

Thin Film Division

Room A105 - Session TF-ThM

Creating Organic-Inorganic Hybrid Materials

Moderators: Devika Choudhury, ASM, Robin Rodriguez, Jet Propulsion Laboratory

8:00am **TF-ThM-1 Functional Ceramic Heterostructures via Vapor and Liquid Phase Infiltration of Polymer Templates**, *Diana Berman*, University of North Texas **INVITED**

Robust and efficient process for synthesis of various composition inorganic coatings with controlled nanoporosity and structure is highly desirable for design of efficient catalytic, purification, and detection systems. Recently, infiltration of a nanoporous polymer template with inorganic precursors using sequential infiltration synthesis with inorganic vapor precursors followed by oxidative annealing was proposed as a new and efficient approach to create porous inorganic structures with tunable porosity and composition. The major limitations of the original water-based thermal sequential infiltration synthesis, though, are the thickness of the patterned structure being limited by vapor penetration depth of the precursors into the polymer template and the resulting material selection being restricted by the availability of high vapor pressure precursors. Here, we propose a swelling-based modification to the polymer infiltration process that allows to overcome these limitations. We summarize the basics of the multi-step infiltration approach, the structure and properties of the resulting materials, and their functional potential for practical applications. We report ultra-high accessibility of the pores when porous films are prepared via the polymer swelling-based infiltration synthesis (SBI). Using a quartz crystal microbalance (QCM) technique, we demonstrate increased solvent absorbing capabilities of highly porous ceramic films as a result of high interconnectivity of the pores in such structures. Our results show that the approach can be extended toward preparing conformal coatings, freestanding membranes, and powders consisting of metal or metal oxide nanoparticles embedded in a porous oxide matrix.

8:40am **TF-ThM-3 Effect of Polymer Templates on Nanoporous Inorganic Coatings Synthesized by Polymer Infiltration**, *Khalil Omotosho, D. Berman*, University of North Texas

Polymer templates infiltration synthesis of all-inorganic metal oxide architectures provides control over their thickness, porosity, and composition. In this study, we provide insights into the synthesis of nanoporous zinc oxide films as a model system via infiltration of polymers such as polymer of intrinsic microporosity (PIM-1) and representative of the block-copolymers family (polystyrene-polyvinyl pyridine block copolymer) that have different mechanisms of interaction with metal oxide precursors. We investigated the polymer infiltration process with both gas (diethyl zinc, DEZ, and water vapors) and solution (zinc acetylacetonate, Zn(acac)₂, dissolved in ethanol) phase precursors. We systematically studied the effect of polymer template and the form of the metal oxide precursors on the properties of synthesized metal oxide thin coatings using the quartz crystal microbalance (QCM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analyses. Our study prove that the infiltration of polymer templates can be efficiently achieved using both gas phase and solution phase precursors. Furthermore, we show that the crystallinity of the synthesized ZnO films is mainly affected by the state of the precursor (gas or solution phase) and is independent of the polymer template type. In turn, the polymer type affects the surface termination of ZnO films. In addition, our findings demonstrate that the surface of porous ZnO coatings synthesized with BCP (here PS-P4VP) is more accessible than the surface of ZnO synthesized with PIM; however, despite the lower surface accessibility for ethanol molecules, ZnO synthesized via infiltration of PIM-1 with solution-phase precursors demonstrates the largest change in resistivity upon its exposure to ethanol vapor at room temperature.

9:00am **TF-ThM-4 Alkylation of Esters by TiCl₄ Vapor Phase Infiltration (VPI) and the Resulting Chemical and Thermophysical Properties of the Hybrid Materials**, *Shuaib Balogun*, Georgia Institute of Technology, USA; *S. Yim*, Georgia Institute of Technology; *B. Jean, T. Yom*, Georgia Institute of Technology, USA; *A. Steiner*, Sandia National Laboratories; *M. Losego*, Georgia Institute of Technology, USA

