Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM-MoA

ALD Supercycle Processes

Moderators: John P. Murphy, Naval Research Laboratory, **Venkateswara Pallem**, AirLiquide

4:00pm **EM-MoA-11 From Inverse Design to Thin-Film Growth: AI-Guided Discovery of ALD Dielectrics***, Ngoc Le Trinh, **Wonjoong Kim**, Bonwook Gu, Minhyeok Lee, Dohyun Kim, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

As atomic layer deposition (ALD) is increasingly applied to complex multicomponent materials, selecting viable compositions and phase windows still relies largely on empirical trial and error. This limitation is particularly acute for emerging dielectric materials, where small compositional changes can strongly affect phase stability and electrical performance. To address this challenge, we present an inverse design framework that integrates a generative diffusion model with a line graph neural network (LGNN) to accelerate materials discovery prior to synthesis. The framework is applied to $La_xTa_yO_z$ ternary oxides, a composition space well represented in the Materials Project database and promising for high-k dielectric and wide-bandgap applications, yet experimentally underexplored. The model directly generates candidate stoichiometries together with predicted structural and electronic properties from a learned generative manifold. Selected compositions and prototype structures were experimentally realized using atomic layer modulation (ALM), enabling atomic-scale compositional control. The resulting $La_xTa_yO_z$ thin films crystallize in the predicted orthorhombic phase, and their electrical properties follow trends consistent with model predictions. These results demonstrate an end-to-end pathway from AI-driven inverse design to thin-film synthesis and device-level validation. More broadly, this framework offers a general strategy to reduce trial-and-error in thin-film fabrication by guiding experiments toward the most promising composition and phase regions.

4:15pm **EM-MoA-12 Spatial ALD of Zinc Tin Oxide by Co-Dosing and Supercycles: The Role of Persistent Ligands***, **Poorani Gnanasambandan**,* Eindhoven University of Technology, The Netherlands*; Melika Motaghian,* Spark Nano, Netherlands*; Mariadriana Creatore, Bart Macco,* Eindhoven University of Technology, The Netherlands

Zinc tin oxide (ZTO) has emerged as a versatile material platform with applications spanning thin film transistors [1] and tandem solar cells [2]. Synthesis of ZTO by conventional temporal atomic layer deposition (ALD) using diethylzinc (DEZ) and tetrakis(dimethyamino)tin(IV) (TDMASn) as precursors has been extensively studied following the supercycle approach, wherein a non-linear growth of ZTO is observed. This stems from persistent ligands - already present in the binary processes - which are strongly enhanced when combined in the supercycle. Specifically, the removal of ethyl (Et) ligands from DEZ is much less effective on SnO_2 surfaces [1,3].

Despite offering transformative advantages in processing speed, low thermal budget, and manufacturing scalability, spatial atomic layer deposition (SALD) of ZTO remains largely unexplored. In this work, we investigate the synthesis of $Zn_{1-x}Sn_xO$ films by SALD using both co-dosing and supercycles, and draw a direct comparison between them. We study ZTO films across composition ranges x = 0.1 to 0.6, and deposition temperature of 100-200 °C.

Our findings reveal that while binary SnO_2 and ZnO films deposited by SALD are free of carbon impurities, both supercycle and codosing resulted in ZTO films with a maximum of 5. at% and 3. at% carbon, respectively, while no nitrogen is detected. The presence of carbon and absence of nitrogen suggests the persistent Et ligands rather than the N-containing amine ligands to be (partially) incorporated. In-situ ellipsometry during SALD shows a strong nucleation delay for ZnO when interrupted by a single cycle of SnO_2, in line with more strongly-bound persistent Et ligands on Sn-terminated surfaces similar to reported behaviour in temporal ALD processes [1, 3]. Given that both approaches demonstrate bulk-carbon presence, our current work focuses on compositional analysis across the full Zn:Sn ratio range and in-depth surface characterization to fully elucidate similarities and differences between co-dosing and supercycle SALD of ZTO. Of particular interest is the codosing approach, which yields well-mixed films, hence understanding its growth mechanism and impact on film properties will be systematically investigated.

[1] Hung, HN, et al. "Enhancing electronic properties by suppressing nucleation delay for low-temperature processed atomic-layer-deposited amorphous zinc–tin-oxide thin films." *Ceramics International* 50, no. 9 (2024), p:15085

[2] Heydarian, M, et al. "Indium-Free Recombination Layer for Perovskite-Based Multijunction-Solar-Cells-with Improved Performance Using Sputtered Zinc Tin Oxide." *Small* 21, no. 50 (2025), p: e11646.

[3] Mackus, A, J., et al. "Incomplete elimination of precursor ligands during atomic layer deposition of zinc-oxide, tin-oxide, and zinc-tin-oxide." *The Journal of Chemical Physics* 146, no. 5 (2017), p: 052802.

Acknowledgement: This work is supported by the European Union co-funded PEPPERONI (No. 101084251) project.

4:30pm **EM-MoA-13 Atomic Layer Deposition of Epitaxial Complex Oxides for Neuromorphic and Photonic Applications***, **Henrik Sønsteby**,* University of Oslo, Norway **INVITED**

Atomic layer deposition (ALD) famously offers precise control over thickness, uniformity and in some cases, composition. However, its use for the growth of crystalline and epitaxial complex oxides, particularly at low temperatures, remains limited**.** This invited contribution reports on recent progress in ALD process development for complex oxide ferroelectrics and semiconductors. The focus is on precursor chemistry, binary process compatibility and growth control in multicomponent systems relevant for neuromorphic and photonic devices. Together, these developments position ALD not only as a tool for dimensional control, but as a chemically tunable platform for engineering functional oxides beyond conventional process limits.

The work centers on water-free, ozone-based ALD processes for ternary oxides, where reliable control of the binary end members is essential. For $Hf_{0.5}Zr_{0.5}O_2$, low growth-per-cycle processes for HfO_2 and ZrO_2 have been established within overlapping temperature windows. These processes show linear growth behavior, good uniformity, and percent-level control of cation composition through supercycle design. They enable the formation of ferroelectric HZO in very thin films, which is particularly relevant for scaled ferroelectric devices used in neuromorphic computing.

In parallel, new barium precursor chemistries have been developed to address long-standing challenges associated with ALD of Ba-containing oxides. These precursors enable controlled deposition of Ba-containing binary phases using ozone-driven ALD processes at low temperatures. When combined with matching TiO_2 and SnO_2 processes, this approach allows systematic investigation of ternary oxide growth, where stoichiometry, sub-cycle arrangement, and thermal budget can be independently adjusted. Such control is required for $BaTiO_3$- and $BaSnO_3$-based material systems relevant for electrooptic and oxide electronic applications. As an additional outcome, ozone-based ALD of TiO_2 has been demonstrated down to room temperature, providing further flexibility for low-thermal-budget process integration.

Overall, the results illustrate how chemically informed ALD process design can be used to approach crystalline and epitaxial complex oxides under CMOS-compatible conditions. Outstanding challenges related to defect control, crystallization pathways, and transfer to larger substrates are discussed in the context of future device integration. In this context, the work outlines a pathway toward integrating functional complex oxides into future electronic and photonic technologies using ALD as a manufacturable deposition approach.

5:00pm **EM-MoA-15 Towards Fast-Growing Metal Phosphate Films with Controlled Stoichiometry Using Plasma-Enhanced ALD***, **Aditya Chalishazar**, Ruben Blomme, Lowie Henderick,* Ghent University, Belgium*; Sylwia Klejna,* AGH University of Krakow, Poland*; Matthias Minjauw, Arpan Dhara,* Ghent University, Belgium*; Frans Munnik,* Institute of Ion Beam Physics and Materials Research, HZDR, Germany*; Christophe Detavernier, Jolien Dendooven,* Ghent University, Belgium

Metal phosphates are promising materials for battery electrodes and coatings, corrosion protection coatings, electrocatalysts, and ionic conductors. The versatility of these materials arises due to different binding modes for the metal (M), phosphorus (P) and oxygen (O), resulting in unique structures, stoichiometries, and functional properties. However, controlling the stoichiometry of metal phosphate thin-films using ALD is non-trivial [1]. In this work, we developed ALD processes for Al, Zn, Ti and Sn phosphates, systematically comparing three different approaches (Figure 1) in terms of their strengths and limitations regarding growth characteristics and composition control.

The first approach relies on supercycles to introduce the phosphate backbone. Inspired by [2,3], we combined one metal oxide (MO) ALD cycle with n phosphorus oxide (PO) ALD cycles, using trimethylphosphate (TMP) as the P-precursor and O_2 plasma as coreactant in both the MO and PO subcycles. We observed increased P content as the number of PO cycles per supercycle (n) was increased, varying from MOs to meta/pyrophosphates (atomic P fraction (P_i): 0–23 %; Figure 2(a,d)). However, increasing n beyond a point resulted in moderately increased growth per supercycle (GPSC) with nearly unchanged P content. Our findings, corroborated by computations, indicate that these trends are caused by self-inhibited growth of PO during the supercycle. As such, achieving high P content (P_i > 20%) with this approach comes at the cost of impractically long deposition times.

The second approach relies on TMP plasma polymerisation [1]. Using ALD cycles of TMP plasma, O_2 plasma and M precursor pulses, we developed and compared fast-growing processes for highly P-rich Al, Zn, Ti and Sn meta/ultraphosphate films. Saturated film growth was observed for $T_{dep} \geq$ 300 °C, while a CVD component arises at lower temperatures. As a result, the P content decreases with temperature, offering some compositional control. However, while high growth rates are achieved, this approach is limited to compositions in the high P-range (P_i: 22–26 %; Figure 2(b,d)).

To overcome the limitations of the first two approaches, we developed a novel third approach to achieve high growth rates as well as compositional control from meta/ultraphosphates to P-doped MOs (P_i: 30–10 %; Figure 2(c,d)). Using a supercycle of one TMP plasma-based cycle with n MO ALD cycles, we demonstrate wide compositional tuneability for Al, Zn, Ti and Sn phosphates with high GPSCs.

[1]Henderick et al., *Appl. Phys. Rev.*, **9**, 011310 (2022)
[2]Hornsveld et al., *J. Phys. Chem. C*, **124(9)**, 5495 (2020)
[3]Di Palma et al., *J. Vac. Sci. Technol. A*, **38**, 022416 (2020)

5:15pm **EM-MoA-16 Uncovering Emergent Electrical Behaviour in ALD Nanolaminates Through Supercycle Engineering for SiC Gate Applications**, ***Jesse Kalliomäki**, Soumen Mazumder, Fernanda Albrechtvechietti, Mustafa Yildirim, Safdar Muhammad,* Applied Materials, Finland

Power electronics based on Silicon Carbide (SiC) are central to the green energy transition, enabling high–efficiency electric vehicle (EV) charging and supporting modern power–grid infrastructure. SiC devices are well suited for this task due to their high thermal stability, low ON-resistance ($R_{s,ON}$), and compatibility with existing semiconductor manufacturing. However, optimal performance requires gate-oxides able to withstand high electric fields without excessive leakage or degradation. Traditional thermally grown SiO_2, which were already at a disadvantage due upcoming high aspect ratio device architectures[1], suffers from high interface trap densities at the SiC/SiO_2 interface, limiting device performance[2]. Consequently, improved dielectric materials are needed to meet increasingly demanding application requirements.

This work presents a gate–oxide solution based on nanolaminate metal oxide stacks deposited by Atomic Layer Deposition (ALD). The nanolaminate structure enables record–high breakdown fields (EBD) combined with low leakage and high dielectric constant (k), while adaptive supercycle approach provides precise tunability of material properties to meet device–specific needs. Films were deposited using Applied Materials™ Picosun® ALD systems. With supercycle optimization, high EBD, low leakage, desired flatband voltage (Vfb), high k-value, low interface trap density (Dit) and minimal residual stress are achieved. Electrical properties were evaluated using Hg–probe from samples deposited on Si substrates (Fig 1).

The performance of the nanolaminate stems from precise control of sublayers that disrupt crystallization pathways of the component films. Resulting stratified film stack gives rise to emergent dielectric behaviour through sub–band formation in the periodic structure[3]. Notably, films that tend to crystalize otherwise remains fully amorphous even after annealing, improving electrical reliability.

Process optimization yielded highly uniform films (≈1% or better) with competitive batch–reactor cycle times. Compositional analyses confirm the targeted layer structure and low impurity levels. Electrical characterization demonstrates EBD up to 12 MV/cm, low leakage (<5E-8 @6 MV/cm) and a k-value of ~8, offering higher equivalent oxide thickness and reduced electric–field stress relative to SiO_2. The films also exhibit low Dit values (10^{11} eV^{-1} cm^{-2} range) near the valence band.

These results highlight how advanced supercycle strategies can produce a nanolaminate to rival SiO_2 as the gate dielectric in next–generation SiC MOSFETs.

[1] Micro Nanostruct., Volume 202, 2025, 208126
[2] Energies 2019, 12(12), 2310
[3] Phys. Rev. B 44, 11260

Emerging Materials and Processes
Room Tampa Bay Salons 5-9 - Session EM-MoP
Emerging Materials and Processes Poster Session

EM-MoP-1 Chromium-Doped ALD Lead Telluride Thin Films with Additional Iodine Coating*, Haifeng Cong*, *Helmut Baumgart,* Old Dominion University*; Tarek Abdel-Fattah,* Christopher Newport University

Thermoelectric materials directly convert heat into electricity, and PbTe is a promising narrow bandgap material due to its high Seebeck coefficient, chemical stability, and ability to operate at elevated temperatures (600–850 K). While PbTe thin films deposited by Atomic Layer Deposition (ALD) have been widely studied, doping thin films to enhance their thermoelectric performance remains less explored.In this study, PbTe thin films were synthesized on silicon substrates with native oxide via ALD using Pb(II)bis(2,2,6,6-tetramethyl-3,5-heptanedionato) and (trimethylsilyl) telluride as precursors. Chromium (Cr) was incorporated into the ALD films to modify electrical properties. An additional surface modification was performed by coating the PbTe:Cr films with iodine, followed by thermal treatment in a furnace at 80 °C for 72 hours, producing films with implanted Cr^{+} and iodine.Comprehensive characterization included X-ray diffraction (XRD) for crystal structure, FE-SEM for morphology, AFM for surface roughness, EDS and XPS for elemental composition and chemical states, and measurements of Seebeck coefficient, Hall effect, and thermal conductivity. Comparative analysis was conducted between Cr-doped PbTe films without iodine top coating and those with the iodine-treated top layer. Results show that the iodine modification further influences the electrical properties and thermoelectric figure of merit (ZT), highlighting the potential of combined Cr doping and surface engineering for high-performance PbTe thin films.

EM-MoP-2 Formation of Multi-Heterojunctions via Atomic Layer Etching for High Performance MoS_2 Photodetectors*, Si Yeon Kim*, *Sun Jae Jeong, Ji Eun Kang, Geun Young Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

In this study, high performance 2D MoS_2 photodetectors incorporating multi-heterojunction structures were fabricated through Atomic Layer Etching (ALE). By precisely controlling the thickness of the MoS_2 thin films using an ALE technique, MoS_2 heterojunctions composed of monolayer and multilayer regions were successfully formed. This engineered bandgap modulation facilitated the generation and separation of photo-induced carriers, thereby significantly enhancing the device's photoresponsivity.

Furthermore, the formation of multi-junction interfaces increased the effective contact area with the electrodes, securing superior electrical characteristics. Unlike conventional approaches that rely on hybrid heterostructures, this work distinguishes itself by simultaneously optimizing electrical and optoelectronic performance within a single material platform. These results demonstrate that ALE is a scalable and effective technique for manipulating 2D materials, paving a new way for next-generation optoelectronic applications.

EM-MoP-3 Plasma-Assisted Defect Engineering of MoS_2 for Controlled N-Type Doping and Phase Transition*, Ga-Hee Oh*, *Sun Jae Jeong, Ji Eun Kang, Geun Young Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Precise control of doping type and concentration in transition metal dichalcogenides (TMDs) is essential for realizing TMD-based electronic devices, including p-n diodes, field-effect transistors (FETs), and tunnel FETs. However, conventional ion implantation techniques are not suitable for two-dimensional materials due to severe lattice damage and structural degradation.

This study presents an approach for achieving controlled n-type doping and structural phase transition in CVD-grown MoS_2 through atomic-scale plasma-assisted defect engineering. Although radical-based surface doping is generally limited by shallow penetration depth, Argon plasma treatment was applied to the MoS_2 surface, creating sulfur vacancies that effectively introduced n-type doping characteristics. The density of these sulfur vacancies and thereby the doping concentration was precisely tuned by varying the plasma exposure duration.

In addition to doping, the defect formation induced a phase transformation from the semiconducting 2H phase to the metallic 1T phase. Raman spectroscopy confirmed the emergence of new peaks associated with the 1T phase. Raman spectroscopy confirmed the emergence of new peaks associated with the 1T phase, while X-ray photoelectron spectroscopy (XPS) provided evidence of both chemical and structural changes during the process. These plasma – induced modifications resulted in substantial improvements in device performance, such as increased field-effect mobility and higher on/off current ratios. The ability to simultaneously control both carrier type and structural phase makes this method particularly promising for the design of high-performance two-dimensional (2D) electronic devices.

Overall, the results demonstrate that plasma-assisted defect engineering offers a scalable and controllable pathway for tuning the electronic properties of 2D transition metal dichalcogenides like MoS_2. This technique opens new possibilities for the development of next-generation nanoelectronics and optoelectronic devices.

