

Emerging Materials

Room 107-109 - Session EM-TuA

Organic-Inorganic Hybrid Materials

Moderator: Virginia Wheeler, U.S. Naval Research Laboratory

1:30pm EM-TuA-1 Simultaneous Enhancement of Toughness and Elimination of the UV Sensitivity of Kevlar with a Combined ALD/MPI Process, *Ixtasne Azpitarte, M Knez*, CIC nanoGUNE, Spain

Kevlar® is among the most prominent high-strength polymers for a use in mechanically demanding applications, such as personal safety, sport equipment and aircrafts. In many of these applications Kevlar is exposed to UV radiation and/or moisture, which seriously affect its mechanical properties. Thus, strengthening or protection of Kevlar is of great interest. So far, the most efficient approaches resulted in heavy and rigid composite materials consisting of Kevlar fibers embedded in a resin [1]–[3].

Kevlar's outstanding strength arises from the highly ordered crystalline structure formed during the extrusion of the polymer. Astonishingly, little attention has been paid to the possibility of enhancing the mechanical properties and stability via chemical post-processing of the polymer. In our previous work [4], we demonstrated that the thermal and UV sensitivity of Kevlar can be suppressed by infiltration of ZnO through Multiple Pulsed Infiltration (MPI). However, still only 90% of the modulus of toughness was retained in this way.

In this work, we present an extraordinary improvement of the properties of the fibers after applying a combined ALD/MPI process. Kevlar fibers have been infiltrated with ZnO and coated with Al₂O₃ in the same process. In this way, not only the loss of the modulus of toughness was suppressed, but the fibers even gained 10% of toughness. Simultaneously its sensitivity to UV-induced degradation was completely eliminated. This new processing strategy is a breakthrough in the improvement of Kevlar and promises further optimization with refinement of the processing conditions and precursors.

[1] J. R. Yeh, J. L. Teply, and A. Laboratories, "Compressive Response of Kevlar / Epoxy Composites," vol. 22, no. March 1988, pp. 245–257, 2015.

[2] a Mittelman and L. Roman, "Tensile properties of real unidirectional Kevlar / epoxy composites," vol. 21, no. 1, pp. 63–69, 1990.

[3] R. J. Morgan, C. Pruneda, and W. J. Steele, "The Relationship between the Physical Structure and the Microscopic Deformation and Failure Processes of Poly(p-Phenylene Terephthalamide) Fibers," *J. Polym. Sci. Polym. Phys. Ed.*, vol. 21, pp. 1757–1783, 1983.

[4] I. Azpitarte *et al.*, "Suppressing the Thermal and Ultraviolet Sensitivity of Kevlar by Infiltration and Hybridization with ZnO," *Chem. Mater.*, vol. 29, no. 23, pp. 10068–10074, 2017.

1:45pm EM-TuA-2 Mutual Synergistic Doping in Conductive Hybrid Materials Obtained after Vapor Phase Infiltration, *W Wang, I Azpitarte, Mato Knez*, CIC nanoGUNE, Spain

Hybrid materials are in most cases blends of inorganic and organic materials and are considered to be key for the next generation of materials research. The main goal while fabricating such materials is to bridge the worlds of polymers and ceramics, ideally uniting the most desirable properties within a singular material. Furthermore, in a well performing hybrid material the individual components will add value to their counterpart in a synergistic way.

In this work, an innovative approach towards creating flexible electronic materials will be presented. Rather than growing thin conformal films, the ALD process technology is applied to controllably infiltrate metals into polymeric substrates, which leads to novel strategies for obtaining conductive polymers. On the one hand, single precursor infiltration processes are applied to dope conductive polymers such as polyaniline or P3HT in a post polymerization process, opening the pathway to easier structuring of the polymer substrates and a more precise control of the doping levels. This is of great importance for those conductive polymers, which upon doping do not allow further shaping anymore due to dopant-induced brittleness.

On the other hand, a completely new concept for fabricating conductive polymers will be presented, which also shows a paradigm shift. Namely, the infiltration strategy with multiple precursors is applied to fabricate polymer-inorganic hybrid materials that are able to mutually dope each other in a synergistic way. The interaction of the semiconducting and the

polymeric phase increases the conductivity of the hybrid material by up to 5 orders of magnitude in comparison to the conventionally doped polymer or the semiconductor. This strategy opens a new pathway to construct flexible conductive materials and enables thousands of new material combinations for the fabrication of flexible electronic materials.