Vapor phase infiltration (VPI) is a post-processing modification technique used to imbue inorganic materials into polymers to create organic-inorganic hybrid materials with new properties. In VPI, inorganic material can become entrapped by reaction with the polymer functional group, by

reacting with a co-reactant or by physical entrapment due to loss of volatility. While several VPI precursor-polymer chemistries have been explored and their chemical mechanisms have been noted, a lack of chemical intuition remains for fully understanding the chemical mechanisms that govern VPI processes. This study seeks to continue to build this knowledge by examining the chemical reaction mechanisms that occur during TiCl₄ infiltration into esters namely PMMA and PLA. In this research, the poly-methyl methacrylate / TiO₂ and poly-lactic acid / TiO₂ hybrid materials are prepared using VPI. The chemical states of the atoms in the polymers pre & post infiltration are studied using x-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectroscopy. The chemical mechanism of infiltration appears to occur via an acid catalyzed SN2-alkylation reaction. As infiltration occurs in PMMA, there is an increase loss of methyl groups in the PMMA ester, whereas, in PLA there is an observed cleavage of the main chain at the methoxy bond, resulting in degradation of the polymer. The kinetics of this reaction and consequently the TiCl₄ infiltration increases with both VPI process temperature and TiCl₄ exposure time. Interestingly, the resulting hybrid materials offer new properties due to the reaction with TiCl₄. Increased titanium loading leads to up to 100% chemical stability in PMMA. Additionally, films infiltrated with up to 6% Ti have a 50 % and 70 % reduction in coefficients of thermal expansion (CTE) below and above T_g respectively. CTE continually reduces with increased titanium loading. In this talk, we will discuss how these chemical and physical changes could be used for various applications.

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9:20am **TF-ThM-5 Free and Simple Simulations of Vapor-Phase Infiltration Process Kinetics Using Google Colab**, *Mark Losego*, Georgia Institute of Technology

Vapor-phase infiltration (VPI) is a post-polymerization chemical modification technique that exposes organic polymers to gas-phase inorganic precursors that sorb and become entrapped within the polymer to create organic-inorganic hybrid materials. The process kinetics for VPI are a complicated convolution of sorption, non-Fickian diffusion, and reaction processes. We recently introduced a reaction-diffusion model to capture many of the VPI process kinetics phenomena, and recent experimental work has demonstrated the validity of this model's process predictions. This talk will introduce our publication of this model on Google Colab, a free, web-based environment for running Python codes without any need for installing or configuring a Python platform on your personal computer. This web-based platform makes it free and simple for anyone to now run our reaction-diffusion VPI process simulation model. This talk will include how to access and run these simulations, defining the important model variables as well as how they relate to physical process parameters. Example simulations will be run and then compared to experimental data we and others have published to demonstrate how this reaction-diffusion model can be used to interpret and help predict VPI process phenomena.

9:40am **TF-ThM-6 High-Throughput Molecular Layer Deposition for the Discovery of Organic-Inorganic EUV Photoresists**, *Duncan Reece*, University of Washington, UK; *E. Crum*, University of Washington; *Y. Choe*, University of Washington, Republic of Korea; *D. Bergsman*, University of Washington

Continued progress in information and communication technologies requires sustained innovations in memory and storage devices' architecture and production processes. However, scaling technology to sub-5nm features may require Extreme Ultraviolet (EUV) sources, which necessitates new photoresist materials that are highly adsorbing of EUV while meeting the formal requirements of a photoresist. Such materials must also be environmentally conscious and abundantly available. One potential solution is a hybrid inorganic-organic thin film produced through molecular layer deposition (MLD), the organic equivalent of atomic layer deposition. However, the discovery process for new MLD materials is typically slow and needs improvement.

