Thin Films
Room 317 - Session TF-TuM

Fundamentals of TF II

Moderators: Devika Choudhury, ASM, **Blake Nuwayhid**, Naval Research Laboratory

8:00am **TF-TuM-1 Argon and Nitrogen Background Atmospheres as Growth Modulators in RIR-MAPLE Deposited $MAPbI_3$ Thin Films**, ***Joshua Ayeni***, *Adrienne Stiff-Roberts,* Duke University

Controlling material delivery during pulsed laser deposition (PLD) is critical for hybrid perovskites, where volatile organic components make film growth highly sensitive to deposition conditions [1]. Resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE) provides a solvent-mediated, low-damage deposition route for delicate hybrid materials. During RIR-MAPLE, inert background gases can alter plume expansion through collisional scattering and thermalization, affecting precursor transport and crystallization. Although RIR-MAPLE has been applied to diverse material systems [2,3], the comparative effects of inert gases on three-dimensional perovskite growth remain largely unexplored.

In this study, methylammonium lead iodide ($MAPbI_3$) thin films were deposited under controlled argon (Ar) and nitrogen (N_2) environments to investigate how inert atmospheres regulate plume propagation, precursor incorporation, and film evolution during RIR-MAPLE growth. $MAPbI_3$ possesses strong optical absorption, long carrier diffusion length, high mobility, and tunable bandgap energy, making it promising for photovoltaic and optoelectronic applications [4,5].

Depositions were performed using a resonant 2.94 μm Er:YAG laser, enabling gentle matrix sublimation and transfer of intact material toward the substrate for nucleation and crystallization. By varying gas species and pressure, distinct growth behaviors emerged due to atmosphere-dependent plume scattering and thermalization. Structural characterization revealed differences in crystallinity, orientation, and crystallite development between Ar- and N_2-grown films, indicating that the background atmosphere strongly influences growth kinetics.

Compared to Ar, N_2 environments promoted improved crystalline evolution (~35–43 nm) and increased film thickness (~150–260 nm), consistent with enhanced precursor retention and reduced loss of volatile species near the substrate. In contrast, Ar atmospheres produced thinner films (~100–147 nm) and stronger evidence of scattering-induced disruption of precursor transport. Optical measurements showed preservation of the characteristic $MAPbI_3$ absorption edge and photoluminescence response across both atmospheres, while subtle spectral shifts reflected atmosphere-dependent variations in structural order and defect-mediated recombination pathways.

Overall, the results demonstrate that inert background environments in RIR-MAPLE act as active growth regulators rather than passive chamber conditions. These findings establish the role of inert gases and pressure in tuning growth dynamics and support scalable RIR-MAPLE deposition of high-quality hybrid perovskite thin films.

8:15am **TF-TuM-2 High Throughput Thin-Film Ion Kinetic Testing Enabled Through Atmospheric-Pressure Spatial ALD**, ***Daniel MacAyeal***, *Ellen Owens, Kaydence Delgado, Alexander Kozen,* University of Vermont

Research in atmospheric pressure spatial atomic layer deposition (AP-SALD) has enabled new capabilities in quickly manufacturing thin metal-oxide coatings for photovoltaics, electrochemical interfaces, and low-cost transparent conductors for flexible electronic devices. Spatial ALD can also be used for rapid materials testing and processing through deposition of high-throughput combinatorial libraries. Here, we utilize this approach to investigate AP-SALD of Nb_2O_5 / TiO_2 mixed metal oxide (MMO) bronzes, which are known to exhibit fast ion transport. Discrete regions of each mixed metal oxide can be varied by an arbitrary material property or manufacturing parameter of our choosing. We construct TiO_2 / Nb_2O_5 bronze test structures with varied alloy composition, precursor flow parameters, nanolaminate thickness, and overall region composition. We use spectroscopic ellipsometry, Raman spectroscopy, AFM, and XRD to evaluate materials structure, composition, and morphology as a function of the aforementioned parameters. We demonstrate the capabilities of AP-SALD and highlight new accelerated methods for high-throughput complex oxide materials development.

