Thin Films Division
Room 317 - Session TF1+SE-WeM

Vapor Deposition and Vapor Infiltration of Organic, Polymeric, and/or Hybrid Materials

Moderator: Siamak Nejati, University of Nebraska-Lincoln

8:00am **TF1+SE-WeM-1 Thermophysical Properties of Organic-Inorganic Hybrid Thin Films Created via Vapor Phase Infiltration (VPI)*, Mark Losego,*** Georgia Institute of Technology

This talk will discuss how thermophysical properties, including the glass transition, thermal expansion, and onset of crystallization, are altered when an organic material is transformed into an organic-inorganic hybrid material via vapor phase infiltration. Vapor phase infiltration (VPI) is a gas-phase technique that exposes organic materials to inorganic vapors (e.g., metalorganics or metal halides) that sorb into the organic, transforming it into an organic-inorganic hybrid. Over the past several years, our lab has examined how the precursor-organic chemistry and VPI process conditions (e.g., temperature) can be used to alter the quantity of inorganic loading and the extent to which the inorganic becomes chemically bound to the organic components. Controlling this physicochemical structure also alters the thermophysical properties of the resultant hybrid material. This talk will describe several examples including altering the glass transition temperature in poly(styrene-co-2-hydroxyethyl methacrylate) (PS-r-PHEMA) random copolymers infiltrated with aluminum oxyhydroxide and in Spiro-OMeTAD hole transport layers infiltrated with titanium oxide. In the PS-r-PHEMA system, random copolymers of varying HEMA composition from 0 to 20 mol% were investigated and the T_g was found to systematically increase with increasing HEMA temperature by as much as 40 °C. Changes in T-$_g$ at low HEMA composition, for which the polymer is fully infiltrated, fit the Fox-Flory model for crosslinking phenomena which, in addition to a dissolution study on these materials, suggests that VPI crosslinks the PS-r-PHEMA, raising its glass transition temperature. Interestingly, according to the Fox-Flory model, these cross-links are 5x to 10x stiffer than usually observed for most organic crosslinks, suggesting an interesting phenomenon for inorganic cross-linking. For the Spiro-OMeTAD system, T_g appears to decrease with inorganic infiltration. This result is attributed to a lack of primary bonding between the inorganic and organic phases; the inorganic clusters now serve to disrupt the natural π-π stacking in the Spiro-OMeTAD, lowering T_g. Conversely, though, this disruption of the intermolecular forces leads to an increased resistance to crystallization in these hybrid films. This reduced propensity for crystallization may be useful for improving long-term stability of Spiro-OMeTAD-based organic electronic devices.

8:20am **TF1+SE-WeM-2 Chemical Vapor Deposition of Soft Materials for Garment-Integrated Sensor Systems and Plant Electronics*, Trisha L. Andrew,*** University of Massachusetts Amherst **INVITED**

Chemical vapor deposition is a single-step processing method for forming functional polymer films on unconventional substrates, such as commodity textiles and living plants, and allows fabrication of rugged and sensitive fabric-, fiber- and/or plant-based sensors for wearable electronics and smart farms. I will the detail the materials science and engineering advances made by my team during the process of assembling various garment-integrated sensor systems and plant-based sensors for longitudinal health monitoring in native environments. In particular, I will highlight our recent work in developing garments for portable brain activity monitoring and activity tracking, systems for in-home sleep monitoring, and conductive living plants for detection of selected abiotic stressors in commercial farms.

9:00am **TF1+SE-WeM-4 Effects of Trimethylaluminum Vapor Pressure and Exposure Time on Inorganic Loading in Vapor Phase Infiltrated PIM-1 Polymer Membranes*, Benjamin Jean,*** *Y. Ren, E. McGuinness, R. Lively, M. Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is a process for synthesizing organic-inorganic hybrid materials by infiltrating polymers with inorganic vapor molecules. Recently, our research team has used VPI to synthesize hybrid membranes with consistent nanofiltration performance in a variety of organic solvents that would otherwise swell or dissolve the parent polymer membrane. The properties of these hybrid materials can vary with the amount of VPI generated inorganic loading. However, the relationship between VPI processing conditions and inorganic loading is still not fully understood. This talk will discuss the effects of VPI dose pressure and exposure time on inorganic loading using the technologically relevant membrane material polymer of intrinsic microporosity 1 (PIM-1). At sufficiently low dose pressures and infiltration times (i.e., before saturation), inorganic loading can be controlled with both vapor pressure and exposure time. However, inorganic loading appears to saturate for this system at around 13 wt% inorganic. This apparent saturation point can be reached by infiltrating for 5 hours at TMA dose pressures above 0.4 Torr or after 40 hours at lower vapor pressures of 0.1 Torr. Inorganic loading appears to saturate for this system when the polymer's functional groups become fully populated with bound VPI precursors. These experimental results can be understood with the use of a recently developed reaction-diffusion model for VPI. Critical to applying this model to these post-deposition measurements is re-normalizing the mass loading to the total number of functional groups in the polymer. These findings suggest that the vapor pressure during infiltration affects the kinetics of this infiltration process but does not appear to alter the thermodynamically determined saturation point for inorganic loading.