EM-MoP-4 Fabrication of p-type Al-doped SnO_x Thin Films via Supercycle ALD using Sn4+-based Precursor*, Suhyeon Park*, *Jiseop Byeon, Minjae Kwon,* Kyungpook National University, Republic of Korea*; Roy Byung Kyu Chung,* Kyungpook National University

Tin oxide (SnO_x) is a promising material for oxide semiconductor devices, such as thin-film transistors (TFTs), due to its tunable electronic properties derived from the multivalent nature of Sn^{2+} and Sn^{4+}. While SnO_2 is a typical n-type semiconductor, SnO exhibits p-type conductivity [1], making it suitable as a complementary material in complementary metal oxide semiconductor (CMOS) circuits. However, SnO is thermodynamically unstable and easily oxidized, requiring precise stoichiometry control. [2, 3] Previous studies have attempted to realize p-type SnO using atomic layer deposition (ALD) processes with Sn^{2+}-based precursors. [4, 5, 6] However, these precursors often suffer from limited commercial availability or high costs, hindering their practical use in research. In contrast, ALD processes employing Sn^{4+}-based precursors tend to favor the formation of stable n-type SnO_2, making p-type conduction difficult to achieve. To overcome these limitations, Al doping was employed as a key strategy to realize p-type SnO_x thin films using Sn^{4+}-based precursors.In this work, p-type Al-doped SnO_x (Al-SnO_x) thin films were fabricated through a supercycle ALD process using Tetrakis(dimethylamino)tin(IV) (TDMASn) as a Sn^{4+}-based precursor and Trimethylaluminum (TMA) as an Al_2O_3 source. The influence of the Al concentration and the spatial insertion position of the Al layer within the supercycle was systematically investigated. The optimal electrical performance was achieved when the Al layer was positioned in the middle of the SnO_2 layers. At an optimized Al concentration of 1.22 at%, the films exhibited a Hall mobility of 1.42 $cm^2/V \cdot s$ and a carrier concentration of 2.35 $\times 10^{18}$ cm^{-3} after post-annealing in a forming gas atmosphere. To evaluate electrical and structural characteristics of the films, Hall effect measurements and Grazing Incidence X-ray Diffraction (GIXRD) were primarily performed.This study demonstrates the feasibility of forming p-type films using cost-effective precursors. The optimization of both Al content and its spatial distribution allowed for precise control over the film's electrical characteristics. Based on these optimized process conditions, the controlled integration of n-type SnO_2 and p-type SnO_x films is expected to contribute to the future realization of tin oxide-based CMOS technology.

EM-MoP-5 Molecular Layer Deposited Hf-Based Hybrid Photoresists for Dual-Tone EUV Lithography*, Thi Thu Huong Chu*, *Dan N. Le, Minki Choe, Dushyant M. Narayan, Minjong Lee, Soham Shirodkar,* University of Texas at Dallas*; Nikhil Tiwale, Chang-Yong Nam,* Brookhaven National Laboratory*; Jiyoung Kim,* University of Texas at Dallas

Hafnium-based hybrid photoresists have emerged as promising candidates for extreme ultraviolet (EUV) lithography due to their high EUV absorption, superior etch resistance, and potential for sub-10 nm patterning.[1,2] Beyond their conventional single-tone behavior, our studies have revealed that Hf-based inorganic–organic hybrid materials can exhibit dual-tone responses under EUV exposure, enabling both positive- and negative-tone patterning within the same resist platform. This unique capability opens new opportunities for process simplification and enhanced patterning flexibility in advanced lithographic applications.

In this work, we demonstrate dual-tone EUV patterning using Hf-based hybrid photoresists and systematically evaluate their lithographic performance under both EUV exposure and low-energy electron-beam lithography (100 V EBL). We show that the resist tone can be switched via post-deposition treatment, which induces chemical changes within the Hf-based resist and results in tone inversion from conventional negative to positive tone behavior. The Hf-based hybrid resist films were fabricated via molecular layer deposition (MLD) using TDMA-Hf as the inorganic precursor and 2,3-dimercapto-1-propanol (DMP) as the organic linker. The MLD-derived hybrid resist exhibits high sensitivity, with the critical doses of 17.6

and 18.5 mJ/cm^2 for negative- and positive-tone modes, respectively. The critical doses required for both negative- and positive-tone patterning are comparable, indicating minimal sensitivity penalty when switching between tone modes.

Mechanistic investigations were conducted using *in-situ* FTIR and XPS analysis. The results indicate that negative-tone behavior arises from exposure-induced crosslinking, which stabilizes the resist film after development. In contrast, post-treated films exhibit positive-tone behavior, where film hardening is followed by bond scission under EUV or e-beam exposure, leading to enhanced solubility in the developer.

These findings highlight the versatility of Hf-based hybrid photoresists as multifunctional EUV resist materials and underscore their potential for next-generation EUV lithography, where adaptable tone control and simplified process integration are increasingly critical.

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[1] N. Mojarad *et al.,* Nanoscale, **2015**,7, 4031–4037.

[2] Y. Wang *et al.,* J. Mater. Chem. A, **2025**, 13, 29860.

EM-MoP-6 Deterministic Resistive Switching via Atomic-Layer Control of 2D WS_2 and Confined Ag Electrodes*,* ***Sihoon Son,*** *Taesung Kim, Hyunbin Choi, Geonwook Kim,* Sungkyunkwan University (SKKU), Republic of Korea

Atomic-scale control of both the active switching medium and the ionic source is a critical requirement for achieving reliable and scalable resistive memory technologies. While two-dimensional (2D) materials offer an intrinsically thin and well-defined switching layer, resistive switching in filamentary memories is still dominated by stochastic variations originating from uncontrolled metal-ion supply. Here, we demonstrate a resistive memory platform in which the resistive switching behavior is deterministically governed by the simultaneous atomic-layer-level control of a 2D WS_2 switching medium and the confined supply of Ag ions, enabled by ALD/ALE-compatible thickness engineering.

The WS_2 switching layer was synthesized with atomic-scale thickness control, allowing systematic modulation of the vertical transport length and defect density. In parallel, the Ag electrode was intentionally confined in both thickness and areal distribution, limiting the total Ag reservoir available for electrochemical metallization. By independently tuning the WS_2 thickness and the Ag supply, we reveal a clear transition in resistive switching behavior from Ag-dominated metallic conduction to vacancy-mediated switching governed by sulfur-vacancy (V_s) percolation. Electrical measurements combined with thickness-dependent statistics show that the high-resistance state is primarily dictated by the WS_2 thickness, whereas excessive Ag supply leads to unstable low-resistance states and increased variability.

Detailed electrical analysis and finite-element simulations indicate that a partially formed Ag tip, generated under confined Ag conditions, produces a highly localized electric-field enhancement at the WS_2 interface. This localized field drives controlled V_s migration along grain boundaries without forming a continuous metallic filament. The resulting sequential switching process—comprising partial Ag filament formation, transient space-charge-limited conduction, and eventual vacancy filament percolation—yields sub-percent switching variability and stable non-volatile memory operation. Importantly, ex-situ structural and compositional analyses confirm the absence of residual Ag within the WS_2 layer after switching, highlighting the non-metallic nature of the final conductive pathway.

By demonstrating that resistive switching characteristics can be deterministically programmed through atomic-scale thickness control of a 2D switching medium and precise limitation of metal-ion supply, this work establishes a materials-level design strategy directly aligned with ALD/ALE processing. The presented approach provides a scalable pathway toward highly uniform RRAM and neuromorphic memory devices, in which variability is suppressed not by circuit-level compensation but by atomically engineered material interfaces.

EM-MoP-7 BEOL Compatible Direct Growth of MoS_2 for Cu free Hybrid Bonding*,* ***Hyunbin Choi,*** Department of Semiconductor Convergence Engineering, Sungkyunkwan University, Republic of Korea*; Sihoon Son,* SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Republic of Korea*; Geonwook Kim, Taesung Kim,* School of Mechanical Engineering, Sungkyunkwan University (SKKU), Republic of Korea

Hybrid bonding technology is emerging as an essential solution for advanced 3D semiconductor integration, enabling the simultaneous bonding of metals and dielectrics. However, conventional hybrid bonding suffers from copper (Cu) contamination during the O_2 plasma activation step required for hydroxyl (OH) group formation on dielectric surfaces such as SiCN. The harsh plasma conditions induce Cu sputtering and migration, causing chamber and substrate contamination that degrades process reliability over time.To address this issue, we introduce a contamination free hybrid bonding approach employing an ultrathin molybdenum disulfide (MoS_2) barrier layer. The MoS_2 film is formed through plasma-enhanced chemical vapor deposition (PECVD) sulfurization of a Mo layer at low temperature. This barrier effectively suppresses Cu sputtering during O_2 plasma processing, preventing metal induced contamination while maintaining plasma activation efficiency.Furthermore, the MoS_2 layer enables post bonding electrical connection via memristive switching. Upon voltage application across the Cu–MoS_2–Cu structure, Cu ions migrate through the MoS_2 and form conductive filaments, ensuring reliable electrical connectivity without damaging the bonding interface.This work demonstrates a novel, BEOL compatible, Cu contamination free hybrid bonding process that preserves device integrity and enables high yield 3D integration. The proposed method provides a practical route toward cleaner, more reliable, and scalable hybrid bonding for next generation heterogeneous semiconductor systems.

EM-MoP-8 Monolithic 3D Artificial Intelligence Hardware Using four-Tier Vertically Integrated IGZO-Based HZO Ferroelectric Transistors*,* ***Geonwook Kim,*** *Sihoon Son, Hyunbin Choi, Taesung kim,* Sungkyunkwan University (SKKU), Republic of Korea

The relentless demand for faster, smaller and more energy-efficient integrated circuits has pushed the semiconductor industry to the performance, power and area (PPA) wall, where interconnect delay and energy dissipation dominate system efficiency. While 2.5D and TSV-based 3D integration offer partial relief, they suffer from long interconnects, thermal hotspots and reliability concerns. Monolithic 3D integration (M3DI) provides a transformative TSV-free paradigm, enabling nanoscale vertical interconnects between front-end-of-line logic and back-end-of-line memory tiers, thereby maximizing PPA efficiency and reducing latency. Here we demonstrate monolithic 3D integration (M3DI) of oxide thin-film electronics, integrating amorphous IGZO field-effect transistors with ferroelectric HZO field-effect transistors in a vertically stacked 1T-1FeFET architecture. These oxide-based thin-film devices are fully BEOLcompatible and highly scalable, providing uniform threshold voltage and I_{on}/I_{off} distributions for logic operations, as well as stable ferroelectric switching with narrow variability for memory functions. The resulting M3DI arrays enable ultra-dense integration, reproducible operation, and low-latency performance within a compact footprint. Beyond binary switching, the M3DI 1T-1FeFET architecture exhibits synaptic functionalities, including multilevel nonvolatile memory, spike-timing-dependent plasticity, and excellent array-level uniformity—key attributes for neuromorphic and AI hardware. This work establishes oxide-semiconductor-based M3DI as a promising platform for next-generation intelligent and energy-efficient computing systems beyond conventional CMOS and von Neumann architectures.

EM-MoP-10 Bias-Modulated ALD of Zinc Oxide*,* ***Jessica Jones,*** Argonne National Laboratory, USA*; Shi Li,* Argonne National Laboratory*; Rajeev Assary, Jeffrey Elam,* Argonne National Laboratory, USA

Biasing substrates during atomic layer deposition (ALD) in gaining popularity as a method to alter the resulting film. This is hypothesized to alter precursor–surface interactions and provide a means to tune material properties. We performed zinc oxide (ZnO) ALD using diethylzinc (DEZ) and water on silicon with native oxide substrates at 150 °C in a sample holder designed to create a static electrical field by biasing one plate of a parallel plate capacitor during deposition. ZnO films prepared in an electric field/on a biased sample holder were thinner, changed relative crystalline composition, and contained more carbon compared to samples grown under identical conditions without bias. Density functional theory (DFT) calculations showed enhanced electron migration between dissociatively adsorbed DEZ molecules and the ZnO (002) facet with increasing force from an electric field at the substrate surface, which strengthens the electronic

interactions between the surface and the adsorbate. These models offer a compelling explanation for the inhibited growth, changes in the crystallinity, and increased carbon content of films grown in an electric field/on biased plates.

EM-MoP-11 Plasma-Enhanced Atomic Layer Deposition of Ferroelectric Aluminum Nitride*, **Nicholas Strnad**,* US Army Research Laboratory*; Gilbert B. Rayner Jr., Noel O'Toole,* The Kurt J. Lesker Company*; Nastazia Moshirfatemi,* General Technical Services, LLC*; Daniel Drury, Brendan Hanrahan,* US Army Research Laboratory*; Glen Fox,* Fox Materials Consulting, LLC*; Jeffrey Pulskamp,* US Army Research Laboratory

Piezoelectric aluminum nitride (AlN) and doped-variant aluminum-scandium nitride ($Al_{(1-x)}Sc_xN$) thin films are commercially essential for RF filters for wireless communication and have additional applications as sensors for piezoelectric ultrasound transducers (PMUTs), and energy harvesters. Recently, there have been a flurry of reports of ferroelectric sputtered $Al_{(1-x)}Sc_xN$ since its published discovery by Fichtner in 2019. Ferroelectric $Al_{(1-x)}Sc_xN$ has enormous potential as a memory thin film due to its extremely large, switched polarization (>>100 µC/cm^2) and Curie temperature > 1000° C, making it suitable for operation in extreme environments. Despite this excitement, there are few reports showing ferroelectricity in nominally undoped aluminum nitride, typically deposited using sputtering, due to the large electric fields (>6 MV/cm) required for switching. Here, we show ferroelectric AlN thin films grown by plasma-enhanced atomic layer deposition (PEALD) grown using ultra-high purity conditions. This is the first demonstration of ferroelectric PEALD AlN and only the second report of any ferroelectric nitride grown by PEALD. The PEALD AlN thin films were deposited at a substrate temperature of 300° C and exhibit room-temperature ferroelectric switching which is enabled by their enormous breakdown fields > 9 MV/cm. Trimethylaluminum (TMA) and alternatively N_2 and N_2/H_2 plasmas were implemented as co-precursors. The PEALD AlN films exhibited the wurtzite phase and grew in the c-axis (0002)-orientation on {111}-oriented Pt bottom electrodes deposited on (001) silicon with a 500 nm-thick thermal oxide.

EM-MoP-12 Thermal Atomic Layer Deposition and Post-Deposition Annealing of Molybdenum Oxide and Sulfide Thin Films*, Wesley Jen, **Nolan Olaso**, Icelene Leong, Steven M. Hues, Elton Graugnard,* Micron School of Materials Science and Engineering, Boise State University

In order to enable further advances in microelectronics, new processes capable of precisely depositing films are required. This is especially true of processes meant for depositing transition metal dichalcogenides such as MoS_2, a material of particular interest due to its high potential mobility even at a thickness of a few atoms. Molybdenum oxide (MoO_x) is a wide bandgap transition metal oxide that has been of growing interest for several different applications in the semiconductor community, including for use as gate dielectrics in ultra-thin transistors, carrier-selective contacts in solar cells, and chemical selective materials in gas detection sensors. In this work, we report on an industry-compatible processes for depositing MoO_x and MoS_x thin films at 200 °C using bis(tert-butylamino)bis(dimethylamino)Mo (BTBDM) with H_2O or H_2S, respectively. Post deposition annealing in oxygen formed MoO3 from MoO_x, while annealing either MoO_x or MoS_x in H_2S formed crystalline MoS_2. ALD processes were characterized using in situ quartz microbalance measurements, while the resulting films were characterized using X-ray photoelectron spectroscopy, atomic force microscopy, optical absorption, Raman spectroscopy, and photoluminescence measurements. These results provide insight into methodologies for both precisely depositing crystalline MoS_2 and its oxide to accelerate the integration of 2D materials into leading edge microelectronics.

EM-MoP-14 Research on New-material Screening Methods toward the Development of Chemical-reaction-based Surface-roughness Reduction Processes*, **Taiki Kato**, Hirokazu Ueda, Mitsuhiro Tachibana,* Tokyo Electron Ltd., Japan*; Peter Ventzek,* Tokyo Electron Ltd.

In semiconductor device manufacturing processes, substrate surface roughness should be minimized because it leads to increased electrical resistance and added parasitic capacitance. Critical for device scaling, this is even more so when considering two-dimensional materials. Conventional methods for reducing substrate roughness include atomic layer deposition (ALD) and atomic layer etching (ALE), but a method that could reduce only the substrate roughness via surface chemical reactions without changing film thickness would represent a major breakthrough. We developed a numerical analysis method to evaluate the roughness-reduction effects of novel materials. The planarization capability of new precursors on various substrate materials was ranked for different topographic structures. The goal of the study at this stage is to prove the feasibility of chemical planarization of common interconnect metals.

Numerical evaluation of roughness-reduction effects followed two approaches: molecular dynamics (MD) and direct evaluation of the reaction-pathway thermodynamics. First, machine-learned potentials (MLP) based MD simulations described how novel precursor molecules interact on various metal surfaces with different roughness features. The analysis produced a picture in which certain reactive precursors, upon impinging on rough metal substrates, bond with surface metal atoms promoting their mobility, diffusion and surface flattening. By comparing the MD simulation temperature conditions at which metal surfaces become flattenable, we can rank the relative ease of planarization among different metals including ruthenium, cobalt and gold. Our second approach employed reaction-pathway (thermodynamics) to evaluate the activation energy for step-edge collapse for various metal surfaces. Smaller activation energies imply an easier to planarize surface. The same three metals in the MD study were evaluated and found to scale consistently. We also found that adsorption of the novel precursors reduces the activation energy for step-edge collapse, clarifying a mechanism in which precursor adsorption promotes diffusion of surface metal atoms and thereby enables surface planarization.

The presentation summarizes scaling trends we see from simulation-based studies of substrate-roughness adsorbate mediated planarization for various materials. Specifically, we show improvements in device characteristics resulting from reduced substrate surface roughness, experimental evaluations of roughness reduction versus film-thickness change, and potential process applications. We finish with an outlook for future development.

EM-MoP-15 Molecular Layer Deposition of Metalcones Using Salicylaldehyde as an Organic Precursor*, **Henry Yu-Jun Tang**,* National Taiwan University, Taiwan*; Hao-Wei Chan, Bo-Yuan Gu, Zhen-Rou Chang, Fang-Yu Lin, Yi-Jung Liao, Feng-Yu Tsai,* National Taiwan University, Taiwan

This study demonstrates molecular layer deposition (MLD) of alucone and hafnicone thin films using a previously unexplored organic precursor, salicylaldehyde, paired with trimethylaluminum (TMA) and tetrakis(dimethylamido)hafnium(IV) (TDMAHf), respectively. MLD of alucone and hafnicone at deposition temperatures between 120 and 190°C was confirmed with in-situ quartz crystal microbalance (QCM) and chemical analyses. The alucone chemistry was observed to be prone to self-termination, which could be mitigated with two methods: using an exposure process, and using H_2O as a coreactant. Conversely, the hafnicone chemistry showed strong resistance to self-termination owing to the high functionality and large ligand-to-ligand steric hindrance of TDMAHf. The potential of the alucone and hafnicone films as low dielectric constant (k) materials was evaluated, with the alucone and hafnicone films exhibiting k value of 4.2 and 4.7, respectively. The alucone and hafnicone films showed good thermal stability, with ~25% and 20% reduction in thickness upon baking in vacuum at 500°C for 15 min, respectively.