8:30am **TF-TuM-3 Accelerated Approaches to Atmospheric Pressure ALD Process Development Using Predefined Test Structures**, ***Ellen Owens***, *Holly Wilson, Dan MacAyeal, Alex Zaccardi, Drew Ledger, Alexander Kozen,* University of Vermont

Process development and associated materials screening for atomic layer deposition (ALD) processes can be long and arduous, particularly for compositionally complex ternary quaternary, and pentanary films. Beyond conventional ALD, Atmospheric pressure spatial ALD (AP-SALD) is an emerging and powerful tool that can produce discrete arrays of deposited material on a single wafer to increase the rate of material optimization of thin-film materials. In this talk, we discuss strategies to dramatically decrease process development and materials characterization timelines for ALD films using atmospheric pressure spatial ALD (AP-SALD) onto prepatterned arrays of test structures and devices.

We use TiO2as a prototype material to demonstrate the high throughput capabilities of AP-SALD process by deposition onto interdigitated electrodes and evaluate the electrical, optical, and structural properties of these films.

We vary combinatorial parameters including precursor, carrier, and sheath gas flow rates, nozzle to substrate gaps, deposition temperatures, and post deposition processes, allowing us to quickly access a wide parameter space on a single substrate.

We evaluate the spatially-resolved deposition characteristics of TiO2 using profilometry, spectroscopic ellipsometry, and electrical measurements including IV, CV, linear& nonlinear impedance, and Hall effect measurements.

8:45am **TF-TuM-4 Facile Optimization of Combinatorial Sputtering Processes with Arbitrary Numbers of Components for Targeted Compositions**, ***Shelby Fields***, U.S. Naval Research Laboratory

Combinatorial thin films and coatings, which display analogue compositions that vary as a function of position, enable high-throughput materials discovery and optimization. For example, when paired with mappable characterization, whole explorations of composition effects on materials properties may be contained within a single synthesis step. However, the applicability of combinatorial films and coatings to many materials challenges is hindered by irreproducibility and constrained processing spaces, which reduce the extent to which these experiments map on to end-use technology. To address this deficiency, this presentation introduces a process development method that enables the reproducible synthesis of *n*-component sputtered combinatorial thin films with targeted compositions at specific coordinates. It is determined that areal mass density profiles of individually sputtered species are well described by two-dimensional Gaussian peak shapes, the amplitude of which possesses a strongly linear relationship with applied target power. In addition, areal mass density profiles are shown to be noncovariant during co-deposition. Based upon these characteristics, an optimization expression is derived that computes the power required to obtain a targeted atomic concentration at a specific coordinate. It is shown that a minimum of two depositions at different powers are sufficient produce an optimized process model, which is subsequently enabled to suggest powers to obtain any composition at a targeted coordinate, permitting the high throughput exploration of entire composition spaces. Furthermore, this optimized process allows for the substitution of substrates of different diameter and material following calibration, is compatible with both direct current and radio-frequency magnetron sputtering, and can suggest powers to obtain identical compositions at different growth rates. As a proof-of-concept, a $Cr_vFe_wMo_xNb_yTa_z$ alloy thin film is synthesized on a 6”-diameter Si wafer with an equiatomic composition at the center that matches well with simulation following calibration. This capability is further demonstrated through the synthesis of alloy combinatorial wafers using reactive and rf sputtering processes for separate materials exploration investigations. In total, this optimization method enables the rapid and reproducible synthesis of combinatorial films with arbitrary numbers of components, which better connects this high throughput experimental method with down-stream applications and technology.

9:00am **TF-TuM-5 Combining Pyroelectric Calorimetry and Multiscale Modeling to Untangle the Interplay of Precursor Delivery, Kinetics, and Byproducts in ALD ZrO2**, ***Ashley Bielinski***[1,2], *Anik Biswas, Cong Liu, Alex Martinson,* Argonne National Laboratory

