreatment of the WSe_2 surface and the HfO_2 ALD process, we investigated the influence of the precursor (both Hf and O) dose times, number of precursor pulses, purge time, and stop flow pumping schemes on the microstructure of the HfO_2 deposited on pre-treated WSe_2. AFM, backscattered electron imaging, and Auger spectroscopy were utilized to determine an optimal combination of plasma exposure and HfO_2 ALD process parameters to yield uniform dielectrics across TMD basal planes.

After process optimization, we evaluated the minimum possible HfO_2 thickness allowed via our plasma pretreatment strategy while still maintaining fully coalesced films using AFM and cross-section TEM. Electrical measurements will demonstrate the capabilities of our technique in depositing high quality, ultra-thin dielectrics onto TMDs with minimal impact on TMD structural properties. This work will further enable the advancement of TMD based top gate and gate all around transistors with ultrathin dielectrics and addresses the concern of maintaining the integrity of underlying TMD channels during pre-treatments prior to ALD.

8:30am **AF1-WeM-3 Comparing HfO_2 Thin Films Grown by Low-temperature Thermal and Plasma ALD for Neuromorphic Functionality**, *Alessandro Cataldo,* CNR-IMM, Italy; *Alan Durnez, Himadri N. Mohanty,* CNRS-C2N, France; *Seyed Ariana Mirshokraee, Sabina Spiga,* CNR-IMM, Italy; *Liza Herrera-Diez,* CNRS-C2N, France; ***Alessio Lamperti***, CNR-IMM, Italy

The need for integration of materials in the fabrication of devices sensible to thermal budgets, such as in flexible, organic and bio-inspired electronics, requires the development and study of low thermal ALD processes. On this scope several attempts have been performed to tackle this issue from different sides, involving the development of innovative precursors and engineering of growth processes, including the extension of ALD regime down to 80 °C in thermal ALD or employing plasma ALD to deliver the energy required for the chemical reactivity.

In this context, HfO_2 has been, and still is, the subject of many efforts, driven by the need of both innovative scientific challenges and functionalities and the existing markets. Recently, its integration in neuromorphic and magnetoionic devices, shifted the attention from qualifying the material properties in terms of compact, dense, defect-free, crystalline films, to consider the type and degree of defects, the selective incorporation of additional elements, typically C, N and OH, in amorphous films. Thus, the need to redefine low temperature ALD processes targeting HfO_2 with such specifications.

Within this framework, here, we compare three processes where thermal or plasma ALD is considered, employing two different equipment. In details, we consider TEMAHf and TDMAH as Hf precursors, H_2O as oxidant in the thermal ALD processes or Oxygen from O_2 in 300 W plasma ALD process, with temperature in the 80 – 100 °C range. We target four HfO_2 thickness, 3, 5, 10 and 20 nm, grown on SiO_2/Si substrate, to have the minimal set for accurately verify the ALD window regime and compare any change in the growth per cycle.

Grown HfO_2 layers are characterized from XRR, XPS and ToF-SIMS to evaluate any change in the electron density, elemental chemistry and stoichiometry. We observe, depending on the growth process, a stoichiometry below the nominal O:Hf=2:1 ratio in all cases, the lowest value in HfO_2 films grown using plasma ALD, with a slight evolution of the stoichiometry with the film thickness. Further, we observe from XPS a significant amount of OH groups depending on the ALD process, in-line with the electron density value from XRR. We explain such changes in terms of purging time and engineering of the oxidant sub-cycle within each ALD cycle, and considering the interplay between oxidation and hydroxilation phenomena.

Further, we integrate HfO_2 films in simple MIM capacitors to extract their dielectric constant (k) and voltage breakdown (V_{BD}). k value results around 17 in HfO_2 films from thermal ALD lowering to k = 12 in HfO_2 from plasma ALD, while V_{BD} varies in the range 3.0-5.5 MV/cm. We tentatively explain such changes in terms of defectivity and ionic species inside the grown HfO_2 films.

Finally, we briefly report on how the so-grown HfO_2 films enable, or not, magnetoionic functionality, depending on the ALD process employed.

Financial support from EIC METASPIN project, grant n. 101098651.

8:45am **AF1-WeM-4 Germanium Oxide with Tunable Composition Using Low-Temperature PEALD**, ***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

Germanium dioxide (GeO_2) is of particular interest in advanced microelectronics and is regarded as an ultrawide bandgap (UWBG) material for next-generation CMOS applications. With exceptional carrier mobility, it shows promise for high-frequency and high-power electronics,[1,2] while its optical properties make it appealing for, e.g., anti-reflection coatings.[3] Furthermore, two-dimensional (2D) GeO_2 has an inherently porous structure with molecular-sized holes and is thus of interest as a material for selective gas-separation membranes.[4,5]

To transition these applications from research to industrial applications, it is necessary to develop scalable processes that enable the deposition of high-quality, defect-free GeO_2 films. Owing to its self-limiting nature, ALD emerges as the most promising solution, offering precise control over thickness and morphology. Yet, ALD strongly relies on the underlying chemistry, and especially the development of low-temperature processes is currently restricted by the lack of suitable Ge precursors.

To address this challenge, we introduce tetrakis-(3-dimethylamino)propyl germanium(IV) [$Ge(DMP)_4$], designed to be highly thermally stable, volatile (see TGA in **Figure 1c**), and reactive, to facilitate low-temperature ALD processing of GeO_2. Using this new liquid, non-pyrophoric, and monomeric precursor (as confirmed by single-crystal XRD and DFT structure analysis in **Figure 1a,b**), we developed a PEALD process for GeO_2 using O_2 plasma as the co-reactant. The process operates across a broad temperature range from 40 °C to 240 °C (**Figure 2a**) with a linear GPC of 0.24 Å at 150 °C. By utilizing different plasma pulse durations (t_{plasma}), the composition of the films can be adjusted: with t_{plasma} = 500 ms, the thin films consist of GeO_2, GeO, and Ge, with a higher degree of sub-stoichiometric GeO_x species at higher deposition temperatures, whereas stochiometric GeO_2 is obtained with t_{plasma} = 50 ms (**Figure 2b, c**). Initial characterization revealed that the composition directly influences the optical behavior of GeO_x thin films, as seen in the UV/Vis spectra of GeO_x thin films deposited using different plasma durations and deposition temperatures (**Figure 3a**). Further, transmission electron spectroscopy revealed closed and uniform thin films with an amorphous structure (**Figure 3b**). Thereby, the rapid nucleation behavior of the process allowed the deposition of a thin film using only eight PEALD cycles. This enabled down-scaling to a film thickness of ≤1 nm (**Figure 3c**), approaching the theoretical thickness required for the bilayer structure and providing a strong foundation to explore the scalable growth and utilization of bilayer GeO_2.