EM-MoP-16 The Effect of Remote Ar Plasmas on the Crystalline Structure of VO_2*, Peter Litwin,* U.S. Naval Research Laboratory*; Neeraj Nepal,* US Naval Research Laboratory*; Andrew Lang,* U.S. Naval Research Laboratory*; David Boris,* US Naval Research Laboratory*; Michael Johnson,* Naval Research Laboratory, USA*; Scott Walton,* US Naval Research Laboratory*; **Virginia Wheeler**,* U.S. Naval Research Laboratory

The effect of chemically inert plasmas on the surface of thin film materials is of interest because it allows for an additional means to deliver energy to a material beyond increasing the material's temperature. This could be of use in cases where energy needs to be delivered to specific layers or interfaces in a heterostructure without subjecting the entire material stack to higher temperatures or to overcome energetic barriers, such as those associated with material crystallization (or amorphization) or the formation of metastable phases. However, plasmas make for a complex environment due to the various energy contributions from ions, electrons, excited species, and photons. Despite this complexity, an increased understanding of energy transfer at the plasmas-surface interface opens additional avenues in material engineering. This may be particularly true for plasma enhanced atomic layer deposition (PEALD) processes where deposited thin films are cyclically exposed to plasmas and thus could benefit from an increased understanding of the interaction between plasmas and material surfaces.

In this work we look at the impact of chemically inert remote Ar plasmas on crystalline VO_2 (c-VO_2) thin films deposited by ALD. Thermal ALD of VO_2 was carried out at 150 °C using TEMAV and O_3 and subsequently crystallized in a dedicated thermal annealing vacuum system using our typical process[1]. We

demonstrate that under certain plasma conditions we can remove the Raman signature of the c-VO_2 films without any change to the surface morphology of the material, and this capability was greater when operating at lower pressures during the plasma exposure. Additionally, by changing the Ar plasma conditions used, we are also capable of recovering the crystalline nature of the previously damaged films; this was accomplished by treating the sample to subsequent plasma exposures of descending power. This presentation will discuss the details of these experiments and, with the aid of in situ plasma diagnostics, attempt to elucidate the mechanisms responsible for the behavior observed.

[1] J. Phys. Chem. C 2017, 121, 19341−19347

EM-MoP-19 Scalable and Controllable Deposition of Extrinsically Doped P-Type MoS_2 via Thermal Atomic Layer Deposition*, **Sungjoon Kim**, Jeffrey Elam,* Argonne National Laboratory

Computational energy consumption is increasing exponentially, making energy-efficient microelectronics and computing an urgent need. Three-dimensional integrated circuits (3D ICs) and neuromorphic computing promise to revolutionize information technology by drastically reducing the energy consumption of computers, and two-dimensional (2D) semiconductors like molybdenum disulfide (MoS_2) can enable such technologies. However, the development of complementary p-type MoS_2 is needed to fully leverage the benefits of 2D semiconductors. Moreover, thermal processes for thin film deposition are preferred over plasma-based techniques in high aspect ratio applications such as vertical gate-all-around transistors and 3D NAND. Here, we demonstrate the uniform and controlled deposition of extrinsically doped p-type MoS_2 using thermal atomic layer deposition (ALD). By varying the dopant cycle ratio, the final MoS_2's resistivity and charge carrier concentration can be precisely tuned. The resulting p-type MoS_2 was characterized using techniques including Raman spectroscopy, X-ray photoelectron spectroscopy, and Hall measurements, and was used to fabricate and test memtransistors. This work offers a pathway to deposit p-type 2D materials with tailored material properties.

EM-MoP-20 Mechanistic Transformation Pathway to Continuous and Impurity-Free Tellurium Films*, **Seung Ho Ryu**, Seungsu Kim, Jihoon Jeon, Gwang Min Park, Seong Keun Kim,* Korea University, Republic of Korea

As Si-based devices approach their physical scaling limits, monolithic three-dimensional (M3D) integration has emerged as a promising strategy for continued performance enhancement. In this architecture, transistors are vertically stacked within the back-end-of-line (BEOL) layers, imposing a strict process temperature limit below 400 °C to prevent degradation of front-end CMOS circuits. This restriction necessitates new channel materials that can be processed at low temperatures while maintaining high performance. Although substantial advances have been achieved in n-type oxides such as In_2O_3 and IGZO, the development of BEOL-compatible p-type channels remains limited.

Tellurium (Te) has attracted attention as a promising p-type semiconductor owing to its intrinsically high hole mobility and low melting point. However, direct ALD growth typically yields discontinuous, island-like films due to poor wettability and weak interchain van der Waals bonding. Previous approaches, such as increasing precursor pressure or introducing TeO_2 adhesion layers, have shown limited success because of poor conformality and interfacial oxygen residues. Here, we present a transformation-based strategy in which ALD-deposited TeO_2 is subsequently reduced to elemental Te. This method enables the formation of ultrathin, continuous, and oxygen-free Te layers with excellent conformality. Comprehensive structural and electrical analyses confirm complete phase conversion, smooth morphology, and stable p-type conduction, demonstrating a viable route for BEOL-compatible p-type channel integration in next-generation M3D electronics.

EM-MoP-21 Atomic Layer Deposition (ALD) on Complex Fibrous Architectures: Pathways to Functional and Smart Textiles*, **Tamer Uyar**,* Cornell University*; Necmi Biyikli,* University of Connecticut

Atomic layer deposition (ALD) offers a powerful platform for engineering the surfaces of fibers, nanofibers, and textile architectures with unprecedented precision. The three–dimensional, high–aspect–ratio morphology of fibrous networks presents significant challenges for conventional coating techniques, while ALD offers a unique opportunity for conformal nanoscale functionalization of fibers and textiles. ALD enables uniform coatings on fibers that impart advanced chemical, electrical, optical, and catalytic properties onto complex textile structures. In our research, we explore the use of ALD on diverse fibrous substrates—including polymeric fibers, nanofiber mats, and textile structures—to develop multifunctional and smart textile systems. ALD–modified fibers demonstrate enhanced performance for applications such as self–cleaning and antimicrobial textiles, conductive pathways for e–textiles, barrier and protective layers, and responsive surfaces for sensing and actuation. Beyond direct functionalization, nanofibers also serve as versatile sacrificial templates for fabricating hollow, core–shell, and hierarchical nanostructures through ALD. These architectures can be used as–is or further processed to yield complex geometries useful in photocatalysis, heterogeneous catalysis, energy harvesting, and environmental remediation. This talk will present an overview of the unique capabilities and advantages of combining ALD with fibrous substrates, highlighting material–substrate interactions, coating strategies, and emerging application domains. Together, these advances demonstrate how ALD on complex fibrous architectures can enable the next generation of multifunctional, adaptive, and smart textile technologies.

EM-MoP-22 Functional Group Dependence of Al_2O_3 Atomic Layer Infiltration in Polymeric Encapsulation Layers for Flexible OLEDs*, **Ye Jin Jeong**, Si Eun Jung, Ji Ho Jeon,* Seoul National University of Science and Technology, Republic of Korea*; Kwan Hyuck Yoon, Woo Yong Sung,* Samsung Display, Republic of Korea*; Jeong Hwan Han, Byung Joon Choi,* Seoul National University of Science and Technology, Republic of Korea

Flexible OLEDs have attracted significant attention as next-generation display devices; however, their susceptibility to moisture and oxygen degrades device lifetime and stability, making it important to secure effective encapsulation technology. Atomic layer infiltration (ALI) is a process that induces precursor molecules to infiltrate not only the polymer surface but also the internal free volume by introducing an exposure step with high-concentration vapor-phase precursors. This enables the formation of an organic–inorganic hybrid structure within the polymer, effectively suppressing gas diffusion while maintaining mechanical flexibility. In this study, Al_2O_3 was infiltrated using trimethylaluminum (TMA) and H_2O on polymer thin films of polyimide (PI), polyethylene terephthalate (PET), and polystyrene (PS). The infiltration behavior and feasibility of barrier layer formation were compared among the three substrates. To control process pressure and enhance precursor infiltration depth, the holding time and N_2 gas flow rate during the exposure and pulse steps were systematically varied. When the same ALI process was applied to an inkjet-printed acrylic monomer substrate and a PI film to compare infiltration behavior, deeper infiltration was observed in the acrylic monomer substrate. This was interpreted as being due to the higher free volume and greater accessibility of reactive sites in the acrylic monomer substrate, whereas the denser surface layer of the commercial PI film limited precursor diffusion.

XPS depth profiling revealed that the thickness of the organic–inorganic hybrid layer was greatest in PET, followed by PI and PS, indicating the deepest Al_2O_3 infiltration in PET. These results suggest that the type and distribution of functional groups within the polymer are important factors governing precursor infiltration and the subsequent ALD growth behavior. Analysis of the XPS O 1s spectra showed that, after the ALI process, both PI and PET exhibited a decrease in the carbonyl-related component and the formation of a new Al–O component, consistent with the FTIR results. XRF analysis further confirmed that samples with thicker infiltration layers contained higher Al concentrations. In addition, TEM and line-scan EDS analyses confirmed the formation of an organic–inorganic hybrid layer in both PI and PET, where Al and C coexisted. In future work, the moisture absorption and barrier properties of the formed hybrid films are quantitatively evaluated through Ca tests.

Acknowledgments : This work was supported by the Technology Innovation Program (RS-2024-00467233, Development of core materials, devices, and process industry source technologies to secure next-generation OLED pixel process technology) funded By the Ministry of Trade, Industry & Energy(MOTIE, Korea).

EM-MoP-23 Full-thickness Organic-inorganic Hybrid Barrier via Atomic Layer Infiltration for Flexible OLED Encapsulation*, **Si Eun Jung**, Ye Jin Jung, Yu Min Lee, Ji Ho Jeon,* Seoul National University of Science and Technology, Republic of Korea*; Kwan Hyuck Yoon, Woo Yong Sung,* Samsung Display, Republic of Korea*; Jeong Hwan Han, Byung Joon Choi,* Seoul National University of Science and Technology, Republic of Korea

Flexible organic light-emitting diodes (OLEDs) have attracted considerable attention as next-generation display technologies due to their bendability, enabling applications such as foldable smartphones, wearable devices, and flexible electronics. However, their long-term stability remains limited because of exposure to moisture and oxygen, as well as mechanical stress

generated during repeated bending. These factors induce cracking, delamination, pixel shrinkage, dark spots, and electrode oxidation, ultimately degrading device performance. Therefore, effective encapsulation technology is essential to ensure the durability of flexible OLED devices.

Although thin-film encapsulation (TFE) technologies have been extensively studied, their practical application to flexible OLEDs remains challenging due to issues such as excessive thickness, pinhole defects, reduced flexibility, and process complexity. In this study, an atomic layer infiltration (ALI) process was employed to form a flexible organic–inorganic hybrid barrier layer for OLED encapsulation. ALI is a modified atomic layer deposition (ALD) technique that incorporates a precursor holding step, allowing inorganic materials to infiltrate into a polymer matrix and thereby improving barrier performance.

In this work, an acrylic monomer film was used as the organic matrix, while Al_2O_3 derived from trimethylaluminum (TMA) and H_2O served as the infiltrated inorganic material. Due to the high reactivity of TMA with carbonyl groups in the monomer matrix, the free volume near the surface is rapidly filled during infiltration, resulting in early saturation of AlO_x penetration. To suppress this effect and achieve deeper infiltration, the reactant ratio was adjusted. As a result, an approximately 2 μm-thick Al_2O_3–monomer hybrid layer was successfully formed, exhibiting superior barrier performance compared with a conventional Al_2O_3 film deposited by ALD. Furthermore, no cracks were observed during bending tests at a curvature radius of 1 mm, demonstrating excellent mechanical reliability. The water vapor transmission rate (WVTR) was evaluated using a Ca test, demonstrating the potential of the proposed structure as a reliable encapsulation layer for flexible OLED applications.

Acknowledgments: This work was supported by the Technology Innovation Program (RS-2024-00467233, Development of core materials, devices, and process industry source technologies to secure next-generation OLED pixel process technology) funded By the Ministry of Trade, Industry & Energy (MOTIE, Korea)

EM-MoP-24 Quantitative Control of ZnO Infiltration in Polyimide via Vapor Phase Infiltration through Reaction–Diffusion Modeling*, **Ji Ho Jeon**, Jeong Hwan Han, Byung Joon Choi, Si Eun Jung, Ye Jin Jung, Su Min Eun,* Seoul National University of Science and Technology, Republic of Korea*; Kwanhyuck Yoon, Woo Yong Sung,* Samsung, Republic of Korea

The rapid advancement of emerging technologies, including wearable sensors, EUV photoresists, and next-generation optoelectronic devices, has driven a growing demand for high-performance organic–inorganic hybrid materials. These applications require a unique synergy of properties, combining the versatility of organic polymers with the chemical robustness and functional stability of inorganic materials. Among various fabrication methods, atomic layer infiltration (ALI) has emerged as a powerful technique for creating such hybrids by introducing gaseous precursors into the free volume of polymer matrices. However, achieving deep infiltration while maintaining a uniform compositional profile remains challenging. In addition, the complex and non-linear interplay between diffusion and reaction kinetics within polymer matrices complicates the establishment of reliable process–structure relationships, often necessitating extensive trial-and-error optimization.

In this study, we fabricated organic–inorganic hybrid films by infiltrating ALD ZnO into a polyimide (PI) substrate via ALI process. By introducing Zn precursor (diethylzinc, DEZ) hold time, ZnO effectively infiltrates and fills the polymer free volume, forming a dense hybrid structure. The infiltration depth (750-3,000 nm) was systematically controlled by tuning the pulse and hold times of DEZ during the VPI process.The total Zn content was quantified by X-ray fluorescence, while infiltration depth and compositional distributions were analyzed using cross-sectional transmission electron microscopy, energy-dispersive X-ray spectroscopy, and XPS depth profiling.

To enable quantitative control of infiltration depth, a reaction–diffusion model was developed to describe the interaction between DEZ and the polymer matrix, from which the reaction rate constant and diffusion coefficient were extracted. Model fitting to experimental data establishes a predictive framework for accurately describing infiltration profiles and precursor transport within the polymer.These results demonstrate that infiltration behavior can be quantitatively predicted and controlled, providing a robust platform for the rational design of organic–inorganic hybrid materials.

Acknowledgement

This work was supported by National Research Foundation of Korea(NRF) grants funded by the Ministry of Education (MOE)(NRF-2021R1A6A1A03039981) and by the Technology Innovation Program(RS-2024-00467233) though the Korea Planning and Evaluation Institute of Industrial Technology(KEIT) funded by the Ministry of Trade, Industry and Energy(MOTIE, Korea).

EM-MoP-25 Impact of Si Doping Approaches on Phase Formation and Electrical Performance of HZO Films for High–k, Low–Leakage DRAM Capacitors*, **Geumbi Mun**, Hyun-Cheol Kim,* IMEC, Belgium and Samsung Electronics, Republic of Korea*; Mihaela Ioana Popovici, Haengha Seo, Gourab De, Gwon Kim, Seohyeon Park, Laura Nyns, Johan Swerts, Jan Van Houdt, Maarten Rosmeulen,* IMEC, Belgium

As dynamic random-access memory (DRAM) capacitors continue to scale, maintaining high capacitance with low leakage becomes increasingly challenging. Among high-k materials, ZrO_2 in combination with HfO_2 has attracted significant interest for DRAM applications. Both ZrO_2 and HfO_2 are polyphasic oxides, where the tetragonal (t)-phase is particularly attractive due to its high dielectric constant.In the t-phases of ZrO_2 and HfO_2, the theoretical dielectric constants are approximately 47 and 70, respectively. However, numerous studies have reported that stabilizing tetragonal HfO_2 is significantly more challenging than stabilizing tetragonal ZrO_2. In particular, HfO_2 typically maintains the tetragonal phase only in ultrathin films with thicknesses below ~3 nm (1). This limitation highlights the intrinsic difficulty of achieving a robust tetragonal phase in HfO_2. To overcome this challenge, various approachessuch as introducing template effects (2) and employing doping strategies using nano–laminated structureshave been explored.

In this study, we investigate a Si–doped HZO process designed to promote formation of the tetragonal phase and elucidate the role of Si incorporation. We hypothesize that Si doping stabilizes the tetragonal phase in HfO_2 by forming strong tetrahedral Si–O bonds while inducing minimal lattice distortion. Furthermore, because both Hf and Si are tetravalent cations, Si substitution does not require charge compensation through oxygen vacancies, thereby minimizing defect–related gap states. Consequently, Si incorporation is expected to reduce the leakage current.To achieve uniform Si distribution within HfO_2 and control crystallization behavior, we employ both a conventional laminated stack and a modified super–cycle (MSC) technique. The MSC sequence consists of the following steps: (Hf or Zr precursor) – (purge) – (Si precursor) – (purge) – (oxidation) – (purge). We expect that Si–doped HZO films prepared using this approach will exhibit reduced leakage current while maintaining or improving the dielectric constant compared to undoped HZO.

Material characterization techniques, including X–ray diffraction (XRD) and transmission electron microscopy (TEM), were performed to analyze crystallinity and phase formation. Electrical evaluationssuch as capacitance-voltage measurements, leakage current density, and extracted dielectric constant (k) valuesare being conducted to establish correlations between phase composition and electrical properties across varying Si concentrations and dosing methods. By comparing the two Si–doped HZO ALD approaches, along with layered structures composed of Si–doped HfO_2 and ZrO_2 with different Hf/Zr ratios and Si contents, this work aims to pave the way for new high–k, low–leakage thin films suitable for next–generation DRAM capacitor applications.

(1) Yeon-Ji Jeon et.al, Journal of Alloys and Compounds 1010 (2025)

(2) Ae Jin Lee et.al, Applied Surface Science 590 (2022)

EM-MoP-26 UV-Assisted Atomic Layer Deposition of TiO_2 for Enhanced Thermoelectric Performance of n-Type $Bi_2Te_3Se_{0.3}$ Powders*, Su Min Eun, **Se Been Jeong**, Jin Kyeong Shin,* Seoul National University of Science and Technology, Republic of Korea*; Yeongtae Choi,* MAJE Technology Co., Ltd., Republic of Korea*; Byung Joon Choi,* Seoul National University of Science and Technology, Republic of Korea

An effective strategyfor enhancing the performance of thermoelectric powder materials is interface engineering through atomic layer deposition(ALD). The thermoelectric figure of merit, zT, expressed as $S^2 \cdot \sigma \cdot T/\kappa$, is a key indicator,and overcoming the trade-off between thermal conductivity(κ) and electrical conductivity(σ) remains a primary challenge in thermoelectric research. ALD is a thin-film deposition technique that offers precise thickness control, high uniformity, and excellent conformality, making it particularly suitable for coating complex powder surfaces. The introduction of ALD films can maintain high electrical conductivity while enhancing the Seebeck coefficient(S) through the energy filtering effect and reducing thermal conductivity via phonon scattering. Therefore, ALD-based

interface engineering is considered a promising route for improving the thermoelectric performance of powder-based materials.