9:20am **TF1+SE-WeM-5 Elucidating the Sequential Infiltration of Trimethylaluminum and Water Into Polycarbonate Membranes and Thin Films*, Rajesh Pathak,*** *R. Shevate, A. Mane , J. Elam,* Argonne National Laboratory, USA

Sequential infiltration synthesis (SIS) enables the creation of inorganic or polymer-inorganic hybrid nanocomposite materials through the diffusion of metal-organic vapor reagents into polymers and subsequent reactions with the polymer functional groups. Here we report a detailed study of aluminum oxide (Al_2O_3) SIS using trimethyl aluminum (TMA) and H_2O in polycarbonate (PC) thin films and membranes. We employed in situ Fourier transform infrared spectroscopy (FTIR) to elucidate the chemical interactions and in situ spectroscopic ellipsometry (SE) to measure the physical and optical changes that occur during Al_2O_3 SIS in PC. During the first SIS cycle, FTIR measurements revealed a rapid and irreversible reaction between TMA and the PC carbonyl groups to form Al-CH_3 species which then converted to Al_2O_3 upon H_2O exposure during.Virtually no spectral changes were observed by FTIR in subsequent SIS cycles.The SE measurements showed that the PC film thickness increased by ~75% and the refractive index (RI) decreased by ~2% during the initial TMA exposure.These effects were partially reversed during the following H_2O exposure such that the net thickness increase was ~36% and the RI returned to its initial value.During subsequent SIS cycles, the thickness and RI remained essentially constant.Ex situ X-ray photoelectron spectroscopy (XPS) depth profiling measurements showed ~30 at% Al uniformly distributed through the depth of the PC film following a single Al_2O_3 SIS cycle. SIS-derived nano/microstructure materials with tunable structural and optoelectronic properties could be developed for a variety of applications.

Keywords: atomic layer deposition; sequential infiltration synthesis; aluminum oxide, polymer-inorganic nanocomposite.

9:40am **TF1+SE-WeM-6 Kinetics of $TiCl_4$ Vapor Phase Infiltration (VPI) into PMMA and the Resulting Thermophysical and Optical Properties of the TiO_2 -PMMA Hybrids*, Shuaib Balogun,*** Georgia Institute of Technology*; A. Steiner,* Sandia National Lab*; M. Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is a post-polymerization modification technique that imbues inorganic materials into polymers to create organic-inorganic hybrid materials with new properties distinct from the parent polymer. While several VPI precursor-polymer chemistries have been explored, a lack of chemical intuition remains for fully understanding the thermodynamics and kinetics that govern the VPI process. This study seeks to continue to build this knowledge by examining the VPI process kinetics for TiO_2 infiltration into PMMA via the use of $TiCl_4$ and H_2O precursors. In this research, polymethylmethacrylate / TiO_2 hybrid materials are prepared using VPI. The depth of infiltration of the TiO_2species into ~200 nm PMMA thin films is studied using x-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy and spectroscopic ellipsometry. The kinetics for TiCl4 infiltration increases with both VPI process temperature and $TiCl_4$ exposure time. However, the rates of infiltration are considerably slower than those observed in the more commonly studied trimethylaluminum (TMA) / PMMA system. Even at 150 °C, process times of at least 12 hours are required to fully infiltrate a 200 nm PMMA film whereas using TMA similar films are fully infiltrated within 1 hour at the same process temperature. Films that we believe to be fully infiltrated at 150 °C and 24 hours of $TiCl_4$ exposure have a 6 at% Ti in the innermost bulk, as determined by XPS. Interestingly, unlike AlO_x-PMMA hybrids, these TiO_x – PMMA hybrids exhibit significant changes in their optical properties.

Increased titanium loading leads to a 4% increase in refractive index and increased UV absorbance in the UV range of 270-350nm. Furthermore, films infiltrated at 150 °C and 24 hours of $TiCl_4$ exposure had a 50 % and 70 % reduction in coefficients of thermal expansion (CTE) below and above T_g respectively. Reduced CTE trends with increased titanium loading. We will discuss possible opportunities to use these new properties for various applications.