By identifying [$Ge(DMP)_4$] as a new and promising Ge precursor, PEALD processing of GeO_2 and GeO_x becomes feasible at near-room-temperature conditions, advancing the use of GeO_2 and GeO_x thin films for new applications based on their unique properties.

9:00am **AF1-WeM-5 Low Temperature Thermal Atomic Layer Deposition of Bismuth Oxide Thin Films Using a Novel Precursor**, ***Taylor Currie***, *Patrick Price, Ronald Goeke, Joseph Klesko,* Sandia National Laboratories

Binary, ternary, and multinary bismuth-containing oxide thin films have been synthesized by chemical vapor deposition and atomic layer deposition (ALD), and utilized in optical, ferroelectric, sensing, and catalytic applications. Binary bismuth oxide (Bi_2O_3) exists in several crystalline phases; however, deposition of a targeted single phase, as well as stoichiometric Bi_2O_3, by ALD remains challenging.

A recent study deposited Bi-rich α-Bi_2O_3 on Si(100) substrates by ALD using triphenylbismuth ($BiPh_3$) and ozone (O_3) as precursor and co-reactant, respectively, within an ALD window of 250-300 °C. Alternative substrates or annealing at temperatures between 700 - 800 °C was required to access additional phases (i.e., β and γ) and stoichiometric composition.

Herein, we report a thermal ALD process for Bi_2O_3 using methyldiphenylbismuth ($MePh_2Bi$) and O_3 as novel precursor and co-reactant, respectively. Saturation was achieved with a $MePh_2Bi$ precursor delivery temperature as low as 90 °C, and a growth per cycle of ~ 0.6 Å/cycle within the range of 100 - 170 °C. $MePh_2Bi$, a liquid, methyl-substituted, and thermally stable precursor exhibits higher volatility than its solid $BiPh_3$ analogue, enabling deposition on temperature-sensitive substrates. Characterization by x-ray photoelectron spectroscopy, atomic force microscopy, and grazing incidence x-ray diffraction of the as-deposited films is presented.

9:15am **AF1-WeM-6 Effect of Initial Surface Silanol Density and Aminosilane Structure on O2 Plasma-Assisted ALD of SiO_2**, ***Andrew Kaye***, Colorado School of Mines; *Bhushan Zopé,* Intermolecular, Inc.; *Xinjian Lei, Agnes Derecskei, Ronald Pearlstein, Haripin Haripin Chandra,* EMD Electronics; *Sumit Agarwal,* Colorado School of Mines

SiO_2 is a commonly used dielectric material in semiconductor manufacturing, and aminosilanes are typically used as the Si precursor during radical-assisted atomic layer deposition (ALD) of SiO_2. This work explores the role of the initial surface Si−OH density, the substrate temperature, and the structure of the aminosilane precursor on the growth per cycle (GPC) for ALD on plasma-deposited SiO_2 substrates. Specifically, we studied O_2-plasma-assisted ALD of SiO_2 using two aminosilanes, di-*sec*-butylaminosilane (DSBAS) and dimethylamino trimethylsilane (DMATMS). The surface reactions during ALD were monitored using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and the GPC was monitored using *in situ* four-wavelength ellipsometry. On an SiO_2 surface with a high initial Si−OH group density, *in situ* ATR-FTIR spectroscopy shows that ~30% more Si−OH groups are consumed by DMATMS than DSBAS because DSBAS contains a bulkier amino leaving group than DMATMS. *In situ* ellipsometry shows that at an ALD temperature of 100 °C, the GPC using DSBAS and DMATMS are ~1.8 and ~1.2 Å, respectively. The higher GPC for DSBAS shows that the initial aminosilane coverage does not influence the GPC. We speculate that during the O_2 plasma step, O radicals can easily insert into Si−H bonds in adsorbed DSBAS. However, for adsorbed DMATMS, surface Si−$(CH_3)_3$ groups must be combusted, and then converted to Si−OH groups from species generated in the O_2 plasma.

On an SiO_2 surface with a low initial Si−OH group density, approximately the same number of Si−OH groups react with DMATMS and DSBAS. Therefore, we conclude that once the initial surface Si−OH density is sufficiently low, steric effects do not play a role in initial aminosilane adsorption on SiO_2. For both DMATMS and DSBAS, at a constant ALD temperature, the initial SiO_2 surface Si−OH group density has no effect on the GPC of SiO_2 ALD. *In situ* ellipsometry shows that on an SiO_2 surface with a low initial Si−OH group density, no nucleation delay is observed compared to a film with a high initial Si−OH group density. This implies that more Si−OH groups are produced during the first few O_2-plasma half-cycles compared to the initial density of adsorbed aminosilanes on the surface, allowing steady-state ALD to be reached within 5 ALD cycles. As ALD temperature for DSBAS increases, the GPC decreases. This is due to the thermal instability of reactive surface groups such as Si−OH and Si−H, and the areal density of these sites decreases with increasing temperature.

9:30am **AF1-WeM-7 Limits of Plasma Oxidation in Cr_2O_3 Ald: Over-Oxidation, Etching, and Defect Control**, ***Soumik Das***, imec USA; *Huiyun Yang,* University of Michigan, Ann Arbor; *Sean McMitchell,* IMEC Belgium; *Becky (R. L.) Peterson,* University of Michigan, Ann Arbor

Plasma-enhanced atomic layer deposition (PE-ALD) introduces highly reactive oxidation pathways that can fundamentally alter growth mechanisms in multivalent oxides. In p-type Cr_2O_3, plasma exposure does not act as a single monotonic oxidant but instead drives two competing processes: stabilization of Cr^{3+} through efficient ligand removal, and over-oxidation to volatile Cr^{6+} species that induce net etching. In this work, we investigate oxygen plasma-based ALD of Cr_2O_3 using $Cr(acac)_3$, with ozone ALD used only to establish a phase-stable reference growth window. At 250 °C, aggressive plasma dosage conditions suppress net growth, consistent with an etch-dominated regime associated with Cr^{3+}→Cr^{6+} conversion and CrO_3 volatilization. Reducing plasma delivery partially restores growth but yields rough, non-uniform films, indicating a transition toward an oxidation-limited regime rather than a conventional ALD window. Atomic force microscopy reveals pronounced surface roughening and poor film uniformity. These results identify stabilization of the Cr^{3+} oxidation state as the central challenge for PE-ALD of Cr_2O_3 and define critical process limits for plasma oxidation in p-type oxide ALD targeting low-temperature electronics.