Thermal atomic layer deposition (ALD) processes are typically described as alternating sequences of self-limiting surface reactions. When we inspect the dynamics of individual reactions as they approach saturation, we see that in addition to simple mechanisms of ligand exchange reactions, this self-limiting nature also depends on an interplay between precursor delivery, reaction kinetics, and the role of reaction byproducts.An investigation of these dynamic processes can provide insights into the results of ALD processes ranging from fundamental reaction thermodynamics and kinetics to reactor design. However, these reactions happen quickly, often at rates faster than the sampling frequency of common in situ measurement techniques.Pyroelectric calorimetry provides in situ measurements of the heat generated and transferred from surface reactions as well as precursor and byproduct flow with sufficient time resolution to measure these dynamics.Here we present how experimental calorimetry measurements can be combined with multiscale computational modeling to untangle the influence of precursor flow dynamics and reaction kinetics for the reaction between tetrakis(dimethylamido)zirconium(IV) (TDMAZr) and water to form ZrO_2. By combining experimental measurements that represent the true conditions of realistic samples surfaces, first principles modeling of reaction mechanisms, and reactor-scale modeling of precursor flow and byproduct generation, we provide insight into the complexities of ALD surface reactions, the non-idealities of which have broader implications for the development of site- and area-selective ALD.

9:15am **TF-TuM-6 Investigation of Lattice Interpenetration in Thin Film Growth of Microporous Coordination Polymers**, *Hallie Matherne,* ***Greg Szulczewski,*** The University of Alabama

Thin films were synthesized from a family of pillared, microporous coordination polymers with the general formula $M_2(BDC)_2L$, where M is Ni^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+}, BDC is benzendicarboxylic acid and L is either is 1,4-diazabicyclo[2.2.2]octane (DABCO) or 4,4'-bypridine (bpy), by a hot-solvent technique and a room temperature layer-by-layer solution deposition. The thin films were grown on gold substrates and characterized by x-ray diffraction, x-ray photoelectron spectroscopy, ion-scattering spectroscopy, vibrational spectroscopy and scanning electron microscopy. The films were activated by heating under high vacuum and adsorption/desorption isotherms were measured for several volatile organic compounds. The mass uptake of the guest molecules into the coordination polymer host strongly depends on the extent of lattice interpenetration. In general, the extent of lattice interpenetration depends on the length of the diamine pillar. In the hot-vapor synthesis technique, lattice interpenetration is observed when using the longer bpy pillar, but not the shorter DABCO pillar. However, at room temperature, lattice interpenetration can be suppressed by using the layer-by-layer solution deposition technique with the bpy pillar. The key to suppress lattice interpenetration is use of a pyridine terminated thiol monolayer which templates the growth of a single phase.

9:30am **TF-TuM-7 Autodoping of Thin-Film Ionic Materials Using Atomic Layer Deposition (ALD)**, ***Steven Douglass****, Daniela Fontecha, Gary Rubloff, Sang Bok Lee, Keith Gregorczyk,* University of Maryland, College Park

Recently, our group has shown that semiconductor manufacturing techniques can be leveraged to add electrochemical functionality and make devices outside of the traditional semiconductor portfolio. These devices include solid-state microbatteries and super capacitors, aswell as electrochemical random-access memory (ECRAM). In the production of these iontronic devices (devices where ions operate as the main carriers of charge), notable intermixing of ionic material layers has occurred between, for example, the vanadium pentoxide (V_2O_5) cathode and the lithium phosphorus oxynitride (LiPON) electrolyte in solid-state microbatteries. This autodoping has been termed "autolithiation" and is believed to occur in two stages: before LiPON film growth and during LiPON film growth. It was first observed as a physical process during sputtering of LiPON onto a V_2O_5 substrate.

Since, we have observed a similar phenomenon while depositing ALD LiPON onto V_2O_5, with the lithium source being lithium *tert*-butoxide (LiO^tBu). In this talk we discuss how autolithiation during ALD depends on temperature in its initial stage. At 300°C, there was no lithiation after 20 pulses of LiO^tBu. However, one pulse at 350°C and 400°C yielded lithiation, followed by a linear trend of increased lithiation state with increased pulsing. Figure 1 displays the trend of lithium inserted through LiO^tBu pulsing at different temperatures, calculated from electrochemical delithiation of the samples. XPS demonstrates that the V^{4+}:V^{5+} oxidation state ratio grows quicker with increased temperature. Raman spectroscopy shows evolution of the bulk away from α-V_2O_5 with higher temperatures and more LiO^tBu exposure. This presentation discusses characterization and quantification of ALD autolithiation of V_2O_5 before film growth. Future work on the subject will be focused on deconstructing autolithiation after film growth.