Thermal ALD typically requires temperatures above 150 °C, limiting compatibility with thermally sensitive or nanostructured substrates and often resulting in impurity incorporation at lower temperatures. In contrast, UV-assisted ALD (UV-ALD) uses photo-induced ligand decomposition under 254 nm UVC irradiation to enable low-temperature growth while reducing impurities, producing dense films with improved interfacial properties.

In this study, the effect of TiO_2 films deposited by UV-ALD and thermal ALD on the thermoelectric performance of $Bi_2Te_3Se_{0.3}$(BTS) powders is investigated. TiO_2 possesses low intrinsic thermal conductivity, a high Seebeck coefficient, and excellent thermal stability. Therefore, it can improve the thermalstability of BTS thermoelectric materials and contribute to reducedthermal conductivity.

TiO_2 films are deposited onBTS powder surfaces by thermal ALD and UV-ALD using a rotary-type reactor at 150 ℃. Titanium isopropoxide(TTIP) and H_2O are used as the metal precursor and oxidant, respectively. The TiO_2-coated powders are consolidated by spark plasma sintering(SPS) at 673 K under 50 MPa for 5 minutes. Compared with thermal ALD, TiO_2 coating by UV-ALD results in a lower carrier concentration and higher mobility, suggesting the formation of a more uniform and denser interface on the powder surface. Morphology and chemical properties of TiO_2/BTS are characterized by transmission electron microscopy and X-ray photoelectron spectroscopy. This work demonstrates that interface engineering via UV-ALD could provide a scalable route to decouple carrier and phonon transport for high-performance thermoelectrics.

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EM-MoP-27 Dense and Thermally Stable SiNx Gate Dielectrics on Diamond by PEALD, *Chengpeng Wang*, ***Xuetong Zhou***, *Li Zheng, Xinhong Cheng,* Chinese Academy of Sciences, China

Diamond is regarded as the preeminent wide-bandgap semiconductor for next-generation power electronics, owing to its exceptional thermal conductivity and high carrier mobility. However, the absence of a high-quality native oxide necessitates the development of advanced deposited gate dielectrics capable of forming a stable and electrically superior interface with diamond. In this work, we demonstrate the fabrication of high-performance SiN_x gate dielectrics on the diamond substrates using plasma-enhanced atomic layer deposition (PEALD) at an elevated temperature of 450℃ , with hexachlorodisilane (HCDS) and NH_3 plasma as precursors.

A key innovation lies in the use of the highly reactive HCDS precursor at 450 °C, which enables the growth of dense, no detectable oxygen, and thermally stable SiN_x films. The elevated deposition temperature promotes efficient ligand removal and fosters robust chemical bonding at the SiN_x/diamond interface, effectively mitigating common issues in low-temperature ALD such as film porosity and precursor residuals. Electrical characterization of the resulting metal–insulator–semiconductor (MIS) structures reveals a low interface state density (D_{it}) extracted via the conductance method, along with negligible capacitance–voltage (C–V) hysteresis, indicating substantial suppression of border traps and deep-level interfacial defects. Furthermore, the 450℃ PEALD SiNx films exhibit a high breakdown field and suppressed leakage current density. These experimental findings demonstrate that the HCDS-based high-temperature PEALD process offers a reliable, high-quality solution for realizing high-reliability vertical diamond power devices.

EM-MoP-28 Oxygen Plasma Assisted Nucleation of HfO_2 ALD on MoS_2 2-d Material for Gate Stack Applications, ***Robert K. Grubbs***, IMEC Belgium; *Pawan Kumar, Pierre Morin, Benjamin Groven, Kaustuv Banerjee, Johan Swerts, Cesar Lockhart De la Rosa,* IMEC, Belgium; *Zsofia Baji,* Center for Energy Research, Hungary

The demand for increased transistor density in logic circuits is forcing the transistor channel lengths to shorter dimensions which is forcing a proportional decrease in the channel height. Because of the conduction limitations of silicon in the small size limit, alternative materials are being considered to replace the silicon channel material. The most promising alternative materials for this application are the transition metal dichalcogenides (TMD). Most notable is the application of MoS_2 for the channel material. Unfortunately, TMDs come with their own set of challenges when integrating them as transistor channels. Three primary integration challenges include: growth of TMD or the material transfer, source-drain metallization of the TMD and high k dielectric gate formation on the TMD channel. Due to the inertness of the TMD surface, conventional dielectric ALD chemistries will only nucleate at defect sites, grain boundaries or at other vulnerable surface morphologies. This incomplete nucleation causes inhomogeneities in the field that controls the channel and can also produce gate leakage paths. The research presented in this talk uses a remote oxygen plasma to induce nucleation sites on the MoS_2 surface. The exposed surface can then conformally nucleate HfO_2 using tetrakisethylmethylamino hafnium (TEMAH) and water at 200C. Experiments were performed on mono and bilayer MoS_2 samples and characterized with AFM, XPS and electrical testing. It will be shown that there are differences in the surface chemistries between the mono and bilayer samples and that the electrical response indicates the underlying layer in the bilayer samples is electrically conducting.

EM-MoP-29 Vapor-Deposition of Hybrid Thin Films for Functional Devices, ***Sampath Gamage***, University of North Carolina at Greensboro; *Swapnil Nalawade,* North Carolina A&T State University; *Robert Bofah-Buoh, Hemali Rathnayake, Shyam Aravamudhan,* University of North Carolina at Greensboro

Hybrid materials such as metal organic frameworks (MOFs) and hybrid perovskites offer exceptional structural and chemical tunability. However, thin-film integration remains a major barrier to device implementation. This poster presents ongoing work on MOF thin films at the interface of vapor-phase deposition and functional electronics. I will briefly discuss our current efforts on oxide thin films for memristive transport, initial wet-chemical deposition attempts of MIL-88B(Fe), and our planned expansion into atomic/molecular layer deposition (ALD/MLD) for controlled growth of hybrid MOF and organic-inorganic thin films. The central objective is to identify deposition-structure-property relationships that govern film continuity, crystallinity, and interfacial functionality in MOF-derived thin films. By combining defect-engineered metal oxides with emerging vapor-deposited hybrid frameworks, this work aims to define a pathway toward scalable thin-film MOFs for adaptive electronics, sensing, and other functional applications. The poster is intended to place this emerging program in the context of current MOF thin-film challenges and to identify key gaps where ALD/MLD can provide unique advantages

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM1-TuM
Molecular Layer Deposition/Hybrid ALD

Moderators: Haripin Chandra, The Electronics business of Merck KGaA Darmstadt, **Mihai E. Vaida**, University of Central Fllorida

8:00am **EM1-TuM-1 ALD Outstanding Presentation Award Finalist: The Impacts of Organic Structures on the Sensitivity of Molecular Atomic Layer Deposited EUV Resist Thin Films**, *Thi Thu Huong Chu, Dan Le,* University of Texas at Dallas*; Markus Langer, Gregrey Swieca,* University of Mississippi*; Doo San Kim, Minjong Lee, Dushyant Narayan,* University of Texas at Dallas*; Nikhil Tiwale,* Brookhaven National Laboratory*; Jean-Francois Veyan,* University of Texas at Dallas*; Michael Eller,* University of Mississippi*; Chang-Yong Nam,* Brookhaven National Laboratory*; **Jiyoung Kim,*** University of Texas at Dallas

Until now, the development of advanced hybrid EUV resists has largely emphasized inorganic metals with high EUV absorption, while the contribution of organic components remains insufficiently explored. In this work, we investigate how organic backbone structures influence the sensitivity and patterning performance of EUV resist materials, focusing on resist thin films synthesized via molecular atomic layer deposition (MALD) for next-generation EUV lithography. Under EUV exposure, negative tone MALD resist thin films consistently show that organic moieties with an aliphatic chain-based backbone exhibit enhanced sensitivity and improved patterning performance compared with those featuring an aromatic backbone.

To elucidate the underlying mechanisms responsible for the observed enhancement, various material characterization techniques, including in situ FTIR, XPS, Raman, and NP-SIMS, were conducted for two Zn-based systems that feature either organic with an aliphatic chain backbone [e.g., 2,3-dimercapto-1-propanol (DMP)], or an aromatic backbone [e.g., 4-mercaptophenol (4-MP)]. IR measurements, obtained from the in-situ FTIR system equipped with an electron flood gun, indicate clear changes in the aromatic ring of 4 MP upon electron exposure, reflected by a decrease in C=C bond. Additional material characterizations further confirm the changes in the aromatic ring and suggest the formation of graphitic-like carbon within 4-MP-based resist materials upon electron exposures. In contrast, while IR measurements of DMP-based resist thin films show evidence of new species formation, as indicated by an increase in various carbon species, NP-SIMS suggests changes in the oxidation state of Zn within DMP-based resist thin films.

Based on these material characterizations, we propose two distinct exposure mechanisms that potentially govern the sensitivity and patterning behavior of Zn/4-MP and Zn/DMP resist thin films. For the aromatic-based system, the organic moiety likely undergoes crosslinking, leading to the formation of a graphitic-like carbon network, whereas the aliphatic chain–based organic forms complex structures with the metal core surrounded by ligands. These findings provide critical guidance for the molecular design of MALD EUV resist thin films, enabling a balance between sensitivity and pattern fidelity to meet next-generation lithography performance targets.

This work is supported by the U.S. DOE Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. This research is also partially supported by the National R&D program (2022M3H4A3052556) through the National Research Foundation of Korea (NRF), funded by the Ministry of Science and ICT in Korea.

8:30am **EM1-TuM-3 ALD 2026 Young Investigator Award Finalist: All-Dry-Processed Zn-Based Inorganic–Organic Hybrid Photoresists for EUV Lithography**, ***Thi Thu Huong Chu,** Dan N. Le, Dushyant M. Narayan, Minjong Lee, Doo San Kim,* University of Texas at Dallas*; Nikhil Tiwale, Chang-Yong Nam,* Brookhaven National Laboratory*; Jiyoung Kim,* University of Texas at Dallas

Extreme ultraviolet (EUV) lithography is the key enabling technology for sub-10 nm metal half-pitch semiconductor nodes.[1] However, one of the primary bottlenecks lies in the development step of the lithography process. Conventional wet development often leads to pattern collapse due to capillary forces generated during solvent evaporation.[2,3] Although this issue is less severe in high- and hyper-NA EUV lithography as a result of reduced resist thickness, wet development can still degrade pattern fidelity through solvent-induced swelling, non-uniform dissolution, and surface-tension-driven stochastic effects, thereby increasing LER and defectivity.

To address these challenges, dry development processes are emerging as a promising alternative, eliminating the patterning issues associated with wet developers and their associated environmental costs. Here, we present a dry development approach of the Zn-based hybrid inorganic–organic resist systems deposited by molecular layer deposition (MLD). The resist films were patterned using both low-energy electron-beam lithography (100 V EBL) and EUVL. Dry development was then carried out by chemical vapor exposure to hexafluoroacetylacetone (hfacH), which reacts with the Zn-based resists, generating volatile products such as $Zn(hfac)_2$ and organic by-products. During wet development, resist–developer interactions cause lift-off problems that hinder accurate sensitivity evaluation, and high-resolution patterning is degraded by resist swelling and spreading. In contrast, the dry development process achieves a tenfold improvement in sensitivity over wet development while resolving features as small as 10 nm with EUVL. This demonstrates the strong resistance of the exposed regions to hfacH vapor and the elimination of capillary-induced collapse, enabling controlled material removal without the limitations of liquid immersion. Among currently reported all-dry-processed EUV resists, we achieved a low critical dose of 27 mJ/cm^2 with a comparable LER of 1.6 nm.

These findings demonstrate a significant step toward realizing an all-dry EUV resist platform. By combining MLD-based hybrid resist materials with vapor-phase development, this approach not only mitigates fundamental limitations of wet processing but also opens pathways for scalable, high-performance patterning required for next-generation semiconductor manufacturing.

This work is supported by the U.S. DOE Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. This research is also partially supported by the National R&D program (2022M3H4A3052556) through the National Research Foundation of Korea (NRF), funded by the Ministry of Science and ICT in Korea.

[1] I. Giannopoulos *et al.,* Nanoscale, **2024**, 16, 15533–15543.

[2] T. S. Kulmala *et al.,* Proc. SPIE, **2016**, 9776, 97762N.

[3] N. Kenane *et al.,* J. Photopolym. Sci. Technol., **2024**, 37, 257–262.

8:45am **EM1-TuM-4 ALD 2026 Young Investigator Award Finalist: Polyurea Polyurea Molecular Layer Deposition using Low Melting Point Precursors for Use in Biosensor Design**, *Jay Werner, Seancarlos Gonzalez, **David Bergsman,*** University of Washington

Molecular layer deposition (MLD) is a promising tool that can take the place of silane-based SAMs in some surface functionalization applications where a multilayer film is acceptable and a precise, conformal film thickness is desirable, such as in biosensor design. However, many organic MLD precursors have low vapor pressure or are solids at room temperature, which can lead to increased purge times and the possibility of condensation-induced valve clogging. This work presents an underexplored polyurea MLD chemistry using 2,4-toluene diisocyanate (TDIC) and ethylene diamine (ED).This process has some benefits over the similar and more common 1,4-phenylene diisocyanate (PDIC) reactant, such as reduced cost and lower melting point (and thus higher vapor pressure at room temperature). Film characterization suggests that this process is similarly well-behaved to PDIC-based polyurea: in situ ellipsometry shows that the process is both linear up to 55 cycles and self-saturating, XPS analysis shows the expected atomic ratio of oxygen and nitrogen in the film, and FTIR shows amide I & II peaks characteristic of polyurea. In addition, the films were analyzed using zeta potential analysis, fluorescence tagging, and water contact angle (WCA) goniometry to characterize their suitability for use in biosensor design.

9:00am **EM1-TuM-5 Conformality of Molecular Layer Deposited Polyurea for Sidewall Passivation**, ***Wallis Scholl,*** Colorado School of Mines*; Thorsten Lill, Mingmei Wang, Wenyu Zhang, Louis Kim, Harmeet Singh,* Lam Research Corporation*; Sumit Agarwal,* Colorado School of Mines

As the semiconductor industry transitions from fluorocarbon plasma chemistries to carbon-free reactive plasmas, new techniques are needed to passivate the sidewalls of high aspect-ratio (HAR) features during etch. Molecular layer deposition (MLD) is a vapor-phase thin film growth technique comprised of alternating surface reactions for deposition of organic and hybrid organic-inorganic chemistries. While MLD is an analogous technique to atomic layer deposition (ALD), the growth mechanism of MLD has added complexity due to the possibility of double reaction of both functional groups in the precursor molecule with the growth surface and physisorption of molecules into the film. Previous work on ALD has found that conformal deposition on HAR features requires very

high precursor doses to supply necessary diffusive flow. However, we have found that MLD polyurea films are surprisingly conformal using the saturation doses for a flat surface.

Polyurea was deposited via MLD using toluene diisocyanate and ethylene diamine as precursors. Figure 1 a) and b) shows scanning electron microscopy (SEM) images of AR~65:1 holes in SiO_2-SiN_x stacks, both with and without ~10 nm of polyurea deposited via MLD. The chips were then exposed to an etching plasma and imaged again [see Figure 1 c) and d)], and the presence of polyurea was found to result in a smaller CD throughout the entire feature. This result shows that during MLD, polyurea was deposited throughout the entire hole and then was able to protect the sidewalls during etch. We have attributed the unexpectedly high conformality of MLD to the physisorption contribution to film growth which we have shown in detail in previous work. This physisorbed material is free to diffuse throughout the film, which may assist in deposition at the bottom of the hole. However, the process must be carefully designed with this effect in mind, as physisorbed molecules can also diffuse out of the film, resulting in chemical vapor deposition when precursor molecules react in the gas phase. Further, we have studied the plasma-surface interactions of polyurea with HF plasma and shown that polyurea can act as a sacrificial layer during HF etch. When polyurea was deposited on top of SiO_2 or SiN_x and then exposed to an HF plasma, only the polyurea film was etched during initial plasma exposure, while the underlying material was protected. Only once the polyurea was completely consumed by reaction was SiO_2/SiN_x etch observed (see Figure 2). This work presents a new technique for sidewall passivation during HF etch.

9:15am **EM1-TuM-6 Extreme Ultraviolet and Electron Beam-Induced Decarboxylation of Hybrid MLD Aluminum Oxalate Photoresists***, **Long Viet Than**,* Stanford University*; Miso Kim,* Hongik University, Republic of Korea*; Oleg Kostko,* Lawrence Berkeley National Laboratory (LBNL)*; Bonggeun Shong,* Hongik University, Republic of Korea*; Stacey F Bent,* Stanford University

Continued device scaling with the introduction of high numerical aperture (NA) extreme ultraviolet (EUV) lithography will require innovations in photoresist materials. Particularly, new resist chemistries are needed to address the photon and material stochastics challenges that define the current resolution limit. Molecular layer deposited (MLD) metal-organic photoresists offer intrinsic advantages in precise thickness control and chemical homogeneity that can address some of these challenges. However, many MLD resists have poor EUV and electron beam sensitivity, leading to the need to explore new molecular designs that better harness the reactions induced by EUV-generated electrons.

In this work, we introduce a rationally designed MLD resist utilizing metal carboxylate groups to provide an efficient solubility switch mechanism by using trimethylaluminum (TMA) and oxalic acid precursors to deposit aluminum oxalate thin films. X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy reveal their chemical structure, showing that the metal oxalate coordination network reorganizes during exposure to air. We investigate the resist patterning mechanism and performance via electron beam lithography and flood EUV exposure. We use XPS and atomic force microscopy (AFM) to study post-e-beam chemical changes and film shrinkage, and in situ residual gas analysis and total electron yield measurements to identify reactions occurring during EUV exposure. Results show that exposure-induced decarboxylation results in CO/CO_2 gas evolution, inorganic Al-O bonding, and negative tone patterning. The photoresist can be developed with water, yielding an e-beam sensitivity of ~8500 $\mu C/cm^2$ (at 100 keV accelerating voltage) and EUV sensitivity of ~200 mJ/cm^2 – among the best for Al-based resists in the literature. Using electron beam lithography, line/space patterns as small as 14 nm half pitch are resolvable, with a line width roughness (LWR) of 5.2 nm. Thus, this work provides a new chemical motif applicable to hybrid MLD photoresists and highlights the importance of the organic ligand in determining the efficiency of the patterning mechanism.