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11:20am **TF1+SE-WeM-11 Effect of the Metal-Heteroatom Bond on Film Growth and Properties in Vapor-Deposited, Hybrid Metal Organic Thin Films***, **Jacqueline Lewis**, J. Shi, A. Ravi, S. I-Cheng Hsu, S. Bent,* Stanford University

Growing energy demand and the transition to clean energy set the stage for novel materials to fill gaps in current technologies. Hybrid metal organic thin films allow useful, active materials in the energy field, such as Al2O3 and ZnS, to reach a wider range of functionality by adding organic linkers via molecular layer deposition (MLD). Varying the organic linker and metal center using MLD modifies the film properties significantly, giving an adaptable, layer-by-layer growth scheme for the formation of novel materials. Previous literature reports have mainly focused on metal alkoxide films, where the organic linker is a multifunctional organic alcohol. Typically using a bifunctional linker, these films degrade rapidly in air, limiting their potential applicability for membrane materials, catalysis, and encapsulation. However, different functional groups, including dithiols, change the film properties substantially, with stability in air as one of the most notable effects. In this work, zinc thiolate films were deposited via hybrid MLD with a thiol bonding group, showing increased air stability as the films retain ~60% of the thiolate character after over 6 weeks in air. Films grown using 1,2-ethanedithiol degrade faster than those grown with 1,4-butanedithiol. The degradation mechanism forms at least three separate species, which we study via X-ray photoelectron spectroscopy (XPS) and synchtrotron-based X-ray absorption spectroscopy (XAS). Despite some degradation observed via XPS, the band gap of the material stays consistently close to 5.0 eV assuming direct band gap. This multi-week decay is much slower than the degradation of the known metal alkoxides, which degrade on the timescale of hours or days. The increased functionality exhibited by these metal thiolate films shows that changing the metal-heteroatom bond can create more stable films as well as increase the domain of materials to examine.

11:40am **TF1+SE-WeM-12 Oxidative Molecular Layer Deposition of Electrochemically Active Polymers***, **Matthias Young**[1], Q. Wyatt, M. Vaninger, N. Paranamana, T. Heitmann, H. Kaiser,* University of Missouri

Conjugated polymers such as polyethylenedioxythiophene (pEDOT), polypyrrole (pPy), and polyaniline (pAni) exhibit high electrochemical capacities, making them appealing as electrode materials for energy storage, electrochemical desalination, and chemical sensing. Recent work has established the growth of thin-films of pEDOT using alternating gas-phase exposures of EDOT monomers and a metal-chloride (e.g. $MoCl_5$) oxidant in a process termed oxidative molecular layer deposition (oMLD). Here, we report on recent work establishing oMLD of amine-containing conjugated polymers. We find that pyrrole (Py) and $MoCl_5$ undergo self-limiting surface reactions during oMLD exposures to form conformal pPy thin films, but oMLD using aniline (Ani) and p-phenylenediamine (PDA) monomers yield unexpected azo functionality. The formation of azo groups is attributed to an $MoCl_5$-amine surface adduct that spatially constrains polymerization reactions near the amine group and produces azo groups when coupling two primary amines. pPy grown by oMLD exhibits a record-breaking 282 mAh/g capacity in aqueous electrolyte, and PDA/$MoCl_5$ oMLD yields azo-polymers of interest as anode materials for alkali-ion batteries. Alternating between Py and PDA monomers during oMLD produces molecularly mixed copolymers with qualitatively different electrochemical responses from the isolated monomer structures. This work lays the foundation for the growth of conformal thin films of conjugated amine polymers with molecular-level control of composition and thickness.

12:00pm **TF1+SE-WeM-13 Towards High Throughput Molecular Layer Deposition of Alucone Films***, **Hardik Shantilal Jain**[2],* Holst Centre / TNO and Eindhoven University of Technology, The Netherlands*; M. Creatore,* Eindhoven University of Technology, The Netherlands*; P. Poodt,* Holst Centre / TNO and Eindhoven University of Technology, The Netherlands

The deposition rate and properties of MLD films are for a large part determined by what happens during the precursor exposure step. In some cases, however, the purge step is of equal importance, for example in the MLD of alucone films using trimethylaluminum (TMA) and ethylene glycol (EG). Due to the porosity of alucone films, the reactants during their exposure step not only react at the film surface but also tend to infiltrate into the film. The subsequent outgassing of the infiltrated reactant can take relatively very long thereby becoming the deposition rate-limiting step. If enough purge time is not provided for the reactant to outgas, it will lead to an additional CVD component alongside MLD in the overall growth. To employ/avoid the CVD component in the deposition process, we have developed a kinetic model to correlate parameters like exposure times, partial pressures, purge times and deposition temperature to the amount of CVD component in the growth. We have also investigated the impact of this additional CVD component on the step coverage of the alucone films and evaluated its usage in superconformally filling dielectric gaps.

Additionally, we also looked into solutions to increase the deposition rate of the alucone films and improve their conformality and amongst others found that using a bulkier precursor like DMAI instead of TMA can overcome the problem of precursor infiltration, increase the deposition rate of alucone processes by at least an order of magnitude and provide quite conformal films. We also performed a detailed investigation of MLD of alucone using DMAI as the aluminum precursor wherein the effect of deposition temperature and reactant purge times on deposition kinetics has been investigated and the DMAI alucone films have been compared with those prepared using TMA for their chemical environment and degradation showing striking similarities between both. We believe that the above work could be extended to other MLD systems and can serve as a guide in designing efficient MLD reactors and processes.

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[1] **2020 TFD Paul Holloway Awardee**

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

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