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

ALD Supercycle Processes

Moderators: Ageeth Bol, University of Michigan, Ann Arbor, **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 ºC.

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

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