9:30am **EM1-TuM-7 Cyclic Siloxane Precursor for Molecular Layer Deposition of Polymer Networks***, **Sanne Deijkers**, Peter Gordon, Seán Barry,* Carleton University, Canada

Phosphane-ene polymer networks, typically made in bulk phase synthesis, are known for their oxygen scavenging properties, making them ideal as protective layers. Molecular layer deposition (MLD) of polymer networks offers the opportunity to engineer thin film polymer networks for flexible electronics, sensors, and other applications. MLD of phosphane-ene was demonstrated using the cyclic siloxane precursor tetramethyltetravinylcyclotetrasiloxane (D_4^{Vinyl}), isobutylphosphine (iBuPH$_2$), and an Ar plasma to generate P radicals to act as a cross-linking agent [1]. The D_4^{Vinyl} ring can remain intact and improve crosslinking in the MLD film, which is what our group proposed what happens during the phosphane-ene MLD process [1], while the Knez group suggested ring opening in their work on MLD of siloxane-alumina films [2,3] . In this work, various growth mechanisms of polymer networks using the cyclic D_4^{Vinyl} precursor have been studied.

It was found that a long-lived radical is crucial to provide cross-linking. Switching from the primary phosphine iBuPH$_2$ to a primary amine tBuNH$_2$ did not result in growth. *In situ* quartz crystal microbalance (QCM) displayed pulsing of the precursors, but no mass gain was observed. The short-lived N radical proved to be unsuitable for MLD of polymer networks through radical-mediated cross-linking.

The deposition reaction mechanisms of phosphane-ene MLD were examined. *In situ* cycle-by-cycle QCM was combined with *ex situ* ellipsometry, atomic force microscopy, and Fourier transform infrared spectroscopy. Together, it can be hypothesized that the reaction mechanism of D_4^{Vinyl} is dependent on the surface chemistry. The presence of a radical species versus a metal atom at the surface decides the favorability of ring-opening, with the π-acid nature of the metal playing a significant role in ring opening. This presentation will detail different mechanisms using the D_4^{Vinyl} precursor and discuss its implications on film density.

[1] J. T. Lomax *et al.*, *Chem. Mater.*, 35, 4, 2023

[2] K. Ashurbekova *et al.*, *Chem. Mater.*, 33, 3, 2021

[3] K. Ashurbekova *et al., Chem. Commun.*, 57, 17, 2021

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM2-TuM

Vapor Phase Infiltration

Moderators: Jiyoung Kim, University of Texas at Dallas, **Il-Kwon Oh**, Ajou University

10:45am **EM2-TuM-12 The Deposition of Metalcones via Atmospheric Pressure Spatial Atomic Layer Deposition***, **Jonathan Ly**, Kevin Musselman,* University of Waterloo, Canada

Flexible hybrid organic – inorganic polymer thin films consisting of metal alkoxide repeating units in the form (–M–O–CH_2CH_2-O–) known as "metalcones", have traditionally been deposited using chamber-based atomic/molecular layer deposition methods that are slow and challenging to scale [1], [2]. These materials are of interest in spaces such as packaging and flexible electronics, offering superior mechanical properties compared to metal oxide thin films. In this presentation, metalcone thin films have been successfully deposited in open air using an atmospheric pressure spatial molecular layer deposition technique (AP-SMLD). The deposition of alucone and zincone was demonstrated using trimethylaluminum (TMA) and diethylzinc (DEZ) metal precursors respectively, while using ethylene glycol as the organic precursor. A custom AP-SMLD reactor head design allowed for the thin film deposition of these air-reactive species in atmosphere. Optimization of deposition parameters was also carried out, with high organic oxidant and low metal bubbling flow rates resulting in a purer metalcone film, which was characterized via ellipsometry, FTIR, and UV-Vis measurements.

Optical properties of the metalcone films were analyzed using UV-Vis absorbance and ellipsometry measurements. Metalcones were then compared to their respective metal oxides, showing a distinct decrease in refractive index and differences in growth-per-cycle. The chemical composition of deposited metalcone films was analyzed using FTIR, XPS, and TOF-SIMS, showing incorporation of carbon and organic functional groups into the films. Metalcone films were exposed to both humidity and water etching conditions, and morphological changes were analyzed using SEM and AFM, demonstrating increased roughness and surface degradation compared to metal oxide controls. Mechanical properties of SMLD-deposited alucone and zincone were measured with nanoindentation and bending studies. These studies demonstrated an increased flexibility of metalcones and resistance to cracking upon bending, compared to AlO_x and ZnO, respectively. Thus, it was demonstrated that metalcone thin films were successfully deposited in open air using AP-SMLD, enabling industrial scale-up options of metal-organic thin films, such as on a roll-to-roll system, and the potential to deposit other air-sensitive materials in atmospheric conditions [1], [2].

References

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11:00am **EM2-TuM-13 Vapor Phase Infiltration as a Route to Precise Atom Number Cluster Synthesis and Cation Substitution***, Kihoon Kim, Nuwanthaka Jayaweera, Taylor Harville, Cong Liu,* ***Alex Martinson,*** Argonne National Laboratory

The energetically favorable formation of atomically precise clusters enables nanoscale synthesis with exquisite uniformity. We report the synthesis of InS- and CdS-core clusters via vapor infiltration of atomic layer deposition precursors directly into polymer thin films. Sequential infiltration of trimethylindium vapor and hydrogen sulfide gas into poly(methyl methacrylate) (PMMA) allows growth of clusters uniform properties consistent with a magic size cluster–$In_6S_6(CH_3)_6$. Most recently we demonstrate that post-synthetic vapor phase cation substitution into InS-core clusters as deposited in the polymer film is possible for a limited number of ALD precursors, consistent with DFT modeling. Gas phase dimethyl cadmium and hydrogen sulfide precursors infiltrated into poly(4-vinylpyridine) thin films also results in the 3D-nucleation of clusters consistent with a cubane-type Cd_4S_4 core with variable ligand capping. Most recently, we have utilized in situ UV/visible reflection/absorption spectroscopy to observe in real-time the nucleation and growth of CdS clusters for greater mechanistic insight, further supported by DFT. Together the novel approach and in situ characterization methods allow access to and insight into cluster syntheses previous restricted to the solution phase, with the added benefits of rapid byproduct elimination through purging under low vacuum as well as avoidance of the purification, concentration, and film casting required for solution phase cluster syntheses.

11:15am **EM2-TuM-14 Activated Direct Reaction between Carbonyl Groups in Poly(Methyl Methacrylate) (PMMA) and Diethylzinc (DEZ) During Vapor-Phase Infiltration***, Nikhil Tiwale,* Brookhaven National Laboratory*; Ashwanth Subramanian, Sayantani Sikder,* Stony Brook University*; Xiaohui Qu, Guillaume Freychet,* Brookhaven National Laboratory*; Eliot Gann, Cherno Jaye,* National Institute of Standard and Technology*; Kim Kisslinger, Jorge Anibal Boscoboinik,* ***Chang-Yong Nam,*** Brookhaven National Laboratory

Vapor-phase infiltration (VPI) enables organic–inorganic hybrid materials by allowing organometallic precursors to diffuse into polymer matrices and react with specific functional groups. In poly(methyl methacrylate) (PMMA), infiltration using highly reactive trimethylaluminum (TMA) is well established, whereas diethylzinc (DEZ) is generally considered insufficiently reactive toward PMMA carbonyl groups and therefore requires alumina priming. The prevailing model assumes that ZnO_x growth proceeds exclusively through reactions between DEZ and hydroxyl groups generated during the AlO_x priming step.Here, we show that alumina priming directly activates neighboring carbonyl groups in PMMA, enabling a previously unrecognized, direct reaction pathway between DEZ and the polymer backbone during VPI [1]. Using in situ quartz crystal microbalance measurements, cross-sectional scanning transmission electron microscopy, infrared reflection-absorption spectroscopy (IRRAS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and density functional theory (DFT) simulations, we elucidate the mechanism responsible for accelerated ZnO_x infiltration in AlO_x-primed PMMA.AlO_x infiltration rapidly saturates due to near-surface free-volume clogging caused by hyperbranched AlO_x network formation, whereas ZnO_x infiltration exhibits increasing mass uptake and deeper, more uniform penetration over successive cycles. Spectroscopic analyses reveal progressive carbonyl consumption during ZnO_x cycles and the emergence of formate-like species, inconsistent with a hydroxyl-only mechanism. DFT calculations support the formation of a stabilized cyclic Zn-Al-O adduct involving an AlO_x-activated carbonyl group, which lowers the energetic barrier for DEZ binding.These results establish a revised mechanistic framework in which alumina priming electronically activates polymer functional groups, enabling direct DEZ-carbonyl reactions and sustained ZnO_x infiltration, with implications for the design of high-fidelity infiltration-based hybrid materials.

[1] N. Tiwale et al., *Chem. Mater.*, in press (2026), https://doi.org/10.1021/acs.chemmater.5c02584

11:30am **EM2-TuM-15 Atomic Layer Processes for UV-Stable Polymers: Synergistic Effects of Infiltration and Deposition of ZnO***,* ***Gil Menasherov,*** *Nidaa S. Herzallh, Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel

Ultraviolet (UV) radiation is the major cause for polymer degradation in outdoor environments, accelerating mechanical failure and color change, leading to plastic waste accumulation. Effective UV-protective strategies that preserve polymer functionality are therefore critical for extending material longevity in UV-intense environments. Here, we present a synergistic approach combining vapor phase infiltration (VPI) and atomic layer deposition (ALD) to engineer nanoscale zinc oxide (ZnO) coatings on poly(lactic acid) (PLA), a UV-sensitive polymer. Individually, ALD and VPI offer minimal enhancement in UV stability; however, their sequential application enables the formation of conformal, polycrystalline ZnO films that dramatically improve UV resistance in both 3D-printed structures and thin-film PLA models. In situ microgravimetry and cross-sectional electron microscopy reveal that VPI introduces ZnO nucleation sites within and atop the polymer matrix, promoting a >10-fold increase in ZnO growth per ALD cycle. The resulting ZnO–PLA hybrids absorb over 90% of incident UV-C radiation while maintaining high optical transparency in the visible range. This low-temperature, scalable process provides a promising platform for the development of transparent, durable UV-barrier coatings on polymers for use in environmentally demanding applications.

11:45am **EM2-TuM-16 Vapor Phase Infiltration of ZnO Nanocrystals into Biodegradable Fibers for Dermatologic Applications***, Martina Rihova,* CEITEC Brno University of Technology, Czechia*; Susan Azpeitia,* CIC nanoGUNE, Spain*; Denisa Fenclova, Zbynek Heger,* Mendel University in Brno, Czechia*; Mato Knez,* CIC nanoGUNE; IKERBASQUE, Basque Foundation for Science, Spain*;* ***Jan Macak,*** CEMNAT, University of Pardubice; CEITEC Brno University of Technology, Czechia

Vapor Phase Infiltration (VPI) enables the incorporation of metal oxides into polymer materials (1,2). Among other applications, allows the development of active antibacterial polymer-inorganic composites (3,4) and photocatalysts (5).

In this study, VPI was used to infiltrate polyvinyl alcohol or cellulose acetate (CA) fibers with ZnO for the treatment of *Acne vulgaris*. The fibers were prepared from biodegradable polymers using an innovative centrifugal spinning technique (6) and subsequently subjected to VPI using diethyl zinc and water, leading to the formation of ZnO both within the fibers and on the fiber surfaces. (3,4)

The fibers were infiltrated with ZnO via VPI using 1 to 128 cycles. Since ZnO-infiltrated CA fibers do not release ZnO nanocrystals, these fibers were treated with oxygen plasma to modify their solubility (4) The resulting fibers with infiltrated ZnO nanocrystals were comprehensively characterized using SEM, TEM, XRD, and XPS. Antibacterial testing revealed that both CA and PVA fibers infiltrated with ZnO nanocrystals starting from 32 VPI cycles effectively inhibited the growth of acne-causing bacteria. Moreover, the homogeneous distribution of ZnO nanocrystals within the fibers enabled the immediate release of Zn^{2+} ions while preserving the fibrous structure, in contrast to fibers containing ZnO nanoparticles, which directly blended into the spinning solution. (3,4)

The presenation will demonstrate that fibrous carriers combined with active ZnO nanocrystals prepared via VPI represent a highly promising material, showing significant potential for the treatment of *Acne vulgaris*.

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3 Rihova et al. "Centrifugally spun and ZnO-infiltrated PVA fibers with antibacterial activity for treatment of Acne vulgaris." *Journal of Controlled Release* (2025): 113777.

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5. Chennam et al. "Carbon fibers with infiltrated TiO2 nanocrystalline layers: photocatalytic performance." *Nanoscale* (2026).

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Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM1-TuA

Next Generation ALD Semiconductors

Moderators: Jessica Jones, Argonne National Laboratory, **Neeraj Nepal**, U.S. Naval Research Laboratory

1:30pm **EM1-TuA-1 Real-time Optimization of Gallium Oxide and Aluminum Gallium Oxide Thin Film Growth via Plasma-Enhanced Atomic Layer Deposition Using In-situ Spectroscopic Ellipsometry**, ***Yousra Traouli****, Ufuk Kilic, Mathias Schubert, Eva Schubert,* University of Nebraska - Lincoln

Ultrawide bandgap metal oxide semiconductor materials have attracted significant interest for high-power, high-frequency, and extreme-environment applications due to their large breakdown fields and thermal stability under harsh operating conditions. In this work, we investigate the growth dynamics of gallium oxide (Ga_2O_3) and aluminum gallium oxide $(Al_xGa_{1-x})_2O_3$ thin films deposited by plasma-enhanced atomic layer deposition (PE-ALD). The deposition process was monitored in real-time using *in-situ* spectroscopic ellipsometry (SE).

Ga_2O_3 ultrathin films were grown using four trimethylgallium pulses with a total exposure time of 20 msec during the metal-precursor half-cycle, followed by a remote oxygen plasma (75 sec, 300 W). Ternary $(Al_xGa_{1-x})_2O_3$ films were deposited using a hybrid ALD process that alternate trimethylaluminum (60 msec)/H_2O (60 msec) cycles for Al_2O_3 and trimethylgallium/oxygen-plasma cycles for Ga_2O_3. While the substrate temperature is maintained at 250° C, argon was used Argon as the carrier gas during the introduction of precursor material (60 sccm) and plasma process (200 sccm) with process pressure of 0.25 Torr.

To interpret the time-resolved SE data, a dynamic dual-box model approach was employed, providing insight into surface processes such as precursor adsorption and ligand removal [1,2]. Periodic oscillations in surface roughness and subsurface layer thickness were observed, reflecting the cyclic nature of molecule attachment and ligand desorption. To maintain accurate analysis of the *in-situ* SE data,the complex dielectric functions of Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ thin films were determined over the spectral range of 0.74–5.04 eV using selected *in-situ* SE data at different film thickness. The growth rates of Ga_2O_3 and Al_2O_3 were 0.918 Å/cycle and 0.575 Å/cycle, respectively. Additionally, by performing *ex-situ* SE measurements in a spectral range from 0.64 eV to 9 eV at select angles of incidence from 45° to 75° by 10° steps, we extracted the broad spectral range complex dielectric function at room temperature and identify the higher order band-to-band transitions based on critical point model dielectric function analysis.

Complementary characterization techniques, including X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy, were used to assess film crystallinity, composition, and surface morphology.

Overall, this study demonstrates the *in-situ* SE technique as a powerful tool for recipe optimization and for revealing in-cycle growth kinetics during PE-ALD of Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ thin films.

[1] Kilic, Ufuk, et al. Sci. Rep. 10.1 (2020): 10392.

[2] Traouli, Yousra, et al. J. Vac. Sci. Technol. 42.5 (2024).

1:45pm **EM1-TuA-2 Conductive Si-Doped Ga_2O_3 via Thermal ALD Followed by Thermal Annealing**, ***Benjamin Greenberg,*** U.S. Naval Research Laboratory*; Katie Gann,* National Research Council Fellow Residing at U.S. Naval Research Laboratory*; Boris Feigelson, Alan Jacobs, Jeffrey Woodward, Daniel Pennachio, Emma Rocco,* U.S. Naval Research Laboratory

Monoclinic β-Ga_2O_3 has a rare combination of ultrawide bandgap (~4.8 eV) and extrinsically controllable electron density, *n*, between ~10^{16} and ~10^{20} cm^{-3}, making it a strong candidate for high-power, high-frequency, and optoelectronic applications. There have been numerous reports of β-Ga_2O_3 thin film growth via metalorganic chemical vapor deposition (MOCVD), thermal atomic layer deposition (ALD), and plasma-enhanced atomic layer deposition (PEALD), including Ga_2O_3:Ge with $n > 10^{20}$ cm^{-3} via MOCVD[1] and Ga_2O_3:Si with $n > 10^{18}$ cm^{-3} via PEALD followed by thermal annealing.[2] In the case of thermal ALD, conformal growth on substrates with high aspect ratio (AR) has been demonstrated, including Si trenches with AR = 11,[3] although doping of the conformal Ga_2O_3 was not investigated. For the development of high-performance, high-AR Ga_2O_3 devices, there remains a need for thermal ALD processes for doped Ga_2O_3 that can simultaneously achieve high *n* and high conformality.