9:45am **AF1-WeM-8 Composition-Tunable Molybdenum Carbonitride Thin Films Prepared by Plasma-Enhanced Atomic Layer Deposition (PEALD) for Diffusion Barriers in Cu and Ru Interconnects**, ***Younjae Shin***, *Chaehyun Park, Minjeong Kweon, Sang Bok Kim, Soo-Hyun Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Mo-based materials (MoC_x, MoN_x, MoC_xN_y) exhibit high thermal and chemical stability as well as extremely low electrical resistivity. [1] Owing to these superior properties, Mo-based thin films are considered as promising diffusion barrier materials for advanced Cu and Ru interconnects. [2] In

MoC_xN_y, C and/or N occupy interstitial sites within the crystal structure, enabling tunable properties. To enable their integration into advanced semiconductor interconnects, MoC_xN_y thin films were deposited by PEALD using a N-free Mo precursor with an H_2+N_2 mixture plasma reactant. By adjusting the H_2:N_2 ratio, the composition of C and N in the MoC_xN_y thin films was systematically controlled. Notably, N incorporation played a decisive role in increasing the growth rate from an extremely low value of 0.3 Å/cycle under pure H_2 plasma to ~1.5 Å/cycle with the introduction of a small amount of N_2, indicating that N_2 promotes surface reactions during MoC_xN_y growth. Under an H_2-rich plasma condition (H_2:N_2 = 8:1), typical ALD behavior was observed, including self-limiting growth with respect to both precursor and reactant pulse times. A stable ALD window was also identified at 225-250 °C, within which a saturated growth rate of ~1.5 Å/cycle and linear thickness evolution with the number of cycles were achieved. Moreover, both the growth rate (1.5-1.9 Å/cycle) and electrical resistivity (590-1490 μΩ·cm) were effectively tuned by varying the H_2:N_2 ratio from 8:1 to 1:8. Structural and compositional analyses using XRD and XPS confirmed the formation of conductive MoC_xN_y thin films with controlled C and N incorporation. Electrical characterization also revealed a strong correlation between film composition and resistivity. Finally, the PEALD-MoC_xN_y thin films were applied as diffusion barrier for Cu and Ru interconnects as well as gate electrode and the results will be presented at the conference.

References

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[2] Tripathi, C. C et al. *Applied Surface Science* (2008): *255* (6), 3518–3522.

Acknowledgements

This work was supported by the Technology Innovation Program (Public-private joint investment semiconductor R&D program (K-CHIPS) to foster high-quality human resources) (RS-2023-00236667, High-performance Ru-TiN interconnects via high-temperature atomic layer deposition (ALD) and development on new interconnect materials based on ALD) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (1415187401).This work was also supported by the Industrial Strategic Technology Development Program (RS-2024-00509266, Development of next-generation dielectric, electrode process equipment, and core materials for logic 1 nm or less and memory × nm level), funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea). The precursor used in this study was provided by UP Chemical Co. Ltd., Korea.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-WeM

Plasma-enhanced ALD of Nitrides

Moderators: Andrew Cavanagh, University of Colorado at Boulder, **Craig Huffman**, Oxford Instruments

10:45am **AF2-WeM-12 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Crystalline Gan Thin Films Using Monovalent Organogallium Precursor***, **Fumikazu Mizutani,** Nobutaka Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan

GaN thin films are promising wide-gap semiconductors, and the low-temperature atomic layer deposition (ALD) of high-quality crystalline GaN films is being actively investigated. In ALD of GaN, trimethylgallium (TMG; $Ga(CH_3)_3$), triethylgallium (TEG; $Ga(C_2H_5)_3$) are widely used. However, there have been almost no reports on obtaining high-purity crystalline GaN films at temperatures below 350 °C.

We have developed a novel liquid precursor (GaCp*; pentamethylcyclopentadienyl gallium) for the ALD of high-purity Ga_2O_3 films [1]. A film with almost no impurities was obtained using ABC-type ALD at a low temperature of 200 °C consisting of precursor adsorption, ligand elimination, and surface oxidation processes. Here, we report the results of investigating a similar ABC-type ALD process to obtain high-purity crystalline GaN at 200 °C.

GaN films were deposited at 200 °C on 150 mm Si wafers with native oxide films using a FlexAL system (Oxford Instruments) with a remote plasma generator and an in situ spectroscopic ellipsometer. In one ALD cycle, GaCp* was used as a precursor, and H_2 plasma followed by N_2 plasma was used as the reactant. In this process, the aromatic anion ligand Cp* was desorbed by H_2 plasma, and the surface Ga was nitrided by N_2 plasma. Self-limiting reactions were observed for GaCp*, H_2 plasma, and N_2 plasma pulse times of 0.5, 20, and 20 s, respectively. Next, we measured the GPC of ALD using the pulse times. The relationship between the number of ALD cycles and film thickness was linear, with a GPC of 0.023 nm/cycle. The sample, which was deposited in 600 cycles and had a film thickness of approximately 14 nm, was subjected to impurity analysis by GDOES and observation of crystallinity by cross-sectional TEM.

GDOES analysis showed that almost no C impurities were detected, suggesting that the ligands were sufficiently removed by H_2 plasma. Clear lattice fringes were observed in the cross-sectional TEM image, indicating that the GaN thin film was highly crystalline. In this study, deposition was performed on a native oxide film of silicon, but it is expected that epitaxial films can be deposited on templates such as sapphire.

The reason why high-purity, highly crystalline GaN could be deposited even at a low temperature of 200 °C is thought to be because GaCp* is a monovalent precursor, meaning that monovalent GaCp* is more advantageous for ligand elimination than trivalent TMG and TEG.

Reference[1] F. Mizutani, S. Higashi, M. Inoue, and T. Nabatame, J. Vac. Sci. Technol. A 38, 022412 (2020).

11:00am **AF2-WeM-13 Plasma-Enhanced Growth of Low-κ Amorphous Boron Nitride: From 25 °C to 400 °C***, **Daehyun Ko**, Fu-Chun Sheu, Luwen Li, Xun Zhan,* UT Austin*; John Carroll, Sergio Gamez-Puente, Hu Li, Peter Ventzek, Jianping Zhao,* Tokyo Electron America*; John Ekerdt, Jamie Warner,* UT Austin

The International Roadmap for Devices and Systems (IRDS) highlights the critical need for new dielectric materials that reduce permittivity and meet reliability requirements for future interconnect architectures. As interconnect dimensions scale into the sub-25 nm regime, conventional silicon-based dielectrics face significant challenges in mitigating parasitic capacitance and crosstalk while satisfying the rigorous mechanical and barrier requirements for integration. Amorphous boron nitride (a-BN) has emerged as a promising alternative for these applications because it offers a unique combination of low permittivity, high mechanical strength, and excellent chemical stability.

