Thin Films
Room 206 B W - Session TF2-WeA

Fundamentals of Thin Films II

Moderator: Qihua Zhang, Pennsylvania State University

4:15pm **TF2-WeA-9 Flipping the Switch on Tin Sulfide Deposition: From SnS to SnS$_2$**, *Christopher Brewer, Hy Nguyen, Reed Woolard, **Amy Walker**,* University of Texas at Dallas

Tin sulfides (Sn_xS_y) are non-toxic and inexpensive materials with low band gaps, making them suitable for semiconductor applications and photovoltaic materials, such as solar cells. Sn_xS_y has three naturally occurring compositions, SnS, Sn_2S_3, and SnS_2. The ability to control the stoichiometry of a Sn_xS_y deposit is of interest for devices like SnS solar cells, where Sn_2S_3 contamination reduces the device efficiency. Tin disulfide is an emerging 2D layered metal dichalcogenide which has applications in electronics and as a photodetector. In this study we investigate the selective deposition of tin sulfides using chemical bath deposition (CBD) on organic substrates. We employ alkanethiolate self-assembled monolayers (SAMs) functionalized with -CH_3, -OH, and -COOH terminal groups as model organic substrates. Our data shows that the substrate functionality does not strongly influence the composition of the deposit. Rather, the tin sulfide deposition can be flipped from SnS to SnS_2 by changing tuning the bath pH. Under basic conditions using tin(II) chloride and thioacetamide, pure SnS is deposited at pH ≥ 11. The data also suggests that the functional group of the SAM directs the phase of the SnS deposited, providing potentially an easier route to the newly discovered cubic SnS phase. In contrast, under acidic conditions SnS_2 is deposited using tin(II) choloride and tartaric acid as a complexing agent. The deposition results will be discussed in the context of our mechanism based approach to tune the bath chemistry to achieve composition control of the Sn_xS_y deposit.

4:30pm **TF2-WeA-10 Homoepitaxial Growth of ZrB2 on a ZrB2(0001) Surface**, *Michael Trenary, **Ayoyele Ologun**,* University of Illinois - Chicago

Zirconium diboride (ZrB_2), a group-IV metal-terminated diboride, is an extremely hard material with a high melting point of 3246 °C. Thin films of ZrB_2 can be grown conformally via chemical vapor deposition (CVD) using zirconium borohydride, $Zr(BH_4)_4$, as a precursor. Homoepitaxial growth of ZrB_2 was studied using scanning tunnelling microscopy (STM). Exposure of $Zr(BH_4)_4$ to the $ZrB_2(0001)$ surface at 1400 K led to the formation of ZrB_2 islands. Coarsening of the ZrB_2 islands into layers via Smoluchowski ripening was observed when the islands were left for 60 minutes at 1400 K before imaging at room temperature. In contrast, exposure at 900 K resulted in high-density clusters. Stepwise annealing at 1400 K led to the transformation of these clusters into a continuous thin film via thermal-induced coalescence, with moiré patterns observed as intermediate structures during this coalescence process.

4:45pm **TF2-WeA-11 Multilayered Films for High Hardness**, ***Nestor Marquez Rios**, Nathaniel McIlwaine, Jon-Paul Maria,* The Pennsylvania State University

Multilayered high entropy carbide films were synthesized by physical vapor deposition (PVD) using bipolar high-power impulse magnetron sputtering (HiPIMS) with methane gas as the carbon source. Shutter automation and asynchronous plasma were used to alternate between two HiPIMS cathodes, enabling modulation of the metal composition leading to superlattice structure formation. The resulting structure consists of two rock salt structured solid solution layers forming a periodic multilayer. Crystallinity was characterized by Xray diffraction (XRD), which demonstrated the ability to grow multilayer sequences with modulated periods ranging from 3 nm to 50 nm, engineered to reach a total film thickness of 1.5 µm changes in the position of low and high order satellite peaks were observed confirming a multilayer period consistent with the designed bilayer thickness. Surface morphology and topography were characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Mechanical properties were evaluated using Knoop and Vickers microindentation techniques to determine the influence of nanoscale engineering by making multilayer on hardness.

