Thin Films
Room 206 B W - Session TF1-MoM

Fundamentals of Thin Films I

Moderators: Jeffrey Elam, Argonne National Laboratory, **Paul Poodt**, Eindhoven University of Technology, Netherlands

8:15am **TF1-MoM-1 Reduced Oxide Epitaxy at Very High Temperatures**, ***Joseph Falson,*** Caltech **INVITED**

In this presentation I will discuss epitaxial growth of reduced oxides at very high temperatures and low oxygen pressures, with a specific focus on binary transition metal oxides. We have stabilized a range of high quality films where in addition to injected oxygen, diffusion of anions from the substrate fuels crystal growth and promotes excellent crystallinity. I will also discuss the use of these atomically flat epitaxial layers as building blocks towards complex heterostructures constructed from dissimilar material classes.

8:45am **TF1-MoM-3 High Entropy Oxide Epitaxial Thin Films via Far-from-Equilibrium Synthesis**, ***Saeed S. I. Almishal,*** *Matthew Furst, Sai Venkata Gayathri Ayyagari,* The Pennsylvania State University*; Pat Kezer,* University of Michigan, Ann Arbor*; Nasim Alem,* The Pennsylvania State University*; Christina Rost,* Virginia Tech*; John Heron,* University of Michigan, Ann Arbor*; Jon-Paul Maria,* The Pennsylvania State University

High entropy oxides (HEOs) are inherently metastable, with properties that are highly sensitive to their thermal history and formation kinetics. Pulsed laser deposition (PLD) stabilizes atomic and electronic configurations far from equilibrium, enabling the exploration of structural and electronic phases inaccessible via conventional bulk synthesis. By precisely tuning growth temperature and rate, PLD directs how materials access metastability and allocate configurational entropy, locally acquiring order within a globally disordered matrix. We exemplify this strategy by growing MgCoNiCuZnO epitaxial thin films, where precise control over substrate temperature and oxygen partial pressure yields up to a 6% variation in the out-of-plane lattice parameter in pseudomorphic thin films across a 200 °C range. By slowing the growth rate or increasing film thickness fivefold, we can induce the formation of two distinct nanostructures: copper-rich nanotweeds and coherent spinel nanocuboids. Incorporating additional cations (e.g., Sc, Cr) facilitates the design of vertically stacked pseudomorphic heterostructures exhibiting exceptional crystalline fidelity and sharp interfaces. Building on these insights, we demonstrate metastable functional oxides—most notably Srx(Ti,Cr,Nb,Mo,W)O_3 films—where engineered chemical disorder while maintaining structural order enhances both electron correlation and spin-orbit coupling. Our work demonstrates how entropy-assisted, far-from-equilibrium synthesis via PLD provides transformative opportunities for designing novel functional oxides, significantly expanding the landscape of crystalline materials.

9:00am **TF1-MoM-4 ALD with Alternative Co-Reactants: Which Work, Which Do Not, and Why**, ***Jay Swarup***[1,2]*, Robert Mercogliano, James Jensen, Geet Chheda, Robert DiStasio Jr., James Engstrom,* Cornell University