In this work, we demonstrate the plasma-enhanced growth (100 MHz capacitively coupled plasma) of a-BN onSiO_2/Si(001) using borazine ($B_3N_3H_6$) as a single-source precursor. We explore a wide processing window, ranging from room temperature (25 °C) to 400 °C. Growth is governed by weak, reversible physical adsorption and plasma exposure time. During a growth cycle, borazine is adsorbed on the substrate, the chamber is purged/evacuated, and an Ar plasma is ignited. The plasma activates the adsorbed borazine by dissociating the B-H and N-H bonds and breaking open the ring structure. *In situ* X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) analyses confirm the formation of stoichiometric, sp^2-bonded films with exceptional purity (<1 at.% carbon) and no resolvable B-C or B-O bonding features over a 25 to 400 °C window. By rigorously defining the thickness of a-BN (~14 nm) grown at 25 °C via cross-sectional scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) of the fabricated metal-insulator-metal (Au/a-BN/SiO_2/Si) capacitors, we extracted a dielectric constant of ~2.94, validating the potential of a-BN for back-end-of-line integration.

We further investigated the temperature dependence of film properties by extending the growth window from 100 °C to 400 °C. Although Fast Fourier transform (FFT) analysis confirms the emergence of short-range lamellar ordering at elevated temperatures, transmission electron microscopy (TEM) and EELS confirm the preservation of a global amorphous phase and an sp^2-bonded network throughout this transition. Consistent with this, X-ray reflectivity (XRR) reveals a linear increase in film density with temperature, reaching ~2.10 g cm^{-3} at 400 °C. This densification correlates with enhanced environmental stability, offering a tunable pathway to synthesize high-quality a-BN dielectrics optimized for diverse thermal budgets.

11:15am **AF2-WeM-14 Comparing the Effect of H_2 and N_2 Plasma on Boron Nitride Surface During Plasma Enhanced Atomic Layer Deposition Using Density Functional Theory***, **Tsung-Hsuan Yang**, Jianping Zhao, Peter Ventzek,* Tokyo Electron America

Boron nitride (BN) has emerged as a promising candidate for next–generation semiconductor and dielectric materials due to its wide bandgap, chemical stability, and compatibility with advanced device architectures. However, the intrinsic inertness of BN surfaces presents challenges for thin–film growth and surface functionalization, particularly when using conventional precursors such as boron trichloride (BCl_3) or borazine

($B_3N_3H_6$), which exhibit limited surface reactivity. Plasma-assisted processes employing hydrogen (H_2) or nitrogen (N_2) are therefore commonly used to activate BN surfaces, although the underlying reaction mechanisms remain poorly understood.

In this work, density functional theory (DFT) calculations are used to investigate the reaction mechanisms and energetics of H_2 and N_2 plasma interactions with boron nitride surfaces. Plasma environments are modeled using atomic hydrogen and nitrogen radicals to represent the highly reactive plasma species. Adsorption configurations, reaction pathways, and activation barriers are analyzed to elucidate key differences between hydrogen- and nitrogen-based plasma treatments.

Our results show that hydrogen radicals preferentially interact with surface nitrogen sites, leading to hydrogen termination and, in some cases, B–N bond dissociation. In contrast, nitrogen radicals promote nitrogen incorporation and surface restructuring through B–N bond formation and the generation of N_2-like dimer species. These distinct reaction pathways produce markedly different surface chemistries, which influence subsequent precursor adsorption and thin–film growth behavior. Based on the calculated energetics, we identify process conditions under which plasma species can selectively tailor surface reactivity, enabling control over film geometry, stoichiometry, and structural evolution.

11:30am **AF2-WeM-15 Precise and Narrow Ion-Energy Distributions in Plasma-Enhanced ALD of Nitrides Using Tailored-Waveform Biasing**, *Arthur de Jong, Silke Peeters, Harm Knoops, Erwin Kessels,* ***Adrie Mackus****,* Eindhoven University of Technology, Netherlands

Plasma-enhanced ALD (PEALD) is a powerful approach for the low-temperature growth of nitride thin films, where controlled ion bombardment can be used to tailor film composition, density, and functional properties. In previous work, we have demonstrated that radiofrequency (RF, 13.56 MHz) substrate biasing provides beneficial ion-energy effects during PEALD, enabling improved electrical and structural properties of a range of dielectrics and conductive nitrides [1,2]. However, the achievable process window can benefit from more precise, narrow, and independent control over the ion energy.

In this contribution, we demonstrate tailored-waveform (TW) substrate biasing at 200 kHz as an advanced ion-energy control scheme [3] for PEALD, offering narrow and well-defined ion-flux energy distribution functions (IFEDFs) without increasing the plasma density [4]. We apply this approach to the PEALD of several technologically-relevant metal nitrides, including AlN_x, TaC_xN_{1-x}, TiN_x, and NbN_x, using Ar–N_2–H_2 plasma mixtures.

By systematically tuning the ion energy via TW biasing, clear and material-specific structure–property relationships are observed. For AlN_x, an increased refractive index and reduced oxygen incorporation are achieved, while for conductive nitrides (TaC_xN_{1-x}, TiN_x, and NbN_x) significant reductions in electrical resistivity are obtained. These results are consistent with, and extend beyond, earlier RF-bias PEALD studies, highlighting the role of controlled low-energy ion bombardment in densification, impurity suppression, and microstructural optimization.

Overall, tailored-waveform biasing provides substantially narrower and better-defined ion-energy distributions, transforming ion energy during ALD into a high-precision knob for materials design.

This work was carried out in collaboration with Oxford Instruments and Prodrive Technologies. An Oxford Instruments FlexAL ALD reactor in the TU/e NanoLab was retrofitted with a Prodrive Technologies prototype low-frequency tailored waveform generator.

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[3] T. Faraz et al., *Precise ion energy control with tailored waveform biasing for atomic scale processing*, J. Appl. Phys. 128, 213301 (2020).

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11:45am **AF2-WeM-16 Characterizing Inductively Coupled Plasmas in $Ar/N_2/H_2$ Mixtures for Plasma Enhanced Atomic Layer Deposition**, ***David Boris****, Jeffrey Woodward, Virginia Wheeler, Michael Johnson, Mackenzie Meyer, Scott Walton,* U.S. Naval Research Laboratory

Low temperature plasmas containing mixtures of Argon, Nitrogen, and Hydrogen are widely used in the plasma enhanced atomic layer deposition of crystalline metal nitrides (e.g. AlN) at low temperatures (<500C) [1,2,3].Generally, the addition of H_2 is beneficial in that it facilitates the removal of precursor ligands and leads to films with low carbon content (<1%). In addition, if the process conditions are properly chosen, highly crystalline metal-nitride films can be grown in $Ar/N_2/H_2$ mixtures.However, the effects of H_2 addition on the downstream plasma properties near the substrate are not well understood in remote, inductively coupled plasma (ICP) geometries.As such, a better understanding of the downstream plasma properties in this gas chemistry will be the focus of this presentation.

