Thin Films Division
Room 316 - Session TF1+SE+SS-ThM
Nucleation, and Interface Phenomena in Thin Films

Moderators: Adrie Mackus, Eindhoven University, Netherlands, **Qing Peng**, University of Alabama

8:00am **TF1+SE+SS-ThM-1 Opportunities of Complex Oxides Prepared by Atomic Layer Depositions***, P. Sallés, P. Machado, **Mariona Coll**,* ICMAB-CSIC, Spain **INVITED**

The rapid development of electronic devices, telecommunication systems, and sensors pushes new functional demands with increasingly stringent requirements like flexibility, light weight, and miniaturization. Transition metal oxides present the richest variety of functional properties due to the large diversity of chemical compositions and structures that they can offer. However, the preparation and manipulation of crystalline yet bendable functional complex oxide membranes has been a long-standing issue as they require specific crystalline substrates and high temperature treatments. We have developed a facile chemical route based on the use of $Sr_3Al_2O_6$(SAO) sacrificial layer to detach oxide thin films of various compositions from the growing substrate and enable their transfer to flexible substrates.[1] Meticulous chemical and structural study of the SAO film have allowed us to identify the formation of an amorphous SAO capping layer and carbonates upon air exposure, which dictate the crystalline quality of the subsequent oxide film growth.[2] Judicious cation substitution in SAO enabled both decreasing reactivity with ambient moisture and modulating the strain state of the subsequent heterostructures grown on it. Upon detailed investigation of oxide adhesion on polymeric substrates and sacrificial etching (figure 1), crystallinity, surface morphology, interface cation diffusion, mechanical and electrical properties of transfer printed heteroepitaxial $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$ membranes have been studied and compared with rigid substrates. From this work it is envisaged many new opportunities to prepare artificial oxide heterostructures and devices offering a whole new dimension for electronics and beyond.

[1] P. Salles, M. Coll et al. Adv. Funct. Interfaces, 2001643 (2021)

[2] P. Salles, M. Coll et al. ACS Appl. Mater. Interfaces , 14, 10, 12845–12854 (2022)

8:40am **TF1+SE+SS-ThM-3 An Atomic-Scale Study of Si Epitaxial Growth on Cl-Si(100)***, **Azadeh Farzaneh**,* University of Maryland, College Park*; R. Butera,* Laboratory for Physical Sciences

Atomically-precise fabrication techniques utilize a scanning tunneling microscope to lithographically define electronic devices and components, where a monatomic layer of H or Cl adsorbed on Si(100) acts as a resist. Unlike traditional resists, these monatomic resists either desorb or remain at the growth front during subsequent growth of Si capping layers.While the body of literature extensively explores Si deposition and subsequent diffusion on H-Si(100), Cl-Si(100) has remained relatively unexplored.A detailed understanding of the thin film growth mechanism enables atomic level control of the interface, which starts with diffusion of adatoms in dilute regimes on the surface. Here we explored the initial stages of Si growth on Cl-Si(100) and characterized thin Si films (~25 nm) grown on this surface. The activation energy for Si adatom diffusion on Cl-Si(100) was extracted from STM observations combined with simulations of a simple random walk model rooted in the mechanism of Si chain formation at different temperatures. Ex-situ characterization of thin Si films grown on Cl-Si confirmed the formation of crystalline layers and the near complete removal of Cl from the Si matrix. The epitaxial film obtained on Cl-Si(100) and absence of Cl from the interface confirm Cl as a viable resist for current atomically precise fabrication schemes. This opens up new pathways for introducing new chemistries and materials into the picture.

9:00am **TF1+SE+SS-ThM-4 The Effect of Oxygen Plasma on the ZnO Growth on Polymer Substrates During Plasma-Enhanced Atomic Layer Deposition***, **Lisanne Demelius**,* Graz University of Technology, Austria*; M. Blatnik,* CEITEC – Central European Institute of Technology, Brno University of Technology, Czechia*; K. Unger,* Graz University of Technology, Austria*; P. Parlanti, M. Gemmi,* Istituto Italiano di Tecnologia, Center for Materials Interfaces, Italy*; A. Coclite,* Graz University of Technology, Austria

Atomic layer deposition (ALD) is a powerful technique to deposit highly conformal thin films the thickness of which can be precisely controlled. However, the use of polymeric substrates often leads to non-ideal ALD processes that result in precursor diffusion and subsurface growth of the deposited material.

Plasma-enhanced ALD (PE-ALD) is known to enhance nucleation due to the surface-activating effect of plasma and can be expected to significantly reduce subsurface diffusion, enabling the surface-limited deposition of thin conformal coatings. However, plasma can also have detrimental effects on polymeric substrates.

Our work contributes to a deeper understanding of how oxygen plasma applied during PE-ALD affects film formation, nucleation, and interface formation of ZnO on polymer substrates. In-situ spectroscopic ellipsometry was used as the main technique to monitor the PE-ALD growth of ZnO on selected polymer thin films. To better understand how the chemical structure of the polymer influences plasma-substrate interactions and ZnO thin film formation, both crosslinked and linear polymers exhibiting varying degrees of reactivity with the ALD precursor were studied.