11:00am **TF-TuM-13 Phase Control in Flash-Evaporated Perovskite Thin Films**, ***Jack Lawton***[3], *Milo V. Ferrara, Carlo A.R. Perini, Juan-Pablo Correa-Baena,* Georgia Institute of Technology

Thermal evaporation has become a well-established technique for the deposition of large area, uniform hybrid metal halide perovskite (MHP) thin films. Despite extensive literature on MHP evaporation, little progress has been made in high-rate MHP deposition, which is key to the eventual commercialization of MHP optoelectronics.Flash evaporation is a deposition technique that can produce MHP films at rates of 500 nm min-1. Such high deposition rates are due to high evaporation temperatures, but these temperatures can also have deleterious effects. In particular, the organic components of the hybrid material may partially decompose. This can lead to organic-deficient, nonstoichiometric films that are rich in secondary phases and possess undesirable properties. Furthermore, high evaporation temperatures can induce precursor powder spitting, whereby powder is ejected from the boat before vaporizing, leading to poor process reproducibility and films with spit defects.In this work, we demonstrate that particle spitting can be eliminated through evaporation boat design. A baffled boat architecture is introduced that hinders the ejection of particles by forcing precursor material to pass through a tortuous path before leaving the boat. We identify that the complex boat geometry produces transient vapor plume stoichiometries, whereby organic species that take longer to exit the boat experience greater heating and are therefore more likely to decompose. Such behavior leads to a gradient in the phase composition, with initial film growth being organic-rich, yet later film growth being dominated by organic-deficient phases.We introduce two novel approaches to achieve phase purity in flash-evaporated MHP films. First, we deposit an organic capping layer atop the MHP and induce intermixing through a modified annealing regimen. This technique replenishes organic material that is deficient in the upper layers of the films and films deposited by this method exhibit phase purity and favorable optoelectronic properties.Second, additive chemistry is shown to control phase composition in evaporated MHP films. Phosphonic acids can be incorporated into precursor powders to increase the organic material's sticking coefficient. Thus, we show that additive chemistry can control film stoichiometry, allowing for phase-pure and high-quality films to be achieved without the need for a second processing step. This work demonstrates how both processing and additive chemistry can be used to control the phase-purity of MHP films deposited at high rates, which could be key in their eventual commercialization.

11:15am **TF-TuM-14 Influence of Substrate Interactions on the Growth of MoO3 on Graphene/Ru(0001) and Highly-Oriented Pyrolytic Graphite**, ***Buddhika Alupothe Gedara****, Zdenek Dohnalek, Zbynek Novotny,* Pacific Northwest National Laboratory

Two-dimensional transition-metal oxides (TMOs) are promising for electronic applications due to their stability and favorable electrical and optical properties. Among them, molybdenum trioxide (MoO_3) stands out for its high dielectric constant, wide band gap (2.9-3.2 eV), and catalytic activity, enabling diverse electronic and energy-related applications. In this work, we investigate the effects of substrate topography and charge transfer on MoO_3 growth on highly oriented pyrolytic graphite (HOPG) and graphene (Gr)/Ru(0001) using scanning tunneling microscopy and X-ray photoelectron spectroscopy (XPS).Small MoO_3 clusters formed on Gr/Ru(0001), whereas large, dendritic, and disordered MoO_3 clusters formed on HOPG following deposition at 300 K. Upon increasing the temperature to 500-700 K, more ordered, crystalline MoO_3 islands form on both substrates. Notably, a distinct height difference of MoO_3 is observed on these two substrates over the studied temperature range. The height of MoO_3 islands on Gr/Ru(0001) corresponds to a single layer of MoO_3 (3.9 ± 0.2 Å), whereas the height of the MoO_3 islands on HOPG is consistent with the previously reported double layer (6.8±0.1 Å) [1, 2]. Single-layer MoO_3