In this work, we use a combination of Langmuir probes, a retarding field energy analyzer, and optical emission spectroscopy (OES) to examine the effects of varying process parameters on the physical characteristics of $Ar/N_2/H_2$ plasmas generated in a remote, ICP geometry.In particular, a range of applied RF powers, gas flows, and pressures are explored with a focus on the resulting changes in atomic species density, plasma density, plasma potential, and the energy and flux of ions at the substrate.Of particular interest is the effect H_2 has on the ion flux and ion energy distribution at the substrate. These changes in plasma properties are then tied to changes in the characteristics of AlN thin films grown via plasma-enhanced ALD using a remote ICP employing $Ar/N_2/H_2$ gas mixtures. This work was supported by the NRL Base program through the Office of Naval Research.

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[3] M. F. J. Vos, et al J. Phys. Chem 122, 39 (2018)

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-WeA

Modeling for ALD Processes I

Moderators: Alex Martinson, Argonne National Laboratory, **Paul Williams**, Pegasus Chemicals

1:30pm **AF1-WeA-1 A Framework Bridging Generative AI Models and Atomic Layer Deposition for $HfxZr_{1-x}O_2$, *Han-Bo-Ram Lee***, *Bonwook Gu,* Incheon National University, Republic of Korea

As atomic layer deposition (ALD) is increasingly applied to complex, multicomponent materials, selecting appropriate compositions and phase windows in practice still relies heavily on trial-and-error. This becomes a serious limitation for functional oxides, where small changes in composition can strongly affect phase formation and electrical properties under thin-film growth conditions. In this work, we present an inverse-design framework for ALD, a general approach that connects recent advances in data-driven artificial intelligence (AI) models for inorganic materials with experimental ALD process development. We first generate many candidate crystal structures by using an AI-based structure generator (a model that proposes plausible crystal structures from composition). This generator prioritizes physically reasonable inorganic structures and compositions, as well as thermodynamically stable candidates (i.e., structures likely to form). These structures are relaxed with machine-learning interatomic potential (a fast surrogate for DFT) to obtain consistent formation energies and the energy above the convex hull (E_{hull}), enabling fast thermodynamic screening across composition. Based on this thermodynamic screening, graph neural network models are used to estimate key electronic properties, allowing composition–structure–property trends to be mapped without extensive first-principles calculations. The framework is demonstrated using the Hf–Zr–O dielectric system. The model captures a clear trade-off between band gaps and dielectric response across composition and highlights an intermediate composition range where low-energy tetragonal and orthorhombic phases are frequently predicted. Guided by these results, $Hf_{1-x}Zr_xO_2$ thin films were deposited by atomic layer modulation (ALM; an ALD sequencing method that tunes the Hf/Zr ratio cycle-by-cycle), which enables atomic-scale control of cation ratios within a single ALD sequence. Structural, electrical, and optical measurements show that the predicted phase evolution and property trends are reproduced experimentally, confirming that the model-guided design window remains meaningful under realistic ALD conditions. Overall, this framework provides a practical way to reduce empirical trial-and-error in ALD by focusing experiments on the most promising composition and phase regions. Although demonstrated here using a Hf–Zr–O system, the framework is not material-specific and can be readily applied to other complex oxides, doped systems, and emerging ALD materials.

1:45pm **AF1-WeA-2 Quantitative Kinetic Monte Carlo Modeling of Al_2O_3 Atomic Layer Deposition by Trimethylaluminum Based on Neural-Network-Potential-Derived Kinetics**, ***Yichen Zou***, *Yuxuan Wu, Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Atomic layer deposition (ALD) is a key thin-film growth technique in advanced semiconductor manufacturing, enabling atomic-scale thickness control and excellent conformality. Despite the technological maturity of the trimethylaluminum (TMA)–H_2O process for Al_2O_3, establishing a quantitative link between atomistic surface reactions and experimentally observed growth behavior remains challenging due to the complexity of the reaction network, finite-temperature kinetic effects, and steric constraints on precursor adsorption.

In this work, we develop a kinetic Monte Carlo (KMC) framework for the TMA–H_2O ALD process by integrating molecular dynamics (MD) simulations with a neural network potential (NNP) trained to near density-functional-theory accuracy. Compared with our previous study, the present model introduces several key improvements. First, the sticking probability of TMA adsorption, previously approximated as an empirical constant, is re-evaluated using explicit MD collision simulations with a chemically irreversible adsorption criterion, yielding a lower and more realistic value. This update enables more accurate estimation of adsorption timescales and surface saturation behavior. Second, the surface reaction network is substantially expanded to explicitly include hydrogen migration as well as H_2O formation and desorption from hydroxyl groups, which were neglected in earlier modeling. Finally, steric effects arising from the bulky methyl ligands of intact TMA molecules are quantitatively incorporated into the KMC model through a local coordination-based descriptor that restricts adsorption in crowded environments.

The KMC simulations quantitatively reproduce key experimental growth characteristics of Al_2O_3 ALD. The simulated mass evolution within a single ALD cycle captures the characteristic rapid-then-slow mass uptake during the TMA pulse, followed by a negative mass change during the H_2O pulse associated with ligand removal and by-product desorption. The predicted saturated mass gain reaches 36.8 ng cm^{-2} $cycle^{-1}$ at 393 K, in good agreement with in situ quartz-crystal microbalance measurements. Furthermore, the simulations indicate that higher temperature and longer H_2O pulse duration promote more efficient removal of methyl ligands, leading to reduced residual carbon in the growing film. These trends highlight the importance of thermal activation and sufficient reactant exposure for minimizing carbon contamination during Al_2O_3 ALD. Overall, the combined treatment of MD-derived adsorption kinetics, expanded surface reaction pathways, and steric constraints provides a physically grounded and quantitatively improved description of Al_2O_3 ALD growth behavior.