Here, we present a high-throughput multi-chamber MLD reactor that can quickly screen hybrid MLD processes for their EUV compatibility. In the reactor, films are deposited with one shared inorganic reactant and six independent counter-reactants in parallel, simultaneously producing

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multiple potential resist materials. In this work, inorganic reactants consisted of highly and non-highly EUV absorbing metals, like diethyl zinc, trimethylaluminum, and tin(IV) t-butoxide, while the organic counter-reactants included ethylene glycol, 1,2,4-trihydroxybenzene, 1,5-hexadiene-3,4-diol, 2-butyne-1,4-diol, cis-2-butene, and 2-methylenepropane-1,3-diol. The resulting films were tested for solvent, developer, and etchant stability before and after exposure to deep UV, electron beam, or X-rays. Promising resists were further characterized and could be used for patterning. Results showed that the inorganic and organic linkers exhibited a range of stabilities and light sensitivities, which could be used to optimize the performance of thin film EUV resists. In addition, this method provides a much faster screening process for potential photoresist materials in a scalable system, allowing for the continued improvement of processor efficiency and progress.

11:00am TF-ThM-10 Understanding the Physicochemical Properties and Structural Evolution of Sequential Infiltration Synthesis Derived Indium Oxyhydroxide Clusters for CO₂ Absorption, *Thabiso Kumene, A. Martinson,* Argonne National Laboratory

Sequential infiltration synthesis (SIS) is a versatile route to hybrid organic-inorganic materials. While SIS is inspired ALD and often utilizes the same precursors and tools, SIS requires infiltration of these vapor phase precursors into a polymer film that includes reversible or irreversible interactions with polymer functional groups. In a second step, the infiltration of an oxygen source (e.g. H₂O) affords reaction to form an inorganic oxyhydroxide that may be chemisorbed at the functional site or physically trapped within the polymer matrix. However, the atomic structure of the first few-atom clusters and the evolution of local coordination environment remain unresolved. Therefore, a more fundamental and detailed understanding of the growth mechanism and structural evolution of indium clusters during SIS is necessary to inform the synthetic design of target clusters for various applications. This talk will discuss the experimental and theoretical efforts to elucidate the growth and structure of indium oxyhydroxide clusters from trimethyl indium (TMIn) during SIS in PMMA polymers. FTIR, UV-vis and DFT calculations suggest the existence of octahedrally coordinated [In]³⁺ species where water ligands complete the coordination sphere. The spectroscopic observations also indicate that the weak adducts formed between trimethyl indium precursor and the Lewis basic carbonyl and ester groups in PMMA are central to the oxyhydroxide growth pathways during SIS. Considering the traditional, solution phase organometallic properties and chemistry of trimethyl indium, we demonstrate a link between solution phase organometallic synthesis and the vapor phase SIS process. DFT calculations and In K-edge EXAFS with PDF analysis suggest the formation of dimeric indium oxyhydroxide species in the very first SIS cycle which is driven by the hydrolysis pathways of TMIn. The talk will also present refined SIS process conditions in which nucleation is only feasible in the first SIS cycle, in order to favor only indium oxyhydroxide cluster growth in subsequent cycles. Furthermore, the nature of SIS-derived InO_xH_y(H₂O)_z clusters as a function size (i.e., SIS cycle number) is examined by vibrational and UV-vis absorption signatures and compared to simulated spectra from DFT simulations. The SIS grown indium oxyhydroxide in PMMA presents opportunities to improve the CO₂ absorption capacity and gas selectivity of inexpensive polymers. The SIS-grown clusters provide a platform for use as a model system to study indium (oxy)hydroxide surface reactivity towards environmentally important transformations such as CO₂ capture and conversion.

11:20am TF-ThM-11 Optimizing Aluminum Oxyhydroxide Vapor Phase Infiltration for the Vapor Phase Mordanting of Natural Dyes to Polyester Fabrics, *M. Losego, Nicole McClelland, E. McGuinness,* Georgia Institute of Technology

Industrial textile dyeing and finishing processes are a significant environmental concern producing large quantities of wastewater that require significant treatment to remove unused synthetic chemicals. Polyester fabrics in particular utilize high temperatures and chemical carrier agents in their dyeing processes. In this work, we present a method for attaching natural dye materials derived from madder root to polyethylene terephthalate fabrics via the introduction of aluminum oxyhydroxides through vapor phase infiltration. Vapor phase infiltration (VPI) is an emerging polymer modification technique that exposes a polymer to metalorganic precursors that diffuse into the polymer and become entrapped as inorganic clusters. The resulting hybrids have unique properties of both organic and inorganic materials. The VPI process has found significant use in modifying the properties of textile materials including their mechanical and optical properties. In this study, we examine