In this work, we demonstrate thermal ALD of Ga_2O_3:Si using trimethylgallium (TMG), bis(t-butylamino)silane (BTBAS), and ozone as precursors, employing supercycles consisting of *x* TMG/O_3 cycles and 1 BTBAS/O_3 cycle. Amorphous Ga_2O_3:Si is deposited on Si(100), α-Al_2O_3(0001), and insulating β-Ga_2O_3:Fe(010) substrates at 220 °C, and some films are then crystallized via thermal annealing under N_2. Comparing as-grown Ga_2O_3:Si with *x* = 15 to undoped Ga_2O_3, Si incorporation is confirmed by an increase in the growth-per-cycle (GPC) from 0.69 to 0.73 Å/cyc and a decrease in the refractive index from 1.92 to 1.84. The as-grown films are electrically insulating, but thermal annealing experiments reveal that low electrical resistivity is possible after crystallization. Ga_2O_3:Si (*x* = 400, thickness = 28 nm) grown on β-Ga_2O_3:Fe and annealed at 900 °C for 10 min exhibits $n = 8.4 \times 10^{18}$ cm^{-3} (dopant activation = 8.8%) and an electron mobility, μ, of 49 $cm^2V^{-1}s^{-1}$ for a resistivity, ρ, of 1.4×10^{-2} Ω-cm. Interestingly, ρ becomes immeasurably high ($\rho > 1$ Ω-cm) when the annealing temperature is increased to 1000 °C. X-ray diffraction (XRD) and transmission electron microscopy (TEM) indicate that annealing at 900 °C produces an epitaxial β-Ga_2O_3:Si layer on top of the β-Ga_2O_3:Fe that spans approximately half of the film thickness (with lower crystalline quality in the top half of the film), whereas annealing at 1000 °C produces fully epitaxial β-Ga_2O_3:Si. The high ρ of the fully epitaxial β-Ga_2O_3:Si—and potential strategies for attaining conformal, conductive β-Ga_2O_3:Si on various substrates—will be discussed in light of known challenges presented by Ga_2O_3 crystallization, including the possible formation of Ga vacancies[4] and γ-Ga_2O_3 en route to β-Ga_2O_3.[5]

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2:00pm **EM1-TuA-3 Low-Temperature Self-Limiting Growth of Crystalline III-Nitride Films: How Far Can We Go?**, ***Necmi Biyikli,*** University of Connecticut **INVITED**

Research efforts on low-temperature (T < 300 °C) synthesis of crystalline III-nitride thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early III-nitride growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, shifting to stainless-steel based hollow-cathode plasma sources revealed highly (002) oriented polycrystalline III-nitride films on Si(100) and sapphire substrates. Upon further modification of the hollow-cathode plasma source and reactor chamber design, we have achieved monocrystalline AlN, quasi-epitaxial GaN and (002) oriented InN films on sapphire substrates at a common growth temperature of 200 °C.The films were deposited using conventional metal-alkyl precursors (trimethylaluminum, triethylgallium, trimethylindium) and various nitrogen plasmas (N2/H2/Ar, N2/H2, N2/Ar, and N2-only) as metal precursor and nitrogen co-reactant, respectively. When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained on c-plane sapphire substrates showed a notable increase. Moreover, a significant improvement of crystalline order has been observed for all binary nitride films grown on sapphire substrates, approaching epitaxial quality films. We attribute this significant improvement in crystal quality to the synergistic impact of customized HCP-ALD reactor, large-diameter third-generation hollow-cathode plasma source, and optimized growth conditions (plasma gas mixture, rf-power, pressure).To gain further insight into how different plasma mixtures and radical species affect III-nitride film quality, we have carried out density functional theory (DFT) based simulations of both metal-organic and plasma half cycles. The computational studies revealed how different adsorbed metal-organic precursor surface groups interact with hydrogen and nitrogen radicals by depicting energetically favorable reaction routes. These results are compared and correlated with the experimental observations, deciphering the critical role of hydrogen radicals. Ongoing computational studies will be used towards perfecting the low-temperature synthesis routes for III-nitride films towards achieving monocrystalline layers with lower impurity content.

2:30pm **EM1-TuA-5 Piezoelectric and ferroelectric $Al_{1-x}Sc_xN$ by plasma-enhanced ALD**, ***Gilbert B. Rayner Jr.***, *Noel O'Toole, Nathaniel Nelson,* Kurt J. Lesker Company*; Bangzhi Liu,* The Pennsylvania State University*; Jeffrey Shallenberger,* The pennsylvania State University*; Gregory Muha, Piush Behera, Suraj Cheema,* Massachusetts Institute of Technology*; Blaine Johs,* Film Sense*; Nastazia Moshirfatemi,* General Technical Services, LLC*; Daniel Drury, Brendan M. Hanrahan,* Army Research Directorate, DEVCOM Army Research Laboratory*; Glen R. Fox,* Fox Materials Consulting, LLC*; Nicholas A. Strnad,* Army Research Directorate, DEVCOM Army Research Laboratory

Wurtzite aluminum–scandium nitride ($Al_{1-x}Sc_xN$) thin films are promising for next-generation electronic and sensing technologies. However, achieving precise composition and uniform coverage on complex three–dimensional architectures remains challenging. Here, we demonstrate the growth of $Al_{1-x}Sc_xN$ by plasma–enhanced atomic layer deposition (PEALD) under ultrahigh purity conditions (UHP-C) using a supercycle sequence composed of alternating AlN and ScN constituent processes. The PEALD process utilized trimethylaluminum (TMA), bis(ethylcyclopentadienyl) scandium chloride [$ClSc(EtCp)_2$] and N_2−H_2 plasma as co-precursors at substrate temperatures ranging from 215−300 °C.

A 60.3 nm-thick PEALD $Al_{0.83}Sc_{0.17}N$ film grown at 300 °C on a {111}-oriented platinum bottom electrode on Si (100) exhibited clear ferroelectric switching. The film showed switched polarization ($2P_r$) of 163 μC/cm^2 and 139 μC/cm^2 for negative and positive pulsing, coercive fields of 5.5 MV/cm and -4.8 MV/cm, and a dielectric constant of 12.8−13.8 at 100 kHz under ±10 V. The effective longitudinal piezoelectric coefficient ($d_{33,f}$) of the $Al_{0.83}Sc_{0.17}N$ film was measured to be -23.6 pm/V and 22.1 pm/V for the N- and metal-polarities, respectively.

Structural analysis revealed that the film on {111} platinum was fully c-axis (0001) oriented out-of-plane, indicating high crystalline quality even along the sidewalls of three–dimensional features. When deposited on single–crystal gallium nitride, the $Al_{0.83}Sc_{0.17}N$ adopted a highly ordered in-plane and out-of-plane arrangement consistent with epitaxial growth. Films deposited over narrow trenches showed uniform, conformal coverage. These results demonstrate that PEALD enables high–quality $Al_{1-x}Sc_xN$ suitable for advanced three–dimensional electronic and sensing applications.

2:45pm **EM1-TuA-6 Low Temperature PEALD of Epitaxial AlN Without Atomic Layer Annealing**, ***Jeffrey Woodward***, *David Boris, Michael Johnson, Daniel Pennachio,* U.S. Naval Research Laboratory*; Michael Mathews,* NRC postdoctoral fellow residing at U.S. Naval Research Laboratory*; Emma Rocco,* U.S. Naval Research Laboratory*; Katie Gann,* NRC postdoctoral fellow residing at U.S. Naval Research Laboratory*; Ben Sekely,* NRC postdoctoral fellow stationed at U.S. Naval Research Laboratory*; Tatyana Feygelson, Jonathan Levine-Miles,* U.S. Naval Research Laboratory*; Jennifer Hite,* University of Florida*; Michael Mastro,* U.S. Naval Research Laboratory*; Henry Chuang,* Boston University*; Virginia Wheeler, Scott Walton,* U.S. Naval Research Laboratory

AlN is a wide-bandgap semiconductor with exceptional thermal conductivity, temperature stability, and piezoelectric properties, making it a promising material for high power and high frequency electronics, deep ultraviolet optoelectronics, and microelectromechanical systems. While AlN PEALD has been the subject of extensive research, it typically results in amorphous or polycrystalline films, which have inferior electrical properties compared to epitaxial AlN. Most reports of epitaxial AlN growth by PEALD involve the use of atomic layer annealing (ALA), in which an Ar plasma exposure is incorporated into each cycle to induce crystallization of the surface.[1] While the effectiveness of ALA is proven, its use also increases cycle duration, which significantly prolongs total process time and can promote impurity incorporation. For these reasons, the growth of epitaxial AlN without ALA is desirable, though this is challenged by the complexity of controlling the plasma properties to achieve suitable growth conditions.[2]

In this work, we demonstrate the growth of 30-50 nm thick epitaxial AlN films on Al_2O_3, GaN, and Ga_2O_3 at 300 °C using PEALD without ALA or thermal annealing. The PEALD process uses the commonly-employed combination of trimethylaluminum (TMA) and $N_2/H_2/Ar$ plasma, and is performed in a standard commercial reactor with remote inductively coupled plasma (ICP) source.Plasma diagnostics were used to identify favorable plasma regimes which produce ion energy and flux characteristics comparable to those of plasmas used in ALA. The films were characterized using x-ray reflectivity (XRR), high resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), atomic force microscopy (AFM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), and optical measurements. The growth per cycle (GPC) and density ranged from 0.90–1.03 Å and 2.998–3.173 g/cm^3, respectively, depending on substrate, with deposition on GaN resulting in the highest GPC and density.The topography of the films closely replicated that of the underlying material with roughness from 0.25–1 nm by AFM and 0.83–2 nm by XRR, indicating that the deposition was highly conformal. The epitaxial nature of the AlN (i.e., exhibiting a highly ordered crystalline structure with well-defined orientational relationship to the substrate) is confirmed by HRXRD and IP-GID, which show the films to be single phase and orientation with 6-fold azimuthal rotational symmetry. While the AlN films on Al_2O_3 and Ga_2O_3 are wurtzite phase with significant mosaicity, the AlN on GaN is metastable zincblende phase with low tilt disorder, as evidenced by narrow out-of-plane rocking curves with FWHM= 0.149 degrees (537 arcseconds). Results of AlN PEALD on nanocrystalline diamond (NCD) and single crystal diamond (SCD) will also be presented.

[1] H. Y. Shih et al., Sci. Rep. **7**, 39717 (2017)
[2] D. R. Boris et al., J. Vac. Sci. Technol. A **42**, 033008 (2024)

3:00pm **EM1-TuA-7 Enabling Blister-Free, Crystalline AlN Thin Films on 200 mm Si Wafers by PE-ALD Using a Microwave Electron Cyclotron Resonance Plasma Source**, ***Shiv Bhudia***, TUM School of Natural Sciences, Technische Universität München; Silicon Austria Labs GmbH, Austria*; Tai Nguyen,* Silicon Austria Labs GmbH, Austria*; Dominik Hartmann,* Evatec AG, Switzerland*; Marco Deluca, Julian Pilz,* Silicon Austria Labs GmbH, Austria

Aluminum nitride (AlN) is an important material for optoelectronics,[1] energy harvesting, and surface-acoustic-wave transducers and resonators.[2–5] It also enables devices operating at high frequencies and in thermally and chemically harsh environments.[6] This interest stems from its combination of a wide bandgap, high thermal conductivity, favorable lattice constant, and piezoelectric properties. In most applications, (002)-textured wurtzite films are required to achieve the desired device performance.[7] Furthermore, when fabricating 3D nanostructures such as microelectromechanical systems (MEMS),[8] memory devices,[9] and through silicon via (TSV) technology,[10] conformal growth and atomic-scale control are essential. Atomic layer deposition (ALD) has been proven to be an enabling deposition method under these conditions.

However, obtaining AlN films with crystal quality comparable to that of other deposition techniques remains challenging for ALD on Si substrates,[11–13] as oxygen and carbon impurities can significantly degrade crystallinity. Surface blistering is also a critical reliability issue in ALD and PE-ALD AlN,[14] yet systematic wafer-scale studies are scarce in literature. Moreover, the use of electron cyclotron resonance (ECR) plasma sources for AlN growth has received limited attention to date.[15]

In this work, AlN films are deposited on 200 mm Si(111) wafers using plasma-enhanced atomic layer deposition with trimethylaluminum (TMA) and NH_3 plasma as reactants. A novel ALD module (Evatec PEALD) is used for film deposition, employing a microwave ECR source for plasma generation. The effects of substrate temperature (200-400 °C) and plasma power (50-200 W) on film properties and blister formation are investigated. It is found that a combination of high power and substrate temperature leads to the formation of blisters on the edge region of the wafer.Applying a combination of characterization techniques, the number of blisters as a function of process parameters could be quantified (0-10 % of wafer area), and the defect formation mechanism was identified as likely caused by stress-induced effects. Fine-tuning of the substrate temperature and plasma power enables the suppression of these defects, resulting in damage-free, crystalline, and chemically pure films on 200 mm Si(111) substrates.

In a nutshell, this work presents effective mechanisms for producing PEALD AlN thin films with preferential c-axis orientation on 200 mm wafers, highlighting the importance of plasma source and parameter selection and giving insights into the suppression of film blistering effects.

3:15pm **EM1-TuA-8 Thermal ALD Tungsten Doped Indium Oxide Film as High Mobility Thin Film Transistor Channel Material**, ***Arnaud Jung***, CEA-LETI, France

Tungsten doped indium oxide (IWO) has proven to be a promising candidate as a high mobility channel material for thin film transistors (TFT) memories and display applications. While sputtered and plasma deposited IWO film have been extensively studied, literature is lacking data on low temperature thermal ALD (atomic layer deposition) deposited IWO. ALD is expected to take over sputtering for this material since it allows for conformal deposition on high aspect ratio 3D structures as well as very precise thickness and defect control for very thin films.

Regarding IWO composition, the indium content has an effect on the effective carrier mobility and tungsten doping is used to control the channel threshold voltage (Vt) by tailoring the oxygen bonding states in the material. The subthreshold slope (SS) describes the rate at which the transistor switches from off to on current state. This metric is highly related to the gate/channel electrostatic coupling and to the materials quality as well as crystalline structure. For aimed applications, we are looking for a material with the highest possible mobility, SS drawing the closest to the thermal limit of 60 mV/decade, and a Vt close to 0 volt because it allows better performance and faster processing rate in memory/display circuits. The film crystalline structure is yet to be explored, as it is known that high effective mobility can be obtained through a strong overlap of the indium 5s orbitals. Currently, amorphous oxide is mainly used since it displays better mobility than a poorly crystallized film, which is mainly due to the small grain boundaries carrier scattering effect. Regarding the oxygen environment, oxygen vacancies act as a carrier donor which shifts the Vt toward negative values.

In this work, we made thermally grown ALD IWO ultra-thin films (thickness < 5 nm) using trimethylindium (TMI) and bis(tert-butylimino)bis(dimethylamino)tungsten as In and W precursor, and O3 as the oxidant. The following ALD approach have been investigated for W doping of In oxide matrix: super-cycles led us to tune the IWO physico-chemical and structural properties. TFT test-vehicles were then fabricated to assess the electrical properties of the channel, in regard to different gate oxides material (SiO2, Al2O3, HfO2, HZO). XPS has been used to identify oxidation states and provide relative elemental quantification. Crystallization and patterning geometry effects on TFT properties have been explored.

Our best TFT was obtained using the supercycle approach with a precursor ratio In:W of 10:1, a deposition temperature of 300°C and using HfO2 as the gate dielectric. This TFT showed a Vt of 0,95 (+- 0,08) V, SS of 303 (+- 41) mV/decade and effective mobility of 14,7 (+- 2,9) cm^2/V.s.

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM2-TuA

ALD for 2D Materials

Moderators: Hanmei Choi, Samsung Electronics, **Christophe Detavernier**, Ghent University, Belgium

4:00pm **EM2-TuA-11 ALD Synthesis of Transition Metal Phosphides**, ***Raul Zazpe**, Jhonatan Rodriguez-Pereira, Jaroslav Charvot, Milan Klikar, Filip Bures, Jan Macak,* University of Pardubice, Czechia

The ever-increasing global energy demand together with the environmental issue originated from the use of fossil fuel, has triggered an intense search for sustainable and clean energy alternatives, such us hydrogen energy, biomass and solar energy among others. In this context, a pivotal key to deliver sustainable and superior energy systems lies on the rational design and development of high-quality and cost-effective catalyst offering enhanced stability, activity and selectivity. Consequently, intense efforts have been devoted in the search and synthesis of new catalyst materials to replace the scarce and expensive traditional noble metals (e.g. Pt, Pd, Au and Ru) for energy conversion and energy storage applications.

Among the recently explored novel catalyst materials, metal phosphides (MPs) have emerged in recent years, attracting significant attention thanks to their intriguing properties [1]. In particular, transition metal phosphides (TMPs) exhibit striking properties. The moderately strong M−P bonds lend outstanding mechanical properties, high thermal stability and outstanding chemical resistance to chemical attack and oxidation in acidic and alkaline solutions. Additionally, Co, Ni, Mo-based phosphides demonstrated excellent catalytic and bifunctional properties towards water splitting as both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [2,3].

Herein, we present the synthesis of TMPs by thermal Atomic Layer Deposition (ALD), including cobalt and titanium phosphide [4], based on the use of different transition metal precursors combined with in-house synthesized P precursors. The physical and chemical properties of the resulting TMPs thin films were extensively characterized by different methods, including atomic force microscopy, X-ray photoelectron spectroscopy and X-Ray diffraction. The presentation will introduce and describe the synthesis of the TMPs and the corresponding characterization toward diverse applications.

[1] Z. Pu, T. Liu, I. S. Amiinu, R. Cheng, P. Wang, C. Zhang, P. Ji, W. Hu, J. Liu, S. Mu, *Adv. Funct. Mater.*, **30**, 2004009 (2020).

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4:15pm **EM2-TuA-12 A Novel Chemistry toward the Atomic Layer Deposition of MoS2 thin films for Heterojunction Photocatalysis**, ***Annmary Anto**, Alexey Ganzhinov, Anjan Deb, Kenichiro Mizohata, Mykhailo Chundak, Mikko Ritala, Matti Putkonen,* University of Helsinki, Finland

Among the transition-metal dichalcogenides (TMDCs), MoS2 is the most extensively studied two-dimensional (2D) material owing to its excellent opto-electronic properties and the semiconducting nature. It is one of the most promising visible-light photocatalytic materials, recognized for potential in electronics to improve device efficiency and enhanced charge retention in energy storage. To harness these applications,researchers have explored a wide range of synthesis techniques,from top-down to bottom-up methods including exfoliation, thermal synthesis, and vapor phase deposition for the development of 2D-MoS2. However, in comparison with any other approach, atomic layer deposition (ALD) offers higher reproducibility and reliability due to its growth insensitivity towards excessive precursors.

Herein, we report a new thermal ALD process to fabricate MoS2 thin films up toa growth rate of 1.5 A°/Cycle at 200–300°C,using Mo(II) acetate dimer and H2S as Mo and S sources, respectively. As-deposited films on Si (100) with native oxide are found to be crystalline in nature, though rough, consisting of flake-like grains, and the X-ray diffraction (XRD) measurements confirmed the presence of (002) plane oriented 2H-MoS2 phase.The ALD-MoS2 films exhibited S/Mo ratio of 2.1–1.3, according to the deposition parameters, with O, C, and H impurities (<10 at.% in total) measured by time-of-flight elastic recoil detection analysis (ToF-ERDA). X-ray photoelectron spectroscopy (XPS) confirmed the formation of chemical bonding from MoS2. The crystalline nature of the films improved with a decline in conductivity along with the temperature. A transformation from in-plane to out-of-plane orientation of the two-dimensional layers as a function of number of cycles was observed.