2:00pm **AF1-WeA-3 Analysis and Design of Nb PE-ALD using Neural Network Potential Molecular Dynamics Simulation**, ***Noboru Sato***, *Akimasa Nakashima, Jun Yamaguchi, Naoki Tamaoki, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Niobium (Nb) is a promising material for semiconductor interconnects, pMOS contacts, and superconducting components for Cryo-CMOS in quantum-computing applications. However, as a group-5 transition metal, Nb is difficult to reduce to the metallic state, and low-temperature CVD/ALD processes remain limited. We have been developing a low-temperature plasma-enhanced ALD (PE-ALD) process using $NbCl_5$ as a precursor and hydrogen plasma as a reducing agent. The resulting Nb films still exhibit high resistivity (~200 μΩ·cm), likely due to residual impurities and small grain size, compared with the bulk value (~15 μΩ·cm). In this study, we analyze the reaction mechanisms of $NbCl_5/H_2$ PE-ALD and explore process-design guidelines using molecular dynamics (MD) simulations based on neural network potentials (NNPs).Reaction analyses were conducted using NNP-based MD simulations implemented in MatlantisTM. The NNP was trained on PBE-based density-functional-theory data with empirical dispersion corrections. First, we examined saturated adsorption of $NbCl_5$ on the Nb(110) surface of body-centered cubic (bcc) Nb, a representative stable surface of metallic Nb. At low coverage, Nb and Cl atoms were largely dissociated on the surface; as coverage increased, Nb atoms aggregated, and at later stages chain-like $NbCl_4$ species formed on the surface.Next, we modeled plasma exposure by injecting H and Ar atoms onto the $NbCl_5$-saturated surface while varying acceleration energy and incident angle. For H atoms, low acceleration energy (0.1 eV) yielded a high probability of reaction with surface Cl to form volatile HCl; this probability decreased as acceleration energy increased. H incorporation into the Nb substrate was most likely at normal incidence (0°) and decreased at higher incident angles. For Ar atoms, $NbCl_4$ desorption was observed when the acceleration energy exceeded 10 eV, whereas surface structural collapse occurred above 100 eV. In contrast to H, Ar showed no strong dependence on incident angle.Experimentally, Nb PE-ALD was performed at 175 °C using an H_2/Ar plasma step with substrate bias. Comparing two bias conditions, (a) 60 W for 7 s and (b) 60 W for 3 s followed by 30 W for 4 s, the lower-bias sequence reduced residual Cl as quantified by XPS from 0.98% (a) to 0.33% (b). The combined simulation/experiment results suggest that suppressing excessive ion energy while maintaining sufficient hydrogen-driven chlorination removal is key to lowering halogen impurities in low-temperature Nb PE-ALD.

2:15pm **AF1-WeA-4 Study of Pd Ald as a Growth Enhancer for Ultrathin CoW Liner/Barrier Layer ALD**, *Noboru Sato, Wataru Mori, Souga Nagai, Yichen Zou, Yuxuan Wu, Yubing Deng, Jun Yamaguchi, Naoki Tamaoki, Atsuhiro Tsukune,* ***Yukihiro Shimogaki***, The University of Tokyo, Japan

Cu interconnects in advanced ULSI employ a bilayer liner/barrier stack to ensure adhesion to Cu and to suppress Cu diffusion. As scaling progresses, however, the effective resistivity of Cu line increases, motivating the use of a single-layer CoW liner/barrier that can provide both adhesion and barrier functions while improving the Cu volume fraction. A major challenge in forming an ultrathin (1–2 nm) continuous CoW film on dielectric surfaces by ALD is the intrinsically low nucleation density of metal ALD on insulators ($<10^{10}$ cm^{-2}), whereas $>10^{14}$ cm^{-2} is typically required for immediate film continuity.

To address this nucleation bottleneck, we explore Pd as a catalytic growth enhancer (GE) for CoW ALD. We previously observed that Co ALD on PVD-Pd/SiO_2 increases the Co nucleation density to ~10^{12} cm^{-2}, i.e., ~100× higher than conventional nucleation on dielectrics [1]. Building on this concept, the present work aims to develop a Pd ALD process capable of forming Pd clusters with nucleation densities ≥10^{13} cm^{-2} on dielectric surfaces, thereby further enhancing the initial nucleation of CoW.

First, we investigated the chemisorption behavior of the Pd precursor $Pd(hfac)_2$ using neural-network-potential molecular dynamics (NNP-MD). The NNP was trained to reproduce dispersion-corrected PBE (Perdew–Burke–Ernzerhof) reference data using Matlantis™. NNP-MD simulations at 450 K showed no chemisorption of $Pd(hfac)_2$ on hydroxyl-terminated SiO_2, whereas adsorption was observed on hydroxyl-terminated α-Al_2O_3 within 100 ps. These results suggest that creating an Al_2O_3-like hydroxylated surface is essential to enable high-density Pd nucleation on insulating substrates.

Guided by the simulation, we experimentally performed Pd ALD on SiO_2 and Cu substrates after surface modification with trimethylaluminum (TMA) at 145 °C to form an Al_2O_3-like overlayer. We compared (a) no treatment, (b) TMA treatment followed by air oxidation, and (c) TMA treatment followed by H_2O exposure. On SiO_2, Pd uptake increased after surface modification. On Cu, a marked increase in Pd uptake was obtained only for condition (c). The higher effectiveness of (c) over (b) is attributed to differences in Al_2O_3 surface termination; notably, our MD simulations also indicated that $Pd(hfac)_2$ does not adsorb on gibbsite-like Al_2O_3 surfaces. These combined computational/experimental results provide a practical route to engineer dielectric surfaces for high-density Pd nucleation as a growth enhancer toward ultrathin, continuous CoW liner/barrier ALD.

Reference

[1] Deng et al., Advanced Metallization Conference 2025, #4-3, Oct. 9-10, 2025, Toyo (2025).

2:30pm **AF1-WeA-5 Design and Performance of AI Agents Based on Large Language Models Interfacing with an Autonomous Atomic Layer Deposition Tool***, **Angel Yanguas-Gil**, Jessica Jones, Sungjoon Kim, Chi Thang Nguyen, Jeffrey Elam,* Argonne National Laboratory

In this work we introduce the design of an atomic layer deposition (ALD) reactor augmented with an AI interface for autonomous materials synthesis. Our modular interface encapsulates the particularities of the hardware behind a Python interface that communicates with the ALD control software via transmission control protocol (TCP). This interface is compatible with model context protocol (MCP) interfaces used in agentic frameworks. To evaluate its performance, we have integrated our tool with a simple AI agent that leverages a large language model to transform user-supplied queries into ALD processes that are then run in our reactor. Our approach uses a JavaScript object notation (JSON) schema to encode ALD processes. Our experimental results show that the AI interface does not impose a significant overhead to our control software, at least within our fastest 10 ms scale. We also carried out a detailed evaluation of the agent performance based on leading models in three types of tasks: basic instruction tasks and process discovery tasks, where the agent is presented with a target material and needs to identify the correct ALD process compatible with the reactor configuration, and process optimization. Despite the simplicity of our agent design, we observed that most of the advanced models excelled at the instruction tasks. However, only recent models such as o1, o3, GPT-5, and Claude Opus 4, with reasoning capabilities, performed well in process discovery tasks. While the results obtained are promising, we identify areas where AI research could help improve the performance of autonomous process discovery and optimization tasks involving atomic layer deposition.