For a number of ALD processes, it is desirable to employ alternative co-reactants to achieve a variety of objectives, which include modifying the temperature window, optimizing the stoichiometry of the thin film, and eliminating undesirable side reactions. Concerning the latter, we have demonstrated that using *t*-BuOH in lieu of H_2O as a co-reactant in ALD with trimethyl aluminum (TMA) results in deposition of a thin film of Al_2O_3 that does not oxidize the underlying Co substrate, while use of H_2O does **[1]**. Here we build upon this previous work using a combination of experiments and theory to examine systematically a series of alcohols—primary, secondary and tertiary—as co-reactants with TMA for the ALD of Al_2O_3. We compare these results to the benchmark TMA|H_2O process and investigate the role of temperature. We have employed a quartz-crystal microbalance to monitor ALD *in situ* and in real-time, and the deposited thin films have been characterized using XPS. In parallel, we utilized density functional theory (DFT) calculations to identify key reaction intermediates and quantify the kinetics of surface reactions. At a temperature of T = 120 °C we find that none of the 8 alcohols examined result in steady growth of a thin film of Al_2O_3. At a temperature of T = 285 °C the situation is quite different, as steady growth is observed, but only by employing tertiary alcohols as co-reactants. Steady growth does not occur with the 6 primary and secondary alcohols examined. For example, concerning structural isomers of C_4H_9OH and $C_5H_{11}OH$, *t*-BuOH and 2-methyl-2-butanol result in steady growth, while 2-butanol and 3-methyl-2-butanol do not. Our calculations using DFT verify the essential role played by the tertiary -OH groups in facilitating the reaction with the chemisorbed species formed in the TMA half-cycle. We find that the important reaction intermediate involves an interaction between an adsorbed alkoxy species with another alcohol, producing -OH(*a*) species. A final issue we addressed concerned the effect of intentionally introducing a small amount of H_2O into the alcohol co-reactants. We find that a mixture of *t*-BuOH and a small amount of H_2O results in steady growth at T = 120 °C, whereas pure *t*-BuOH did not. Similarly, a mixture of *i*-PrOH and a small amount of H_2O results in steady growth at T = 285 °C, whereas pure *i*-PrOH did not. Overall, our study highlights the critical roles played by alcohol order, process temperature, and the influence of small amounts of H_2O impurity on the efficacy of using alcohols as co-reactants in ALD.

[1]J. V. Swarup, H.-R. Chuang, A. L. You, and J. R. Engstrom, ACS Appl. Mater. Interfaces **16**, 16983–16995 (2024).

9:15am **TF1-MoM-5 Enhancing Atomic Layer Deposition Reactor Efficiency for Iridium Thin Films: Balancing Sustainability and Performance in Film Growth**, ***Jaron Vernal Moon****, Timothy J. Gorey,* Los Alamos National Laboratory

Atomic layer deposition (ALD) is a useful technique that enables atomic layer-by-layer growth of conformal films, but the technique is inherently wasteful due to the conventional viscous flow of chemical precursor injection, where the flow stream results in faster film growth at the stream-sample interaction point, reducing coating conformality. This work presents a new, “hold-step” ALD reactor that greatly increases efficiency of conformal film growth while reducing chemical use for improved sustainability. This work specifically focuses on iridium and iridium oxide thin films. By delving deeper into the understanding of the iridium precursor physical properties at temperature, the ALD recipe is tuned to best promote efficient iridium film growth kinetics. By introducing a “hold-step”, the reaction zone is isolated from the vacuum pump during dosing and the pressure is held constant for a set amount of time, resulting in improved film growth as the dosing gases are permitted to diffusively permeate and chemisorb onto embedded surfaces more efficiently. Additionally, characterizing the iridium precursors using techniques such as gas chromatography and thermogravimetric analysis, the ALD reaction can be fine-tuned for effective film growth. By changing from viscous to static flow and better understanding of the precursor kinetics, the total amount of gas required per deposition cycle is substantially reduced. A hold- step reactor design will be presented and compared to traditional ALD reactor designs. For comparison, precursors quantities and the resulting film qualities will be compared. The innovative yet simple design of a hold-step reactor not only enhances film quality but also promotes sustainability by reducing waste gas usage.

9:30am **TF1-MoM-6 Diffusion, Reaction and Thermodynamics of Organic Vapor Phase Infiltration to Overcome Shortcomings of Inorganic Hybridization**, ***Brian Welch,*** Technion Israel Institute of Technology, Israel*; Bratin Sengupta,* Argonne National Laboratory, USA*; Ruoke Cai,* Technion Israel Institute of Technology, Israel*; Vepa Rozyyev,* Argonne National Laboratory, USA*; Eitan Feldman,* Rice University*; Anil Mane,* Argonne National Laboratory, USA*; Alon Grinberg Dana,* Technion Israel Institute of Technology, Israel*; Jeffrey Elam,* Argonne National Laboratory, USA*; Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel

Vapor phase infiltration (VPI) enables tailoring of polymeric materials through incorporation of inorganic components. However, the benefits of VPI (also known as sequential infiltration synthesis, SIS) – are often paired with drawbacks such as compromised mechanical stability. Furthermore, the resulting organic-inorganic bonds are often prone to degradation through hydrolysis. To overcome these limitations, we investigate all-organic VPI using step growth molecular layer deposition (MLD) chemistries as a strategy for enhancing polymer properties. We examine the reaction-diffusion kinetics and thermodynamic behavior of three aromatic step-growth polymerization reactions: polyamide, polyurea, and polyimine. Their material growth occurs via MLD at the surfaces of non-absorbing silicon and zirconia. Organic VPI occurs within the bulk of nucleophile-rich polyvinyl alcohol (PVA), but not through physical entrapment in unreactive polystyrene and poly(methyl methacrylate). Using a reaction-diffusion model, we quantify diffusion-limited polyamide and reaction-limited polyurea nucleation behavior in PVA, identifying key parameters: diffusivity,

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[1] **TFD James Harper Award Finalist**

[2] **JVST Highlighted Talk**

reaction rate, and Damköhler number. Unlike inorganic alumina treatment, organic modification enhances dissolution-resistance in PVA, preserving polymer integrity and resisting hydrolysis even in harsh pH 13 solutions. This study demonstrates the potential of all-organic material deposition for synthesizing novel polymers with improved durability and solvent resilience.

9:45am **TF1-MoM-7 Tailoring Ba-Based Thin Films for Security Imaging: Role of H_2O Reactivity and Al_2O_3 Supercycle Integration in ALD***, **Adnan Mohammad**, Chi Thang Nguyen, Nuwanthaka Jayaweera, Jacob Kupferberg, Jeffrey W. Elam,* Argonne National Laboratory, USA

Microchannel plate (MCP) electron amplifiers are important components in large-area photodetectors, particularly for security-related applications such as night vision, radiation monitoring, and surveillance. Enhancing their performance and gain depends on advanced thin film coatings with high secondary electron yield (SEY). Barium-containing materials, recognized for their high SEY properties, are highly promising candidates for emissive coatings in MCPs. Atomic layer deposition (ALD) has emerged as a leading fabrication technique for such films, offering advantages in uniformity, pinhole-free morphology, and atomic-scale thickness control at low processing temperatures. However, despite ALD's potential, research on barium-thin films via this method remains under-explored. Notably, no prior work has investigated ALD-synthesized barium-based coatings in MCPs, presenting a significant opportunity to bridge this gap.

In this study, we demonstrate the thermal atomic layer deposition (ALD) of barium-containing thin films using bis(tri(isopropyl)cyclopentadienyl)barium ($Ba(iPr_3cp)_2$) as the barium precursor and water (H_2O) as the co-reactant. We further investigate the structural and functional impact of incorporating alumina via super-cycle deposition within the $Ba(iPr_3cp)_2/H_2O$ process. The $Ba(iPr_3cp)_2$ precursor was vaporized at 175°C, and depositions were performed in a hot-wall reactor at 250°C under a pressure of ~1.2 Torr. Systematic saturation studies were conducted to optimize precursor temperature, dose time, purge duration, and co-reactant exposure. Real-time thin film growth was monitored using in-situ ellipsometry, which enabled rapid saturation analysis while providing valuable insights into surface reactions during each ALD cycle.

The barium-containing films were characterized using X-ray photoelectron spectroscopy (XPS) for chemical composition, X-ray diffraction (XRD) for crystalline structure, X-ray reflectivity (XRR) for density, and atomic force microscopy (AFM) for surface topography. Moving forward, we aim to integrate ALD-grown barium layers onto microchannel plate (MCP) substrates and systematically evaluate their resistance, gain, and temporal stability. These metrics will directly assess secondary electron yield (SEY) performance, validating the material's potential as a high-SEY coating to enhance MCP efficiency.

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