[1] **JVST Highlighted Talk**

[2] **TFD Paul Holloway Young Investigator Award Winner**

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

on Gr/Ru(0001) comprises a planar MoO_2 sheet aligned parallel to the Gr/Ru(0001) surface, with Mo atoms terminated by additional oxygen atoms. We observed a brick-style pattern on the MoO_3 islands on Gr/Ru(0001) substrate and the formation of this characteristic pattern is due to the ordered removal of terminal oxygen atoms. Double-layer MoO_3 islands grow on HOPG with a staggered arrangement of corner- and edge-sharing MoO_6 octahedra [1, 2]. XPS data show that Mo in the islands on HOPG are predominantly in (6+) oxidation state while on Gr/Ru(0001) at least half is reduced to (5+) over the temperature range of 500-700 K. The formation of lower oxidation states is attributed to charge transfer from the substrate due to the electron chemical potential difference at the interface, and the presence of oxygen vacancies. Our results demonstrate that substrate-induced interfacial interactions play a key role in controlling the nucleation, growth mode, and structure of MoO_3 on graphene-based supports, providing a pathway to tailor 2D TMO heterostructures for electronic and catalytic applications.

References

[1] D.A. Kowalczyk et al., ACS Appl. Mater. Interfaces, 14 (2022) 44506-44515.

[2] J.H. Kim et al., 2D Materials, 6 (2019) 015016.

11:30am **TF-TuM-15 Atomic Growth Mode of Capping Layers for Surface Passivation of Nb***, **Van Do**, Robert Burnley, Margaret Hall, Helena Lew-Kiedrowska, Sarah Willson, Steven Sibener,* University of Chicago

Nb is the standard material for superconducting radio-frequency (SRF) cavities, but the accelerating performance of these cavities is limited by the spontaneous growth of Nb oxides on the surface. These oxides are insulating and dielectric in nature, which can lead to hot spots and vortex penetration, ultimately degrading cavity performance. To address this challenge, we are improving Nb surface stability through the implementation of two types of capping layers: an inert capping layer and sacrificial capping layer. A chemically inert Au film can suppress oxidation by protecting the underlying Nb surface from environmental exposure. In contrast, a sacrificial Zr layer, owing to its higher oxidation affinity, preferentially oxidizes and thereby shields the underlying Nb. In addition, Zr can intermix with Nb to form a substitutional Zr–Nb alloy with a predicted superconducting transition temperature of 17.7 K. Using scanning tunneling microscopy, we have visualized Au capping layers ranging from sub-monolayer coverage to 10 monolayers, as well as Zr capping layers from initial adsorption through alloy formation on the (3×1)-O/Nb(100) surface. We further evaluated the passivation efficiency of these modified surfaces by leaking oxygen and observing the chemical evolution using x-ray photoelectron spectroscopy. These results provide atomic mechanistic insight into surface treatment methods for enhancing the oxidation resistance and superconducting performance of Nb-based SRF cavities.

11:45am **TF-TuM-16 Distal electrofabrication and Microfluidic Integration of Chitosan Anion-Exchange Membranes for Low-Cost Direct Methanol Fuel Cells***, **Phuc Long Duong**,* College of Engineering, Physics and Computing, Catholic University of America*; Xiaolong Luo,* Catholic University of America

Commercial adoption of hydrogen fuel cells remains limited by high material costs and the lack of a dedicated hydrogen infrastructure. Direct Methanol Fuel Cells (DMFCs) offer a compelling alternative by using an easily refuelable liquid fuel with high energy density. However, conventional DMFCs face significant economic and technical hurdles due to their reliance on expensive proton exchange membranes (e.g., Nafion) and noble-metal catalysts, as well as issues with methanol crossover and sluggish reaction kinetics.

This work demonstrates the design of a microfluidics DMFC (DMFC) that uses ultra-low-cost, non-platinum-group-metal (non-PGM) catalysts and a sustainable, biopolymer-based anion exchange membrane (AEM). We apply a patent-pending distal electrofabrication technique to deposit freestanding chitosan thin films directly within microfluidic channel networks. The electrofabrication provides precise control and utilizes the biopolymer's naturally low methanol permeability to significantly minimize fuel crossover.

Material characterization, including Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD), confirms our hypothesis that distal electrofabrication induces high molecular alignment and a distinct crystallographic ultrastructure compared to standard cast membranes. Furthermore, Electrochemical Impedance Spectroscopy (EIS) validates enhanced hydroxide-ion conductivity within the thin-film networks.

Initial device performance testing demonstrated a peak power density of 70 mW/cm^2, with structural and crosslinking optimizations promising commercial adoption at 5%-10% the cost of existing commercial fuel cells. The success of this project may open a cost-competitive pathway for portable zero-emission energy solutions.

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