Thin Films
Room 206 B W - Session TF1-WeA

VSHOP V – Vapor Synthesis of Hybrid Materials and Their Properties

Moderators: Yifan Cheng, Virginia Tech, **Matthias Young**, University of Missouri

2:15pm **TF1-WeA-1 Hybrid Molecular Layer Deposition of Multi-Metal Alkoxide Resists for Electron Beam and Extreme Ultraviolet Lithography**, ***Long Viet Than***, *Stacey F Bent,* Stanford University

Molecular layer deposited (MLD) metal-organic photoresists have the potential to address the material challenges of extreme ultraviolet (EUV) lithography due to their advantages in thickness control and chemical homogeneity. Previous studies have utilized simple MLD schemes with a single precursor and counter-reactant pair to achieve patterning close to industrially relevant length scales. However, for further optimization, layer-by-layer deposition of multi-component films via a supercycle approach may be required to adjust properties such as sensitivity, contrast, etch resistance, mechanical strength, and others.

In this work, we explore the properties of multi-component MLD photoresists by depositing multi-metal alkoxide ('metalcone') films via both trimethylaluminum (TMA) and diethylzinc (DEZ), and ethylene glycol as the counter-reactant. Using a supercycle approach in which cycles of alucone growth (TMA and EG) are evenly distributed with cycles of zincone growth (DEZ and EG), we grow the multi-metalcone films with a range of Al/Zn ratios and characterize their properties. X-ray photoelectron spectroscopy (XPS) shows that significant transmetalation of Al and Zn occurs during deposition. However, the metal fraction can still be controlled between 40% and 95% Al (normalized against Al + Zn) by varying the fraction of alucone cycles within the supercycle between 0.25% and 50%. To assess the effect of the Al/Zn ratio on resist performance, line/space gratings with 24 nm half pitch are patterned on ~25 nm thick resist films via electron beam lithography as a proxy for EUV lithography and developed with hydrochloric acid at varying concentrations. The results show that compared to pure alucone or zincone films, the multi-metal resists have similar e-beam sensitivity (~70-100 mC/cm^2 depending on development conditions), but enhanced lithographic contrast (improving from a value of γ = 0.38 for alucone to a value of γ = 6.3 for the multi-metalcone) and pattern quality (reduced bridge defects and scumming). The improvements are observed even for minimal Zn incorporation in the multi-metalcone (~95% Al). From XPS studies of the resists after partial development, we attribute the improvement to the preferential dissolution of zincone from the unexposed multi-metal resist, which enhances solubility contrast. This work demonstrates the potential of supercycled MLD schemes to enable emergent interactions between components, vastly expanding the design space for this class of photoresists.

2:30pm **TF1-WeA-2 High-Throughput MLD Screening of Photoresists for EUV Lithography via UV and E-Beam Exposure**, ***Duncan Reece***, *David Bergsman,* University of Washington

As semiconductor patterning pushes toward sub-5 nm features, next-generation photoresists must deliver high resolution, environmental and chemical stability, and compatibility with extreme ultraviolet (EUV) lithography processes. However, EUV photoresist materials explored to date still face challenges such as ease of deposition and achieving sub-nanometer chemical uniformity. Molecular layer deposition (MLD) offers precise control over thin-film structure and composition, enabling the design of hybrid materials tailored to meet these challenges. Previous work has demonstrated MLD-based EUV photoresists incorporating aluminum (Al) and tin (Sn); however, the influence of the organic reactant on the final photoresist properties remains largely underexplored. Using our custom high-throughput multi-chamber MLD system, we synthesized 18 organic–inorganic hybrid films from two organometallic precursors—trimethylaluminum diethylzinc, and tetrakis(dimethylamino)tin(IV)—paired with six organic linkers: hydroquinone bis(2-hydroxyethyl) ether, 1,2,4-trihydroxybenzene, 1,5-hexadiene-3,4-diol, 2-butyne-1,4-diol, cis-2-butene-1,4-diol, and 3,4-dihydroxy-1-butene. Film candidates were screened for growth rate, ease of deposition, uniformity, and ambient stability. To assess potential photochemical reactivity, UV-induced crosslinking, or structural rearrangement, we measured thickness changes before and after solvent exposure, both with and without deep UV treatment.Selected high-performing films were subjected to electron beam lithography as a stand-in for EUV testing, followed by development to evaluate feature resolution and pattern fidelity using scanning electron microscopy and profilometry. Mechanical durability was assessed via nanoindentation, while chemical transformations were characterized with Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS).Our results identify material systems that combine robust environmental and chemical resistance with promising lithographic performance and photo-reactive behavior. While EUV lithography remains the ultimate target application, e-beam serves as a high-resolution surrogate to guide photoresist development. This integrated approach demonstrates the power of high-throughput MLD and multi-parameter screening for accelerating the discovery of advanced materials for next-generation lithographic technologies.

2:45pm **TF1-WeA-3 Transforming Photo-Polymerized Organic Networks into Ceramics via Vapor Phase Infiltration (VPI)**, ***Ronan Neill***, *Li Zhang, Mark Losego,* Georgia Institute of Technology

Micropatterning of 3-dimensional structures from arbitrary ceramic materials is complicated and often expensive. In this work, we explore a new platform technology for converting an easily patterned photopolymerizable resin into a 3D ceramic structure using vapor phase infiltration (VPI) and subsequent thermal combustion.VPI is a gas-phase technique in which inorganic vapors are sorbed into a polymer, creating an organic-inorganic hybrid material.Here we are interested in studying how the chemical design of this hybrid material can affect the thermal combustion process and its conversion to a final ceramic component, without significant cracking.Ethoxylated trimethylolpropane triacrylate (ETPTA) photo-polymerizable monomers are used because they are already known to create compliant networks that readily sorb high fractions of inorganic precursors during VPI.After VPI with trimethyl aluminum (TMA) and water, the hybrid films were thermally annealed to fully combust all organics.In this talk, we will discuss how process parameters including reactor temperature and precursor exposure duration affect cracking, shrinkage, and ceramic density.In general, increased precursor loading during VPI results in reduced cracking of the alumina film, and upwards of 60% of the original film thickness could be retained after organic burnout.To assess changes in the lateral dimension micro-patterned structures were also tested, and minimal change in lateral size were detected, likely due to substrate clamping.