the use of VPI to act as a mordant for natural dye adsorption and how the inorganic loading can be optimized for both dyeability and mechanical performance. Specifically we examine VPI of trimethylaluminum (TMA) into polyethylene terephthalate (PET) fabrics. Inorganic loading is controlled by varying the dose pressure of TMA (moles of TMA) and fabric mass (moles of carbonyl functional group) during VPI and quantified using thermogravimetric analysis (TGA). The resulting hybrid AlO_x-PET fabrics have various inorganic loadings from 1 wt% aluminum oxyhydroxide to >20 wt%. The hybrid fabrics were then dyed with alizarin (derived from madder root) and the dye absorbance was quantified with UV-Vis spectroscopy. At low inorganic loadings the strength of color varied with inorganic content, but a steady-state absorbance was reached at around 1.8 wt% inorganic loading. At these low inorganic loadings, hybrid fabrics maintain key mechanical behaviors such as stiffness (as measured by drape) which is seen to increase significantly with additional inorganic loading. This change in texture was quantified using the Cusick drape test to determine shear and bending stiffness changes as a result of higher inorganic loading. By exploring dye saturation curves for different inorganic loadings, kinetics information was gathered to further optimize this dyeing process for industrialization. Overall, using VPI as a vapor phase mordanting process to fix natural dyes to PET fabrics illustrates the impact that even small quantities of the vapor deposited inorganic can have on approving dyeability, highlighting the practical use of these fabrics in the field of textile sustainability.

11:40am TF-ThM-12 Tuning the Thermal Stability of Vapor Phase Infiltrated Polyacrylonitrile Fabrics, *Téa Cook, B. Jean, E. McGuinness, A. Gonzalez, M. Losego,* Georgia Institute of Technology

VPI creates hybrid organic-inorganic materials by infiltrating polymers with vapor phase metalorganic precursors that sorb and permeate into the bulk of the polymer. Polyacrylonitrile (PAN) is a polymer previously unexplored in VPI. PAN is used in textiles and filtration, but one of its most common applications is as a precursor to carbon fiber. The metalorganic precursor trimethyl aluminum (TMA) has been shown to form a reversible adduct with the nitrile functional group, which is found on the backbone of PAN polymer chains. The VPI process has been shown to alter numerous properties of materials and, specifically, to reduce the thermal stability of hybrid materials. This work will discuss the role of VPI in modifying the thermal properties of infiltrated PAN fabrics as a function of VPI processing conditions such as exposure time, desorption time, and processing temperature. To explore the effects of inorganic loading on the thermal properties of this system, PAN is infiltrated with TMA and co-reacted with water vapor under varied processing conditions to tune the inorganic in each hybrid PAN/AlO_x fabric. PAN infiltrates with high quantities of inorganic loading that can be tuned from 1% to 17% inorganic by weight, as measured by thermogravimetric analysis (TGA). TGA is further used to study the thermal degradation profile of the hybrid PAN/AlO_x, and the kinetics of degradation via the Flynn-Wall-Ozawa analysis method. Through this analysis, the thermal stability of the PAN fabric is shown to decrease after infiltration. The temperatures of the first degradation event in the hybrid fabrics are about 100°C lower than the temperatures of the first degradation event of neat PAN fabric. The activation energy to degrade a PAN/AlO_x hybrid of 7.5 wt % alumina is 67% of that required to degrade a PAN/AlO_x hybrid of 15 wt % alumina. While infiltration reduces the activation energies of each degradation event relative to neat PAN, the change in activation energy varies with loading, suggesting that the thermal stability of hybrid PAN fabrics can be tuned by altering VPI processing conditions which may prove advantageous in the energy-intensive carbon fiber manufacturing process. Overall, this work explores a new VPI system: infiltration of TMA into PAN. Additionally, this work explores the vapor phase modification of PAN fabrics and how processing conditions can be used to tune the inorganic loading of AlO_x/PAN hybrid fabrics and their thermal stability.

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