Optical analysis indicated an energy gap ranging from 2.1 to 1.5 eV for films deposited on soda lime glass, increasing with higher S content. In addition, photocatalytic activity was demonstrated using solar sensitized methylene blue degradation. Further results on the development of heterojunction photocatalyst by integrating the developed MoS2 thin films with suitable oxides will be presented.

4:30pm **EM2-TuA-13 The Role of Plasma Conditions on the Properties of MoS_2 Films Grown by PEALD Using H_2 plasma and Di-tert-butyl Disulfide**, ***Paula Arellano**,* University of Michigan, Ann Arbor; *Ian E. Campbell,* IMEC; *Aashi Gupta, Pavlina Metaxa, Vasiliki Nousia, Ray Duffy,* Tyndall National Institute, University College Cork, Ireland; *Ageeth A. Bol,* University of Michigan, Ann Arbor

The presence of plasma species during PEALD enables film growth at temperatures lower than those usually required for thermal ALD and other deposition methods. We recently demonstrated a low-temperature PEALD process for molybdenum disulfide (MoS_2), based on $Mo(tBuN)_2(NMe_2)_2$ and di-tert-butyl disulfide (TBDS) in combination with H_2 plasma as the coreactant. TBDS is a safer and less hazardous alternative to hydrogen sulfide (H_2S) for PEALD of MoS_2 thin films.[1] Raman spectroscopy however showed that MoS_2 films grown using the TBDS process exhibit higher defect densities than those grown using a H_2S PEALD process. In this work, we study the effect of the H_2 plasma conditions on the quality of the resulting MoS_2 films and demonstrate how careful optimization of the plasma conditions (plasma power, plasma feed gas composition, pressure and flow rate) can reduce the plasma-induced damage and improve the crystallinity of the MoS_2.

The use of H_2 plasma during the TBDS process is thought to remove the Mo precursor ligands and reduce chemisorbed Mo^{6+} species to Mo^{4+} before the TBDS exposure. After characterizing the effects of H_2 plasma parameters on PEALD MoS_x, the defects-to-intensity ratio in the Raman spectra ranged from ~2.7 to ~1.0, revealing a substantial decrease in defect density for PEALD recipes with low power, high pressure H_2 plasma exposure. However, the surface roughness (R_q) of 6 nm thick MoS_x films, as measured by AFM, increased under these conditions due to out-of-plane fin growth.

To reduce fin formation in MoS_x films, we incorporated a low flow rate, low power, long duration Ar plasma step in our ALD cycle scheme. As a result, the R_q of ~6 nm thick MoS_x films decreased from 2.09 nm to 0.435 nm, while the defects-to-intensity ratio in the Raman spectra increased from 1.6 to 2.0. Thus, a tradeoff between fin growth and higher structural disorder exists when tuning the parameters of H_2 and Ar plasma exposures.

Finally, the electrical properties of MoS_x films with varying crystallinity and morphology will be compared. This work shows that the incorporation and optimization of plasma steps during PEALD of MoS_2 can further improve the quality of the resulting MoS_2, enabling the use of safer sulfur chemistry while achieving scalable, damage-controlled thin-film growth.

(1) Campbell, I. E.; et al. *Chem. Mater.* **2025**, *37* (4), 1478–1490.

4:45pm **EM2-TuA-14 ALD-Induced Doping Effect in 2D MoS_2 FETs: Roles of Oxidant Chemistry and MoS_2 Quality***, **Minjong Lee**, Thi Thu Huong Chu, Inhong Hwang, Doo San Kim, Dushyant Narayan, Dan Le, Soham Shirodkar, Jiyoung Kim,* University of Texas at Dallas

As scaling pushes device platforms toward three-dimensional (3D) integration, ultrathin gate dielectrics must be deposited directly on two-dimensional (2D) channels [1]. Atomic layer deposition (ALD) is a leading method for enabling such gate-stack integration. However, the surface chemistry required for nucleation can also unintentionally modulate carrier density in the 2D channel [2]. In MoS_2 field-effect transistors (FETs), this deposition-induced “atomic-layer doping (ALDo)” can alter key device metrics in ways that are often difficult to separate from nucleation-driven interfacial reactions and trap generation.

This work presents an *in-situ*/*ex-situ* characterization framework to track MoS_2 device evolution throughout the ALD gate-dielectric process. *In-situ*, we monitor electrical changes associated with individual ALD half-cycles to capture the initial deposition-induced shifts. *Ex-situ*, we quantify net performance evolution after dielectrics growth to few-nanometer thicknesses. Across ALD cycles, the most pronounced performance changes occur in the initial-growth regime, indicating that interfacial reactions dominate the ALDo response. MoS_2 film quality further sets the baseline sensitivity to ALDo. Exfoliated single-crystal MoS_2 exhibits minimal performance perturbation following few-nanometer gate-dielectric formation, whereas chemical vapor deposition (CVD)-grown MoS_2 shows clear degradation, implicating stronger interfacial reactions. Oxidant chemistry further modulates device behavior: O_3 tends to induce more severe surface perturbation, while H_2O_2 can promote S-O bond formation and yield qualitatively improved electrical characteristics.

Building on these insights, we outline practical routes toward quasi-single-crystal-like behavior in CVD-grown MoS_2 films by scaling channel length to confine transport within a single grain with suppressing excessive oxidation in the defect states. This study demonstrates a device-level diagnostic that accelerates mechanism-guided optimization of ALD gate stacks on 2D channels. The presentation will cover the measurement methodology, integration strategies, and prototype workflows for engineering ALDo, with implications for reliable 2D-FET operation toward future 3D-integrated electronics.

This work was supported by Samsung Electronics through GRO program (IO250621-13116-01) and the KEIT grant funded by MOTIE (RS-2023-00235484, No, 1415187770). The ozone generator was provided by TMEIC, and the BRUTE® Peroxide was provided by RASIRC Inc.

[1] K. S. Kim et al. Nat. Nanotechnol. 19, 895–906 (2024).

[2] S.-E. Yu et al. ALD/ALE Conference (2025).

5:00pm **EM2-TuA-15 Processing MoS_2 and WS_2 using ALD and Patterning on 8-Inch Wafers***, **Nils Boysen**, Leon Doman, Rahel-Manuela Maas, Anjana Devi,* Fraunhofer IMS, Germany

Processing 2D materials using various deposition and patterning methods on larger wafer scales is a major challenge in developing next-generation devices, such as ultra-sensitive sensors for photo-, gas-, and biosensing. In particular, ultra-thin films of layered 2D materials such as MoS_2 and WS_2 exhibit promising properties for sensing applications due to their semiconducting nature, high surface-to-volume ratio, and intrinsic selectivity for different analytes. One of the main challenges to date is the deposition and subsequent patterning of such delicate layers on larger areas, such as 8" silicon wafers. Because of their high sensitivity to oxidation and delamination, standard patterning routes cannot be readily adopted. Typically, MoS_2 and WS_2 are exfoliated and transferred to the target substrates. However, this top-down route adds a significant number of processing steps and is not easily scalable to larger scales. Furthermore, the layers must be on the uppermost layers of the device stack to be accessible for sensing applications, which rules out thick protective capping layers typically used in such stacks.

To overcome these challenges, we introduce a feasible approach to deposit MoS_2 and WS_2 via bottom-up ALD as the uppermost layer on pre-structured metallization layers. Subsequently, we enable patterning of MoS_2 and WS_2 via lithography and ion-beam etching, using in situ ALD Al_2O_3 capping layers that can be later porosified for sensing applications. Accordingly, we developed an ALD process at low deposition temperatures of 100 °C for MoS_2, and at higher deposition temperatures of 350 °C for WS_2 using $[Mo(NMe_2)_4]$, $[W(NtBu)_2(NMe_2)_2]$, and H_2S as precursors (Fig. 1). This resulted in ultra-thin layers that were amorphous for MoS_2 and crystalline with a 2D layered structure for WS_2. Subsequent patterning of the MoS_2 and WS_2 by photolithography and ion-beam etching (IBE) with the help of in-situ deposited Al_2O_3 capping layers prevented delamination and severe oxidation of the amorphous and crystalline layers, as proven by Raman spectroscopy and transmission electron microscopy (TEM) (Fig. 2) of the resulting structures. The integrity of the layers was preserved after porosifying the Al_2O_3 capping layer in boiling water, enabling sensing applications (Fig 3). In the case of patterned MoS_2, selective gas-sensing of relevant gases such as NO_2, NH_3, and H_2S could thus be achieved.

In summary, the new and promising developments in bottom-up 2D material processing via ALD have enabled us to realize sensing structures at a larger wafer scale and will facilitate the adoption of these materials for other device applications.

5:15pm **EM2-TuA-16 Exploiting Atomic Layer Deposition for Contacts to Semiconductors***, **Suzanne Mohney**, Chan-Wen Chiu, M. Saifur Rahman, Ryan Wang, Sree Palaniappan,* Pennsylvania State University

Electrical contacts to semiconductors in transistors and other electronic devices are typically formed by physical vapor deposition techniques such as sputtering or evaporation. Atomic layer deposition (ALD), however, offers unique opportunities for engineering electrical contacts across a wide range of semiconductor families. For example, we previously used an ultrathin ALD-grown dielectric to reduce the metal/semiconductor Schottky barrier height and achieve low-resistance ohmic contacts to silicon [1]. We also compared thermal ALD [2] and remote–plasma ALD [3] processes for depositing conductive films on gallium nitride, producing high-quality Schottky diodes. Most recently, we employed ALD for hole injection in source-drain contacts to the two–dimensional (2D) semiconductor WSe_2, motivated by the promise of 2D semiconductors for device scaling and integration with silicon platforms. Achieving low contact resistance for *p*–channel 2D field effect transistors is often challenging, but we obtained a contact resistance of 10 kΩ·μm [4] using semimetallic TiS_x contacts with MoO_x capping. The TiS_x was grown by thermal ALD from tetrakis(dimethylamido)titanium and hydrogen sulfide at 100 °C. Because contact yield was impacted by nonuniform coverage of TiS_x on WSe_2, we are investigating remote-plasma ALD processes to improve nucleation of TiS_2 on WSe_2 and are examining the interplay between deposition parameters and device performance. The presentation will conclude with an analysis of the outlook for using ALD for contacts to semiconductors across technologies. The authors acknowledge support from the National Science Foundation (NSF) through ECCS 2227346. WSe_2 epilayers were provided by the Penn State 2D Crystal Consortium–Materials Innovation Platform (2DCC-MIP) under NSF DMR 2039351.Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM1-WeM
ALD for Next-Generation Electronics and Quantum Technologies

Moderators: Robert Grubbs, IMEC, Belgium, **Henrik Sønsteby**, University of Oslo

8:00am **EM1-WeM-1 Platinum Growth on Li-Based Thin Films Using Thermal ALD**, ***Manon LETICHE***, *Sylvain POULET, Nicolas MASSONI, Violaine SALVADOR, Hélène COURDERT-ALTEIRAC, Nicolas GAUTHIER, Messaoud BEDJAOUI,* CEA-LETI, France

Lithium-based layers are key players in developing nanostructured energy storage systems. As such, ultrathin lithium phosphorous oxynitride LiPON deposited by Atomic Layers Deposition (ALD) is incorporated as solid-electrolyte between two electrodes for on-chip microsupercapacitors[1,2]. To avoid battery-like behavior it is crucial to select electrode material that doesn't interact with Lithium while providing efficient capacitive behavior and high electrical conductivity. To that purpose, using thermal ALD, noble metals are very good candidates but suffer from low nucleation[3]. This study aims to evaluate the implementation of ultrathin noble metals (such as platinum) deposited by ALD as electrodes for lithium-based capacitances.

Pt thin film was obtained by thermal ALD using Trimethyl(methylcyclopentadienyl)platinum(IV)and O_2 reactants. Pt nucleation on LiPON layers (20 nm thin) has been studied in comparison to lithium free substrates. In order to promote Pt nucleation surface treatment like TriMethylAluminium (TMA) pre-pulsing or TiN interfacial layer were used. Pt growth was morphologically, structurally and electrically characterized on SiO_2 and LiPON substrates using AFM, SEM, TOF-SIMS and spectroscopic ellipsometry.

Primarily, more than 300 cycles were required to obtain viable and continuous Pt film of 8nm on LiPON without any surface treatment. It was found that, whether using TMA pre-pulsing or a TiN interfacial layer, the nucleation delay could be reduced to 200 cycles on LiPON and 85 on SiO_2 substrate to achieve continuous Pt of 8 with a uniformity <3% and low resistivity (20 µΩ.cm) at 200mm wafer scale. Top view imaging and AFM characterizations show island growth without surface treatment on SiO_2 and LiPON substrates with high roughness. Same characterizations when TMA or TiN surface treatment is used evidence a high surface coverage with very low surface roughness on both substrates.

Focusing on the interface LiPON/Pt using TMA pre-pulsing, a thickness evaluation of LiPON with and without Pt capping under air exposure was performed using spectroscopic ellipsometry. Surprisingly, same behavior was observed in both cases. Ongoing interfacial characterizations are expected to assess the compatibility of these materials and Li diffusion through Pt.

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8:15am **EM1-WeM-2 The Stability Study of ITO Film Deposited by Thermal Atomic Layer Deposition**, ***Yongqing Shen***, *Zhengying Jiao, Liguo Chai, Fengbin Tian, Kaiqiang Zhao, libin Jia, Jie Shen, Jianqi Chen, Jinjuan Xiang,* Beijing Superstring Academy of Memory Technology, China*; Weihan Fan,* Beijing Superstring Academy of Memory Technology, Taiwan*; Hongbo Sun, Guilei Wang, Chao Zhao,* Beijing Superstring Academy of Memory Technology, China

Metal oxide thin-film transistors (TFTs), especially InGaZnO TFTs have attracted considerable attention for 3D dynamic random access memory (DRAM) applications, owing to their lower off-state leakage and suitable carrier mobility. A thin Tin-doped In_2O_3 (ITO) has been employed as an inserting layer at contact region to reduce the Schottky barrier from IGZO channel, so as to get higher on-current. [1] Given the promising potential of ALD-grown ITO thin film for 3D DRAM applications, investigating its thermal stability and the impact of contact materials on its performance are critical for back-end-of-line (BEOL) compatibility evaluation.In this work, the thermal stability of ALD-grown ITO film was systematically evaluated via annealing experiments. The film is stable after annealing in an N_2 atmosphere at 600 °C, and has a mixed polycrystalline–amorphous phase structure. Prolonged annealing time, however, induced a significant increase in oxygen-related defects. When the annealing temperature was elevated to 800 °C, the ITO films became rough and initiated decomposition. Considering that ITO may come into contact with interconnect materials (e.g., TiN and W) during subsequent process integration, the effect of TiN deposition on ITO property was also investigated. Deposition of TiN at 530 °C in a hydrogen-containing ambient caused partial damage to the ITO film. In contrast, no obvious changes in ITO properties were observed after annealing in N_2 at 600 °C, indicating that reducing gases (e.g., H_2) can degrade ITO stability. At 400 °C (without H_2), TiN deposition did not cause significant ITO damage; nevertheless, a slight reduction in ITO thickness was detected. This thickness loss is speculated to result from reactions between the byproduct HCl and the ITO surface, as well as the breaking of In–O and Sn–O bonds due to oxygen scavenging by TiN. Collectively, the results demonstrate that the temperature, atmosphere, and process byproducts of subsequent steps all contribute to ITO film damage or thickness loss. This study provides reliable experimental data to guide the integration of ITO for advanced 3D DRAM applications.

8:30am **EM1-WeM-3 Atomic Layer Deposition of TiN layer in Interposer Chip for Superconducting Quantum Processor Unit**, ***Kestutis Grigoras***, *Harshad Mishra, Jukka-Pekka Kaikkonen, Joel Hätinen, Elsa Mannila, Wisa Förbom, Rishabh Upadhyay, Mikael Kervinen, Isabel Gueissaz-Mattelmäki, Marco Marin Suarez, Jorden Senior,* VTT Technical Research Centre of Finland, Ltd, Finland

The increasing complexity of interconnects on a chip and the potential for crosstalk between qubits present significant challenges for scaling up a superconducting quantum processor unit (QPU). The commonly adopted solution is 3D integration, where a QPU interposer chip is employed to reduce parasitic capacitance and inductance, as well as to facilitate signal routing between qubits and control electronics. For higher levels of integration, the interposer typically incorporates through-silicon vias (TSVs). The purpose of TSVs is to minimize the so-called chip resonance mode and to route signals between qubits and control electronics. Due to the growing density of interconnects, the diameter of superconducting TSVs must be as small as possible, on the order of several tens of micrometers. The most reliable method for conformally coating the sidewalls of such high-aspect-ratio structures is the atomic layer deposition (ALD) technique. There are only a few material candidates suitable for superconducting coatings, with titanium nitride (TiN) being one of them.

In this work, we have fabricated and tested silicon interposer chips with coplanar waveguide (CPW) type signal lines and resonators formed by patterned TiN/Ta or Nb layers. These structures were prepared by sputtering [1]. Several types of TSVs were etched using deep reactive ion etching (DRIE) and then coated with a TiN layer using either thermal or plasma ALD. The performance of these structures was measured and compared to reference chips without TSVs. We also compared different characteristics of TiN layers obtained by sputtering and by thermal or plasma ALD. We found that both the microstructure and the critical temperature (T_c) of TiN films prepared by different methods were quite similar. On the other hand, the film stress and selectivity in wet or dry etchants depended on the preparation method, with differences reaching even an order of magnitude. Depending on the fabrication step, these differences could either complicate or, conversely, simplify chip fabrication.

K. Grigoras et al., "Qubit-compatible substrates with superconducting through-silicon vias", IEEE Trans Quant Eng, 3 2022, doi:10.1109/TQE.2022.3209881
[https://doi.org/10.1109/TQE.2022.3209881]

8:45am **EM1-WeM-4 Achieving Ultra-Low Resistivity in TiN Thin Films via Supercycle PEALD: The Critical Role of Ti:N Stoichiometry over Impurity Content**, *Van Long Nguyen,* ***Christophe Vallee***, *Natalya Tokranova, Bryant Colwill,* University at Albany-SUNY

Titanium nitride (TiN) has attracted significant interest in microelectronics due to its excellent chemical resistance, thermal stability, and low resistivity. Low-resistivity, stoichiometric TiN films are essential for realizing high-performance interconnects, diffusion barriers, and electrodes in next-generation microelectronic and quantum devices. While Atomic Layer Deposition (ALD) offers superior conformality, conventional low-temperature processes often yield nitrogen- or titanium-deficient films with high electrical resistivity due to poor stoichiometry and excessive impurity incorporation. We introduce a supercycle PEALD approach that periodically alternates two distinct plasma chemistries (TMSDMA + Ar plasma and TMSDMA + $N_2/H_2/Ar$ plasma with bias to play with energetic ions) (**Figure 1Sa and 1Sb**) to precisely control the TiN film composition and structure. The resulting TiN supercycle film demonstrates a significantly lower

electrical resistivity than its constituent films (**Figure 1Sc**). Surprisingly, this performance gain is achieved even with relatively high residual concentrations of C and O impurities. XPS analysis confirms that the resistivity minimum directly correlates with an approximately stoichiometric Ti:N ≈ 1:1 ratio derived from the relative populations of TiN-related Ti2p and N1s chemical states (**Figure 1Sc**). This result indicates that precise Ti:N stoichiometry, rather than impurity concentration, is the dominant factor governing the electrical performance of TiN films. This supercycle strategy provides a scalable, low-temperature method for fabricating high-conductivity TiN suitable for advanced nanodevice integration.