3:00pm **TF1-WeA-4 Measuring the Coefficient of Thermal Expansion for Vapor Phase Infiltrated Ultra-low-k Dielectric Materials for Advanced Packaging**, ***Pragna Bhaskar***, *Li Zhang, Mohanalingam Kathaperumal, Mark Losego,* Georgia Institute of Technology

Advanced interposers consist of alternate layers of copper and polymer dielectric materials. While copper has a low coefficient of thermal expansion (CTE) of 16 ppm/ ^{0}C, ultra-low-k dielectric materials have CTEs in the range of 50-150 ppm/ ^{0}C. This mismatch in CTE between copper and ultra-low-k dielectric materials results in lower thermomechanical reliability. Most methods available in literature involve the addition of oxide fillers to reduce the CTE of polymers. In this study, vapor phase infiltration (VPI) treatment is considered as a possible method to introduce AlO_x into dry films or spin-coated and cured films. Another challenge with respect to ultra-low-k dielectric films is the measurement of CTE. Conventional CTE measurement techniques such as thermomechanical analysis (TMA) require a sample thickness of the order of few millimeters. The films in the present study have thicknesses in the range of 0.5 to 5 µm matching closely with the typical dielectric layer thickness employed in advanced packaging substrates with very high-density interconnects. Therefore, TMA cannot be used for CTE measurement of these films. Instead, temperature dependent spectroscopic ellipsometry is used to track the thermal expansion of the films and determine their CTE.These measurements demonstrate the effectiveness of the VPI process to lower the CTE of low dielectric constant polymers by about 4 to 15 times depending on the dielectric polymer, placing them near the CTE of copper.The chemical mechanisms for this lowering of the CTE will be discussed in this talk.

3:15pm **TF1-WeA-5 Machine Learning Predictions for Selecting Organic Small Molecules in Atomic Layer Processing**, ***Lucas R Kuehnel***, *Erick A Gutierrez-Monje, Anthony A Khoury, Campbell A Sweet, Matthias J Young,* University of Missouri-Columbia

Selecting organic small molecule inhibitors for area-selective atomic layer deposition and organic precursors for oxidative molecular layer deposition requires knowledge of chemical properties such as pKa, oxidation potential, physical phase, and vapor pressure. However, these data are not readily available for many candidate molecules. Machine learning using moleculebased message passing graph neural network (MPNNs) provides a strategy to establish statistical models connecting molecular structure to these physical properties using tabulated data. These models can be used to rapidly predict the properties for compounds where this data has not been measured. Here, we employ Chemprop, an established user-friendly MPNN framework, to predict chemical properties of organic small molecules relevant to atomic layer processing applications. We report on MPNN models to predict boiling point, melting point, pKa, oxidation potential, and vapor pressure given only SMILES strings as user input. At the time of submission, the mean absolute errors of baseline model predictions on unseen test data are 15.0 K for boiling point, 29.4 K for melting point, 0.749 log units for pKa, and 0.353 V for oxidation potential. The median absolute percent error is 12.5% for vapor pressure. We describe opportunities to integrate such models into semi-autonomous workflows for chemical innovation and discovery relevant to the atomic layer processing communities.

3:30pm **TF1-WeA-6 Physical Vapor Deposition of Metal Iodide Thin Films for Radiation Detections***, **Jun Wang,*** Radiation Monitoring Devices Inc.*; Matthew Loyd,* Oak Ridge Natinal Laboratory*; Nicholas Anastasi, Lakshmi S. Pandian, Vivek V. Nagarkar,* Radiation Monitoring Devices Inc.

Metal iodides, when doped with lanthanide elements, are crucial materials in radiation detection, medical imaging, and high-energy physics applications. They belong to a class of materials called scintillators, which emit photons (fluorescence) when exposed to ionizing radiation. Metal iodide scintillators offer high light output, good energy resolution and scalability, especially in the thin film format. They can be scaled up to a few inch^2 or more for practical applications. However, the hygroscopic nature of these materials hinders the development and commercialization of such scintillators. At Radiation Monitoring Devices, Inc., we specialize in overcoming these challenges and developing such metal iodide scintillators through a controlled growth environment and hermetic sealing techniques. Here we present the development of a well-known lithium iodide (LiI) scintillator, in a large micro-columnar thin film of up to 4 inch^2 in size via a physical vapor deposition in a special integrated glovebox system. The developed LiI film doped with europium (Eu) scintillator boasts a remarkable ultra-high brightness of approximately 22 times that of GS20 (commercially available screens), while the cerium (Ce) doped LiI film offers an ultra-fast decay time of 50 ns. Both films offer a high spatial resolution, excellent gamma-neutron discrimination and high detection efficiency for advanced thermal neutron imaging applications, which are especially suitable for integration with special neutron detectors in national neutron facilities such as Spallation Neutron Source (SNS) and High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. We report recent advancements in the fabrication and characterization of such next-generation LiI scintillator films for thermal neutron imaging applications.

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