Our results show that while the plasma efficiently activates the polymer surface to enable rapid ZnO nucleation, it can also cause significant substrate etching that dominates the initial stage of growth until, at a certain point, ZnO growth takes over and the regime of normal ALD growth behavior is entered. The strength and extent of etching strongly depends on the type of polymer. Despite the initial etching, the resulting thin films exhibit sharp interfaces and a quality, in terms of surface roughness, crystallinity and ZnO density, comparable to those of ZnO deposited on silicon.

A closer examination of the first 25 PE-ALD cycles showed that, on the nanometer scale, the simultaneous etching of the polymer and ZnO nucleation leads to a certain degree of intermixing at the interfaces, the extent of which depends on the type of polymer. It was also revealed that, during the first few cycles, no stochiometric ZnO is yet formed but instead Zinc is found to be bonded to hydroxyl groups and presumably oxygen-carbon species from the polymer, forming hybrid bonds. This points to a strong interaction between the polymer substrate and the forming ZnO, which can be expected to result in good film adhesion, a property that is critical in all applications involving mechanical stress and strain.

9:20am **TF1+SE+SS-ThM-5 Measuring Local Atomic Structure Variations Through the Depth of Ultrathin ALD Aluminum Oxide***, **Nikhila Paranamana**, M. Young, R. Gettler, H. Koenig, S. Montgomery-Smith, X. He,* University of Missouri, Columbia

Understanding the atomic structure of ultrathin (<20 nm) atomic layer deposition (ALD) coatings is critical to establish structure property relationships and accelerate the application of ALD films to address technological needs. Previous studies have measured the atomic structure of nanoscale ALD films using cryogenic electron diffraction with a large (~200 nm) beam diameter. However, for ultrathin ALD coatings, these measurements provide only ensemble average structural information and cannot be used to directly measure differences in atomic structure through the depth of the ALD film. In this study, we localize the electron beam to a small (~ 5 nm) spot size using cryogenic scanning transmission electron microscope (STEM) and we collect electron diffraction data at multiple points along the depth of a 12 nm thick ALD AlO_x film deposited onto a CNT substrate without a contribution from the substrate. We couple these diffraction measurements with pair distribution function (PDF) analysis and iterative reverse Monte Carlo-molecular statics (RMC-MS) modeling to compare atomic structure metrics at different positions in the film depth. We interpret the modeling results considering the 3D concentric cylindrical sample geometry of a CNT with uniform AlO_x coating. These measurements confirm a two-phase bulk/interface structural model proposed previously for ALD AlO_x, and indicate that the interfacial layer at the CNT-AlO_x interface is 2.5 nm thick – five times larger than previously reported. This report demonstrates direct measurement of atomic structural variations across ultrathin films that is of broad interest for understanding local differences in atomic structure across material interfaces.

9:40am **TF1+SE+SS-ThM-6 Interfacial Reactions and Energy Transfer in Sputter Deposited Thermite Reactive Nanolaminates***, **Chloe Skidmore**, J. Maria,* Pennsylvania State University

Cost effective energetic materials with highly tunable ignition and actuation have important applications in both military and commercial sectors. Recently, interest has grown in nanoenergetic composites due to their potential as stand-alone explosives with greater reliability, heat release, and combustion efficiency. Thermite is a versatile inorganic energetic of specific significance due to the highly exothermic reduction-oxidation reaction that occurs between metal and oxide constituents, resulting in self-sustaining heat production. However, if the high energy release and improved tunability provided by the diverse chemistries of inorganic energetics is to be utilized, a fundamental understanding of the initiation and propagation processes in new nanoenergetic materials such as thermite is necessary. Thin film deposition of multilayered stacks of alternating metallic and oxide layers with well defined interfaces offers a streamlined process to observe energy transduction and the chemical reactions that mitigate interface reactions. These multilayered stacks, termed reactive nanolaminates (RNLs), facilitate control over reactant thickness, diffusion distance, interface quality and the total material involved, while also reducing premature intermixing of metal and oxide layers. This presentation explores energy release in sputter deposited CuO-Mg RNLs as a function of bilayer thickness, plasma energetics, and metal-oxide layering sequence. These samples are analyzed via in-situ high temperature x-ray diffraction (XRD) and differential scanning calorimetry (DSC), as both probe the oxygen exchange process by structure evolution and energy production, respectively. The bulk properties associated with the Mg-CuO thermite system suggests extensive oxygen dissolution in the starting metal and the possibility of transient eutectic liquid formation during reaction. XRD results indicate that CuO/Mg RNLs exhibit eutectic liquid formation during reaction, with Cu_xMg_yintermetallics temporarily appearing around 565°C. DSC analysis reveals exotherm maxima at temperatures associated with critical points in the Mg-Cu phase diagram. More precisely, as interfacial area is increased the max exothermic peak shifts from ~650°C (T_m Mg) to ~565°C (T_m Mg_2Cu) before finally occurring at ~483°C (T_m eutectic Mg/Mg_2Cu). Preliminary DSC analysis also suggests that, relatively speaking, sputtering energetics resulting in smoother, more crystalline Mg interlayers, shifts the maximum exothermic peak to higher temperatures. These findings provide insight into the mechanisms of energy transfer in thermite RNLs, allowing for highly tunable, reliable energetic materials.

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