9:00am **EM1-WeM-5 Characterization of Superconducting Niobium Nitride Thin Films Grown by Thermal Atomic Layer Deposition*, Annika Häkkinen,*** *Oona Turpeinen, Jaakko Julin,* University of Jyväskylä, Finland*; Mikko Laitinen,* University Of Jyväskylä, Finland*; Timo Sajavaara,* University of Jyväskylä, Finland

Metal nitrides are a promising group of superconducting materials for a wide range of quantum technologies and advanced electronic applications. In applications requiring superconducting functionality, such as quantum computing, thin-film quality plays an essential role in device performance. Among metal nitrides, niobium nitride (NbN) is especially interesting due to its relatively high theoretical critical temperature (17 K) and compatibility with thermal ALD processes, which provide a straightforward implementation without added process complexity. [1]

In this work, superconducting NbN thin films were grown with TFS-200 ALD system from Beneq Oy operated in thermal mode at 400–500 °C using $NbCl_5$ and NH_3 as precursors. Film thicknesses varied between 25 and 100 nm and the depositions were done on silicon and sapphire substrates. The effects of film thickness, deposition temperature, substrate choice, and post-deposition annealing (650–1000 °C) on the superconducting and structural properties were investigated. Film characterization was carried out using electrical resistivity and critical temperature measurements, Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), and Time-of-Flight Elastic Recoil Detection (ToF-ERD).

Deposited films exhibited promising superconducting properties with critical temperatures up to 13.6 K after post deposition annealing. Films were slightly nitrogen rich and contained low concentrations of impurities such as O (< 4.6 at.%), Cl (< 3.6 at.%), C (< 3.8 at.%) and H (< 4.7 at.%). Superconducting critical temperature was dependent on the film thickness but even the thinnest films (25 nm) had a transition temperature of 10.6 K. These results highlight thermal ALD as a viable method for producing high-quality superconducting NbN thin films.

[1] G. K. Deyu et al." Recent advances in atomic layer deposition of superconducting thin films: a review" *Mater. Horiz*. **12**(15):5594-5626 (2025)

9:15am **EM1-WeM-6 Ferroelectric and Antiferroelectric Ultrathin Materials by Ald for Memory Applications*, Imane Zriba,*** CEA-University Grenoble Alps, France*; Rabei Barhoumi,* CEA-LETI, France*; Patrice Gonon,* LTM - CEA/LETI, France*; Simon Martin, Vincent Jousseaume, Laurent Grenouillet, Messaoud Bedjaoui,* CEA-LETI, France

$Hf_xZr_{1-x}O_2$ (HZO) ferroelectric devices are promising for memory applications but suffer from wake-up, fatigue, and limited endurance. Improving endurance and remnant polarization at low voltage is challenging due to increased leakage in thinner films [1]. Antiferroelectric HZO with higher Zr content offers better endurance and lower power consumption, but shows low polarization and phase instability. Combining ferroelectric and antiferroelectric layers is therefore a promising strategy to enhance device performance [2].

The study aims to develop bilayer and triilayer HZO structures by ALD by alternating ferroelectric (FE) and antiferroelectric (AFE) phases for metal–ferroelectric–metal (MFM) capacitors targeting non-volatile memory applications. Monolayer, bilayer, and trilayer stacks are designed by tuning composition and thickness to investigate the coupling effects between FE and AFE HZO. The goal is to combine the high polarization of FE HZO with the superior endurance of AFE HZO, while reducing coercive fields and operating voltage.

Experimental analysis of as-deposited films provides insights into structural and compositional properties after ALD deposition. X-ray reflectometry (XRR) and X-ray fluorescence (XRF) confirm the high precision of the ALD technique for the growth of stacked thin films, highlighting an accurate control of thickness and Hf-Zr composition in both, bilayer and multilayer structures. As shown in Fig. 1, the increase in annealing temperature enhances the diffraction peak intensity, indicating improved crystallinity of the HZO films. The diffraction patterns reveal a coexistence of tetragonal and orthorhombic phases evolving as a function of Zr content, where higher Zr percentages lead to more intense diffraction peaks, suggesting an increased fraction of the tetragonal phase in the film. This structural evolution is directly reflected in the electrical behavior presented in Fig. 2. Films with higher Zr content exhibit typical double-hysteresis loop with null remanent polarization characteristic of AFE response, consistent with dominance of the tetragonal phase. In contrast, compositions with lower Zr content show more pronounced hysteresis and larger remnant polarization, indicating a stronger contribution from the ferroelectric orthorhombic phase. Overall, the correlation between XRD and P–E results confirms that phase composition, controlled by annealing temperature and Zr ratio, governs the ferroelectric or antiferroelectric behavior of HZO films.

This work investigates the morphological and electrical properties of ALD-grown HfZrO-based structures for embedded ferroelectric memories. Results on monolayer HZO films show a clear link between composition, phase, and electrical behavior. These findings establish a basis for controlling ferroelectric and antiferroelectric responses. Future work will focus on bilayer and trilayer FE/AFE stacks to evaluate their electrical performance and potential for memory applications.

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM2-WeM

Energy-enhanced ALD

Moderators: John Conley, Oregon State University, **Jean-François de Marneffe**, IMEC

10:45am **EM2-WeM-12 Let There Be Light: Photo-Assisted ALD of Pt Using $Pt(acac)_2$ and O_3*, Robin Petit,*** *Kinanti Aliyah, Matthias Minjauw, Ruben Blomme, Arno Depoorter, Seppe Van Dyck,* Ghent University, Belgium*; Martin Rosenthal,* ESRF, France*; Zeger Hens, Christophe Detavernier, Jolien Dendooven,* Ghent University, Belgium

Global trends such as the transition to green hydrogen production and advancements in microelectronics are increasing the demand for high performance Pt-based electrodes. ALD enables Pt deposition in various morphologies, from size-controlled nanoparticles to continuous thin films, by tuning the nucleation behaviour and the number of ALD cycles. In thermal and plasma-enhanced Pt ALD, nucleation depends on parameters such as temperature, precursor dose, co-reactant choice, and substrate pretreatments.

This work focuses on photo-assisted ALD (photo-ALD), which uses ultraviolet (UV) illumination as an additional parameter to control growth. Building on our earlier study using $MeCpPtMe_3$ and O_2, where photon-precursor interactions enabled lower temperature Pt growth with shorter nucleation delays [AVS-ALD2024], we developed a new Pt photo-ALD process using $Pt(acac)_2$ and O_3 under 365 nm illumination. $Pt(acac)_2$ is a more economically viable precursor due to its straightforward synthesis and established large-scale production.

Continuous illumination at 100°C results in metallic Pt (Fig. 1a) and increased Pt loading compared to thermal ALD. To investigate nucleation and growth, in-situ X-ray fluorescence (XRF) and grazing-incidence small angle X-ray scattering (GISAXS) were performed at the European Synchrotron Radiation Facility (ESRF). Tracking the Pt growth kinetics with XRF reveals an enhanced nucleation with illumination (Fig. 1b). GISAXS indicates that, at similar Pt loading, photo-ALD produces smaller particles with higher areal density, while thermal ALD yields larger particles with wider spacing (Fig. 2). SEM images confirm these trends and show a broader size distribution for thermal ALD, indicating more disordered growth where nucleation and particle growth occur simultaneously (Fig. 3).

To understand the impact of photon-precursor interactions during each ALD step, the timing of the illumination is varied, showing that illumination during the $Pt(acac)_2$ half-cycle is critical to achieve photo-enhancement, yet reaction with O_3 remains necessary for further ALD growth. Notably, enhanced growth occurs not only when illuminating the precursor in the gas phase: illuminating surfaces bearing adsorbed $Pt(acac)_2$ and then dosing additional precursor, before the O_3 step, also increases Pt uptake relative to thermal ALD. Ongoing spectroscopy studies aim to clarify the effect of illumination on the precursor ligands.

In summary, our work shows that UV-illumination promotes Pt nucleation for both $MeCpPtMe_3$- and $Pt(acac)_2$-based ALD, providing insights that

support the development of photo-ALD for other metals and advance the technique toward practical applications.

11:00am **EM2-WeM-13 Microwave Enhanced Atomic Layer Deposition (MW-ALD) of Ta2O5**, ***Jessica Haglund***, Oregon State University; *John Conley, Jr.,* Oregon State Univesity

A limitation of some ALD processes is the required low deposition temperature. Low temperature can allow incorporation of residual impurities from unreacted precursors which in turn may degrade electrical, physical, and optical properties. A way to reduce impurities and improve film quality while still maintaining a low thermal budget is known as energy enhanced ALD (EE-ALD), in which extra energy is incorporated into the ALD cycle to improve the film while it is growing. EE-ALD using *in-situ* treatments with either rapid thermal, flash lamp, plasma, or UV exposure have all demonstrated improvements over standard ALD films.[2-10] We recently demonstrated a new EE-ALD technique we call microwave enhanced ALD (MW-ALD) using Al_2O_3.[11] Here we present MW-ALD results on Ta_2O_5 and compare with MW-ALD of HfO_2 and Al_2O_3.

MW-ALD of Ta_2O_5 was performed at 120 and 200 °C using $Ta(OEt)_5$ and H_2O using a Picosun R200 modified with a custom MKS microwave generator and helical antenna. 400 W MW exposures (without plasma generation) were performed following the $Ta(OEt)_5$ purge, starting 15 s into the 120 s N_2 purge and lasting for 30 s. Film thickness and refractive index were analyzed using a mapping Film Sense FS-1 ellipsometer.

On Pt substrates, MW exposure at both 120 and 200 °C resulted in improved uniformity, an increase in median Ta_2O_5 thickness from 8.1 to 8.7 nm, and a slight increase in refractive index. For Si substrates, MW exposure at 200 °C also improved uniformity but had the opposite impact, reducing Ta_2O_5 median thickness from 5.7 to 4.7 nm. For HfO_2 (TEMA-Hf/H_2O), MW pulses during the TEMA-Hf purge resulted in a ~50% increase in thickness and an increase in refractive index, while MW during the H_2O purge had minimal impact. For Al_2O_3 (TMA/H_2O), MW exposure during the TMA pulse improved film quality compared to exposure during the H_2O pulse.Additional investigation of MW exposure during other parts of the ALD cycle, thicker depositions, and electrical data on MOS and MIM devices will be presented at meeting.

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11:15am **EM2-WeM-14 Electron-Enhanced Atomic Layer Deposition of Tunable TiCxNy Ternary Nitride Films Using Tetrakis(dimethylamido)titanium with Ammonia Reactive Background Gas**, ***Zachary Sobell***, *Andrew Cavanagh, Steven George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) of amorphous tunable titanium carbonitride (TiC_xN_y) films was obtained at low temperatures. Amorphous ternary nitrides are important as diffusion barriers for back-end-of-the-line metallization in microprocessor fabrication. The TiC_xN_y EE-ALD was achieved using sequential exposures of tetrakis(dimethylamido)titanium (TDMAT) and low energy electrons in the presence of a continuous NH_3 reactive background gas (RBG) (**Figure 1**). The composition of the TiC_xN_y films was tuned by varying the NH_3 background pressure and the electron exposure time. The TiC_xN_y EE-ALD was performed utilizing a hollow cathode plasma electron source (HC-PES). The HC-PES delivered a high electron flux into background gases at pressures up to several mTorr. TDMAT was used as the source of Ti, C, and N. The NH_3 RBG served both as a source of additional N and a method for the removal of C from the TiC_xN_y films. The TiC_xN_y EE-ALD film growth was monitored using in situ ellipsometry. The TiC_xN_y EE-ALD was conducted at temperatures of 30-130°C using NH_3 pressures of 0 to 3 mTorr.

The C content in the TiC_xN_y films could be tuned using the NH_3 RBG pressure (**Figure 2**). Lower NH_3 pressures led to the incorporation of more C into the TiC_xN_y films. The C:Ti ratio varied from ~0.3 to ~0.05 as measured by XPS at a constant electron exposure time of 10 s. Electron exposure time was also used to modulate the C content in the TiC_xN_y films (**Figure 3**). Shorter electron exposures led to more C incorporation. The C:Ti ratio varied from ~2 to ~0.1 as measured by XPS at a constant NH_3 background pressure of 2 mTorr. In situ 4-wavelength and ex situ spectroscopic ellipsometry were able to estimate electrical resistivities for the TiC_xN_y films. Resistivity decreased from >2000 μΩ-cm to ~200 μΩ-cm with decreasing C content. XRR measurements were able to determine film densities. The film density for TiN films was 4.6 g/cm^3 and the film density decreased with increasing C content.

The C content in the TiC_xN_y films could also be varied using a CH_4 RBG. Carbon could be added by carbon EE-CVD using electron exposures together with CH_4 RBG. The carbon could also be removed using electron exposures together with NH_3 RBG. However, the C content in TiC_xN_y films was difficult to control using a supercycle approach with TiN EE-ALD and carbon EE-CVD.

11:30am **EM2-WeM-15 Pulsed Excimer Laser Processing to Promote Room-Temperature Crystallization of ALD HfO_2 Films**, ***T. Jude Kessler***, *Hans Cho, John P. Murphy, Sarah Brittman, Saikat Mukhopadhyay,* 1. US Naval Research Laboratory; *Peter Litwin,* 2. NRC Research Associateship Program; *Bradley De Gregorio, Virginia Wheeler, F.K. Perkins, Margo Staruch,* 1. US Naval Research Laboratory

Ferroelectric hafnia compounds, including Hafnium Oxide (HfO_2), are of interest to realize advanced neuromorphic devices. The metastable, polar orthorhombic phase of HfO_2 is required to achieve the necessary ferroelectric device properties. Typically, this phase is stabilized at elevated temperatures, a significant barrier to producing thin films by atomic layer deposition (ALD). The lower deposition temperature of ALD enables direct, conformal integration of HfO_2 films on a variety of materials at any fabrication step but produces non-ferroelectric amorphous or monoclinic phase. Excimer Laser Annealing (ELA) has an edge over conventional annealing because it uses short laser pulses to heat only a thin surface layer, which rapidly cools due to a sharp thermal gradient with the underlying material. This process creates a heating and cooling cycle with insufficient time for the elevated state of the thin film to relax, promoting crystallization and stabilization of metastable phases. Thus, in this work, we apply ELA process to crystallize ALD HfO_2 films and determine the parameters that produce the ferroelectric, orthorhombic phase.

Ultrathin (10-20 nm), amorphous HfO_2 films were deposited by plasma enhanced atomic layer deposition on thermal SiO_2 substrates at 200°C using TEMAHf and Ar/O_2 plasma. To enhance the absorption of the pulsed laser, all films were capped with 50nm PEALD TiN. Films were processed using 20ns ELA pulses from 308nm broad bandwidth XeCl Coherent COMPex 201 laser homogenized by a fly's eye system illuminating a 5mmx5mm square with gaussian temporal profile onto the film surface. Parametric ELA testing was initially conducted, varying fluence and number of pulses, to determine the experimental range with sufficient energy to alter the film without causing delamination or photochemical ablation. Experiments investigating the influence of raster pattern and fluence on resulting HfO_2 structure were then performed.

Initial results show that controlling the ELA process parameters, we can both crystallize and influence the phase of HfO_2 films produced. Crystalline films were achieved without any observed damage to the film or underlying surface, exemplifying an advantage of ELA. Using TEM and glancing-incidence x-ray diffraction (GIXRD), we identified the ability to stabilize films with either orthorhombic, tetragonal, or a combination of both phases. Under the right parameters, films were single phase without any residual amorphous or monoclinic phase. Details establishing process-structure-property relationships using this promising technique to achieve relevant and scalable ferroelectric films will also be discussed.

11:45am **EM2-WeM-16 Thermally Activated Atomic Layer Annealing (ALA): A Plasma Free Approach to Densification of Hafnia Thin Films**, ***Dushyant Narayan***, *Thi Thu Huong Chu, Dan Le, Minjong Lee, Doo San Kim, Soham Shirodkar, Jean-Francois Veyan, Jiyoung Kim,* The University of Texas at Dallas

As device length scales continue to scale and transition from 2D planar to 3D structures, device architectures require precise control of step coverage and involve increasingly stringent requirements on electronic performance of high-k dielectrics. One of the immediate challenges is achieving growth of high-k dielectric materials with low defectivity and high density in high-aspect-ratio (HAR) structures within a low thermal budget. In this regard, Atomic layer annealing (ALA) methods offer low-temperature deposition with superior film quality compared to conventional thermal ALD, which has been reported for nitride-based materials such as AlN, and GaN.[1-3]These ALA methods typically utilize plasma to transfer energy to the film during growth to facilitate the migration of adatoms on the surface and also

eliminate unreacted ligands, leading to a more organized and compact thin film.[4] However, plasma based methods suffer from serious limitations in high-aspect ratio structures, where plasma recombination effects can limit the concentration of plasma radicals in trenches.

In this work, we will discuss a chemical approach to densification which we term Thermal-ALA. This method is plasma-free, enabling deposition in HAR structures, and introduces a chemical annealing step into the reaction chamber after each deposition cycle. Here, we will present *in-situ* characterization of the reaction mechanisms involved in this process via Reflective Absorption Infrared Spectroscopy (RAIRS) as well as *ex-situ* characterization of the resulting film properties. By varying the dose of oxidant and substrate temperature we show that resulting hafnia films grown with this technique have improved wet-etch rate (WER), density, and can even crystallize during deposition at substrate temperatures as low as 300 °C. By demonstrating this technique, we show that densification of hafnia thin films can be achieved with purely thermal and chemical techniques, thereby providing another engineering parameter by which film properties can be controlled.

This work is supported by Samsung Electronics through the GRO program(IO250621-13116-01).

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