2:45pm **AF1-WeA-6 Generalized Reaction Networks for Atomic Layer Deposition***, **Simon Elliott**,* Schrödinger, Ireland*; Thomas Ludwig,* Schrödinger*; Thomas Hughes, Chloe Luyet,* Schrödinger*; Jacob Gavartin,* Schrödinger, UK

ALD processes are defined in terms of their underlying chemistry, namely self-limiting gas-surface reactions. Much work has been done to determine the reaction mechanism in specific cases, but a general understanding is lacking regarding the criteria for ALD and the resulting limits on growth rates and sticking coefficients. In this work, we develop a generic reaction network for the deposition or etching of metal oxides by ALD or CVD and use microkinetic modelling (MKM) to compute these measurable process characteristics as a function of process parameters. We use ZnO, Al2O3 and HfO2 as illustrative examples that span a range of metal valences and restrict ourselves to water as the co-reagent, though the extension to sulfides or nitrides in similar Bronsted acid-base chemistry would be straightforward. Building on past mechanistic studies, we identify the elementary forward reactions that together comprise the reaction network as (i) precursor/co-reagent adsorption, (ii) ligand or proton exchange, (iii) elimination of protonated ligands as by-products and (iv) densification into solid film. The reverse of each reaction is also included in the reaction network. We streamline the network by omitting linearly dependent reactions. Since these elementary steps convert one surface intermediate into another, the size of the network scales in principle with the square of the number of intermediates. We therefore restrict the number of surface intermediates to the minimum for the number of ligands per precursor and number of protons per water molecule. Activation free energies for each elementary step would typically be computed with DFT, but here our interest is in how the pattern of relative activation energies across the network affects the overall process. Running MKM simulations of multiple pulse-purge cycles, we establish the bounds for ALD versus CVD behavior in terms of the reactivity of individual metals and ligands. The relative kinetics of ligand transfer and proton transfer are found to be the crucial factor.Having used MKM to identify the chemical spaces where ALD is viable, we then derive the corresponding ranges of growth/etch per cycle and sticking coefficients, which are measurable characteristics of the growth/etch process and can be used as inputs to higher-scale simulations. We present the dependence of these characteristics on precursor mass, metal valence, process temperature and pulse pressure.

3:00pm **AF1-WeA-7 Active-Learning PES Exploration: Fast Reaction Discovery in ALD Chemistry***, Nicolas Onofrio, Nestor Aguirre, **Fedor Goumans**,* Software for Chemistry & Materials, Netherlands

Understanding elementary reaction mechanisms of ALD precursors and plasma species is critical to predict nucleation, film microstructure, and process windows. We describe an automated, active-learning workflow that uses a foundation M3GNet interatomic potential to accelerate potential-energy-surface (PES) exploration and discover mechanistic pathways for ALD chemistries. Starting from a compact DFT seed set, the M3GNet model is fine-tuned and used to propose adsorption states, intermediates and transition-state candidates via ML-guided scans and NEB initializations. An uncertainty-aware query policy identifies high-value configurations for targeted DFT verification; verified results are fed back to the MLIP in iterative retraining. This loop expands PES coverage by orders of magnitude for a fixed DFT budget while maintaining DFT-level accuracy for kinetically relevant energetics. Verified elementary steps parameterize kinetic models (kMC) to evaluate nucleation, lateral growth and defect incorporation under varied pulse timing, temperature and co-reactant conditions. In ALD case studies (high-k precursor screening and Ru–H chemistries) the ML-augmented exploration uncovered low-probability dissociative channels and alternate TSs that materially affect predicted growth and electronic proxies. The approach enables faster, physics-grounded mechanism discovery and targeted DFT allocation, shortening precursor screening cycles and providing mechanistic insight for process engineers.

3:15pm **AF1-WeA-8 in-Silico, High-Throughput Exploration of Ald Reaction Mechanisms***, **Martin Siron**, Luis Pinto,* Entalpic AI, France*; Tristan Deleu,* Entalpic AI, Canada*; Alexandre Duval,* Entalpic AI, France

Understanding and ultimately controlling the elementary surface reaction steps that govern atomic layer deposition (ALD) remains a fundamental challenge for rational precursor design, growth selectivity, and process optimization. Although ALD is often idealized as a sequence of perfectly self-limiting half-reactions, practical film growth frequently proceeds through a complex interplay of competing ligand-exchange pathways, surface restructuring, precursor fragmentation, parasitic decomposition, and coverage-dependent kinetics. Quantitative prediction of reaction barriers, mechanistic branching, and rate-determining steps is therefore essential to connect molecular-scale surface chemistry with macroscopic deposition behavior such as growth-per-cycle (GPC), conformity, and selectivity.

Recent advances in high-throughput in silico reaction discovery, automated reaction network construction, and machine-learning interatomic potentials (MLIPs) are enabling mechanistically informed exploration of ALD chemistry at unprecedented length and time scales. By combining algorithmic reaction enumeration, accelerated transition-state refinement, and ML-driven reactive sampling, emerging computational frameworks

provide a systematic route to map ALD reaction landscapes, identify kinetic bottlenecks, and evaluate competing pathways across broad precursor–surface chemical spaces.

At Entalpic, we develop agnostic and scalable workflows for the automated construction of complete ALD reaction mechanisms by integrating state-of-the-art cheminformatics and quantum chemistry methodologies. Using bond–electron formalism–based reaction enumeration, we generate comprehensive sets of chemically plausible surface reactions, intermediates, and mechanistic pathways. Thermodynamic screening of reaction networks is rapidly performed using MLIPs, enabling efficient evaluation of large chemical spaces beyond the limits of conventional density functional theory.

To characterize kinetic accessibility, we compute activation barriers through a combination of transition-state sampling strategies, including advanced methods such as Popcornn, alongside generative approaches for transition-state structure proposal and refinement. Through the LeMaterial initiative, we are assembling the largest curated database of transition-metal–organic complex reaction pathways, which directly supports the training of predictive and generative models for mechanistic inference. In parallel, we have benchmarked key elementary reactions for technologically relevant ALD precursors, establishing mechanistic descriptors that correlate with experimentally observed growth-per-cycle trends.

ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-WeA
Modeling for ALD Processes II

Moderators: Simon D. Elliott, Schrödinger, **Michael Nolan**, University College Cork

4:00pm **AF2-WeA-11 Validation of the Direct Simulation Monte Carlo Method for the Numerical Modelling of ALD Conformality***, **Paul Nizenkov**, Asim Mirza, Stephen Copplestone, Julian Beyer,* boltzplatz - numerical plasma dynamics GmbH, Germany*; Simone Lauterbach, Marcel Pfeiffer,* Institute of Space Systems, University of Stuttgart, Germany

Atomic layer deposition (ALD) processes span a wide range of length scales and operating pressures, from nano-scale semiconductor features to micrometer-scale structures in MEMS. This means that diffusion processes can range from free molecular flow to the transitional Knudsen regime, where conventional fluid models may require empirical corrections to accurately predict film conformality.

Direct Simulation Monte Carlo (DSMC) offers a reliable approach to the simulation of rarefied gas dynamics on a molecular level. The method has been extensively validated against experimental measurements in different applications including turbo-molecular pumps, spacecraft re-entry aerothermodynamics, and vacuum systems in general. Its ability to accurately resolve gas flow across a wide range of Knudsen numbers, makes it ideally suited for ALD applications spanning multiple flow regimes.

We apply the DSMC method using the open-source plasma simulation framework PICLas to simulate Al_2O_3 ALD conformality from TMA/H_2O in lateral high-aspect-ratio channels. The method is validated against experimental thickness profiles from Arts et al. (2019), then employed to evaluate the extended slope method by Gonsalves et al. (2024) in the transitional regime. DSMC enables seamless multi-scale coupling between reactor-level transport and feature-scale deposition, providing a framework for determining sticking coefficients across industrially relevant conditions. Additionally, PICLas offers the capability to investigate plasma-enhanced ALD processes in the future.

4:15pm **AF2-WeA-12 Multi-Scale Model for Optimization of HfO_2 ALD in High Aspect Ratio Structures***, **Ivan Petras**, Andrey Smirnov, Yury Shustrov,* Semiconductor Technology Research d.o.o. Beograd, Serbia

ALD is characterized by two self-limiting steps and purging. Each step requires a certain time to ensure complete coverage of the surface by precursor and complete removal of excess precursor from reactor volume and surfaces during purging. DRAM capacitors have a complex structure, so it is important to form high-k thin film conformally with excellent step coverage to reduce leakage current. Thus ALD is a key technology for scaling of deep trench DRAM capacitors, where film thickness required is low. HfO2 ALD presents a challenge for conformal deposition in high aspect ratio (HAR) structures due to specific processes such as narrow temperature window due to precursor properties or film quality. In this sense, multi-scale models with coupled reactor- and feature-scale simulations can be applied for reducing process development costs and achieving conformal trench coverage. Focus of this work is aimed at improvement of HfO2 ALD process with consideration of patterned wafers by tuning type of precursor, dosing and purging duration. HfCl4 is known for its thermal stability and ease of use but has the disadvantage of having corrosive by-products, whereas hafnium amides are considered promising due to their high reactivity, non-corrosiveness, and suitability for low temperature processes. An integrated modeling approach was developed with self-consistent coupling of modeling tasks on different scales. Reactor-scale model of Hf-delivery by either HfCl4 or TDMAHf, oxidation and purging include unsteady mass transport with surface chemical reactions. Trench-scale model includes tracing Hf- and oxide precursor species, as well as products of surface chemical reactions.We demonstrate results of process recipe optimization for conformal deposition of HfO2 on patterned wafer within the smallest possible ALD cycle time using multi-scale model. It is shown that optimization of purging is important to keep as few impurities and conformal deposition as possible. Increasing of trench AR leads to remarkably longer time for achieving ALD conformality during precursor delivery, especially for HfCl4 due to secondary effects such as H2O adsorption or etching by HCl by-product. Effect of temperature and H2O purge step duration on resulting film stoichiometry is shown, demonstrating the importance of purge duration due to adsorption of additional H2O. Coating of deep trench surface with each of the precursors has its own characteristics that must be taken into account when optimizing the recipe. Due to its lower reactivity, chloride covers the trench surface more evenly than organometallic precursor. In addition, reactivity of both precursors is sensitive to temperature in different ways. Step coverage dependence on precursor pulse duration is shown for different precursors, pressure and trench AR. Optimal process parameters of HfO2 ALD in HAR trenches are discussed according to temperature range and precursor choice.

4:30pm **AF2-WeA-13 Engineering the Interlayer Materials to Improve Interfacial Thermal Conductance***, **Saikat Mukhopadhyay**,* U.S. Naval Research Laboratory*; Neeraj Nepal, Brian Downey, James Champlain, Shawn Mack, James Lund, Peter Litwin, Virginia Wheeler,* US Naval Research Laboratory

The heterogeneous integration of diverse material components is crucial for developing advanced, multi-functional microelectronic circuits. A significant challenge in this approach is the thermal boundary resistance at material interfaces, which can impede heat dissipation and compromise the performance and reliability of devices. As device sizes shrink and power densities rise, enhancing the interfacial thermal conductance (TBC) has become a critical aspect of thermal management. Recent research on GaN/SiC and AlGaN/Diamond interfaces suggests that introducing an interlayer material can effectively improve TBC.

However, the impact of different interlayer materials and their thickness on TBC is not well understood, and conventional theoretical models like the Acoustic Mismatch Model (AMM) and Diffusion Mismatch Model (DMM) are insufficient as they do not account for the critical role of interfacial states. To address this, our study focuses on the TBC of GaAs/Diamond and GaN/Diamond interfaces, both with and without interlayer materials. We employed advanced transport approaches, including the Non-Equilibrium Green's Function (NEGF) method and Reverse Non-Equilibrium Molecular Dynamics (RNEMD), to accurately calculate TBC incorporating the chemical reconstructions that happen at the interface.

Our calculations find that TBC through GaN/AlN/Diamond is significantly higher than GaN/Diamond. This can be explained in terms of much higher TBC associated with GaN/AlN and AlN/Diamond interfaces compared to the direct GaN/Diamond interface. This motivated a broader investigation using a series of interlayer materials (AlN, TiN, and TaN). We found that all interlayer materials improved the TBC for the GaN/Diamond interface, with TiN yielding the maximum improvement. Additionally, a nearly linear increase in TBC was observed when the TiN layer's thickness was increased from 3nm to 6nm, resulting in a 10% enhancement. Conversely, for the GaAs/Diamond interface, we did not observe a similar improvement in TBC, but the introduction of an AlN interlayer was found to improve the structural stability of the interface. This work provides guidance for future ALD experiments with carefully selected interlayer materials to optimize thermal management in next-generation electronic devices.

4:45pm **AF2-WeA-14 Closing Remarks and Award Presentations***,*

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