5:00pm **TF2-WeA-12 Hot Complex Oxides – Unlocking New Materials and New Physics via High Temperature Adsorption Controlled Molecular Beam Epitaxy** , ***Brendan Faeth**,* Epiray*; Matt Barone, Tobias Schwaigert, Anna Park, Vivek Anil, Dylan Sotir, Yorick Birkholzer, Kyle Shen, Darrell Schlom,* Cornell University

It has long been understood that molecular-beam epitaxy works best for materials that can be grown in an adsorption-controlled regime where thermodynamics automatically provides composition control.This approach has found greatest success for GaAs and other compound semiconductors, fundamentally underlying the capability of MBE to produce semiconductor films with the highest reported purity and mobilities. To date, however, adsorption control processes in complex oxide materials have been limited to specific systems, as the majority of binary oxide constituent compounds (SrO, BrO) remain non-volatile up to ~1000 °C, the typical limit for conventional MBE substrate heater technologies.Here, we utilize a powerful CO_2 laser for MBE substrate heating, allowing access to growth temperatures up to and beyond 2000 °C on virtually all commercially available oxide substrates.Utilizing this approach, we have grown an increasing number of complex oxides in unconventional, ultra-high temperature adsorption-controlled regimes by MBE, some realized here for the first time in epitaxial thin film form.In each case we observe substantial improvements in structural and electronic properties as characterized by transport, XRD, and/or in situ angle-resolved photoemission spectroscopy measurements.In this talk, we outline the technical basis and future possibilities for CO_2 laser heating in MBE, specifically discussing recent results for SrTiO3, BaTiO3, SrMoO3, and Sr2MoO4 grown at substrate temperatures in the 1200-1500 °C range.

5:15pm **TF2-WeA-13 Machine-Learned Relationships between Particle Flux, Kinetic Energy, and Experimental Conditions in Pulsed Laser Deposition**, *Zahra Nasiri, Dorien Carpenter, Jacob H Paiste,* University of Alabama at Birmingham*; Sumner B Harris,* Oak Ridge National Laboratory, USA*; **Renato P Camata**,* University of Alabama at Birmingham

In pulsed laser deposition (PLD), the kinetics of crystal growth is strongly dependent on the flux (Φ) and the kinetic energy (K) of plume species arriving at the substrate. These factors vary widely with target materials and deposition conditions. While scaling laws and prior experience provide some guidance, quantitatively predicting the dependence of Φ and K on the laser fluence (F) and spot area (A) is challenging. Even in well-established PLD laboratories, it is typical for only limited regions of the functions $\Phi(F, A)$ and $K(F, A)$ to be known for specific materials and laser wavelengths. Moreover, these regions often shift due to target surface evolution and subtle experimental variations, demanding time-consuming and costly re-optimization experiments.

Machine learning (ML) algorithms can process PLD plume diagnostic data in real time and generate high-quality dynamic models of $\Phi(F, A)$ and $K(F, A)$. These can be integrated into decision-making workflows to control experimental actuation, either to maintain or deliberately adjust thin film growth conditions according to specified protocols.

In this work we show how high-fidelity representations of $\Phi(F, A)$ and $K(F, A)$ can be generated by Gaussian Process Bayesian Optimization (GPBO) from a small number of experiments. A Gaussian process regression model is trained on progressively accumulating data to produce surrogate models of the objective functions $\Phi(F, A)$ and $K(F, A)$. We compare active learning workflows using different acquisition functions and GP kernels with random sampling. We evaluate the process using synthetic PLD data generated by laser ablation-fluid dynamics simulations. The model produces physically plausible $\Phi(F, A)$ and $K(F, A)$ for specific PLD conditions and target materials. Typical results for PLD of copper (Cu) with F = 1–10 J/cm^2 and A = 0.8–13 mm^2—obtained from 1000 model runs starting with random 3-point seed pairs of (F, A)—show that our GPBO process can discover optimum flux and kinetic energy conditions after as few as three iterations (i.e., experiments) using the probability of improvement (PI) acquisition function. Finally, we will show how introducing a physics-informed, structured mean in the Gaussian process—based on the well-known scaling behavior of Φ and K with vapor density (proportional to F) and Mach number of the expansion (proportional to A)—affects the performance of the GPBO.

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