2:00pm EM-TuA-3 Infiltration Synthesis of ZnO in a Non-reactive Polymer Facilitated by Residual Solvent Molecules, *X Ye, J Kestell, K Kisslinger, M Liu*, Brookhaven National Laboratory; *R Grubbs*, Stony Brook University; *J Boscoboinik, Chang-Yong Nam*, Brookhaven National Laboratory

Infiltration synthesis is an atomic-layer-deposition (ALD)-derived organic-inorganic material hybridization technique that enables unique hybrid nanocomposites with improved material properties and inorganic nanostructures replicated from polymer templates. The process is typically perceived to be driven by the binding reaction between reactive chemical groups of polymers and infiltrating vapor-phase material precursors. In this work, we discover that residual solvent molecules from polymer processing can react with infiltrating precursors to enable the infiltration synthesis of metal oxides in a nonreactive polymer. The experimental investigation, combining in situ quartz crystal microgravimetry, polarization-modulated infrared reflection-absorption spectroscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy, reveals that the ZnO infiltration synthesis in a nominally nonreactive, cross-linked SU-8 polymer is mediated by residual processing solvent cyclopentanone, a cyclic ketone whose Lewis-basic terminal carbonyl group can react with the infiltrating Lewis-acidic Zn precursor diethylzinc (DEZ). Additionally, we identify favorable roles of residual epoxy rings in the SU-8 film in further assisting the infiltration synthesis of ZnO. The discovered rationale not only improves the understanding of infiltration synthesis mechanism, but also potentially expands its application to more diverse polymer systems for the generation of unique functional organic-inorganic hybrids and inorganic nanostructures.

2:15pm EM-TuA-4 Thermal Conductivity in Layer-engineered Inorganic-Organic Thin Films, *Fabian Krahl*, Aalto University, Finland; *A Giri, J Tomko*, University of Virginia; *T Tynell*, Aalto University, Finland; *P Hopkins*, University of Virginia; *M Karppinen*, Aalto University, Finland

The combined atomic/molecular layer deposition (ALD/MLD) offers unprecedented opportunities to design exciting layer-engineered film structures not readily achievable by any other fabrication technique. We utilize this to design hybrid inorganic-organic thin films structures that suppress the thermal conductivity of the inorganic component. Such thin films are desired for example for thermal barrier coatings and wearable thermoelectrics.

Our material system is the semiconducting ZnO matrix with thin benzene layers embedded within the thicker oxide layers. In our previous works we already could show that a significant reduction in thermal conductivity can be achieved by introducing a superlattice, most likely caused by phonon scattering at the layer interfaces.^[1,2] Now we extend our work towards irregular and gradient structures in which the layer thickness is not constant (as it is in regular superlattices), see Figure 1.^[3] Our results show that the layer design is playing an important role and that a cleverly designed gradient structure can surpass the superlattices in regards to the suppression of thermal conductivity.

Our research extends the data for engineered hybrid thin films to gradient layered systems that have, to the best of our knowledge, not been provided before. We believe this approach is not limited to our present ZnO:benzene material system and hope it can help understanding the interaction of film design and properties in thin films.

[1] T. Tynell, A. Giri, J. Gaskins, P. E. Hopkins, P. Mele, K. Miyazaki, M. Karppinen, *J. Mater. Chem. A* **2014**, *2*, 12150.

[2] Giri, J.-P. Niemelä, T. Tynell, J. T. Gaskins, B. F. Donovan, M. Karppinen, P. E. Hopkins, *Phys. Rev. B* **2016**, *93*, 115310.

[3] F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins, M. Karppinen, *Adv. Mater. Interfaces*, in press (2018).

[4] J. Alvarez-Quintana, E. Martínez, E. Pérez-Tijerina, S. A. Pérez-García, J. Rodríguez-Viejo, *J. Appl. Phys.* **2010**, *107*, 063713

2:30pm EM-TuA-5 Reversible Trans-cis Photoisomerization of ALD/MLD-fabricated Azobenzene-based Inorganic-Organic Thin Films, *Aida Khayyami, M Karppinen*, Aalto University, Finland

We report the successful incorporation of photoresponsive azobenzene molecules through atomic/molecular layer deposition (ALD/MLD) in inorganic-organic thin films. Together with azobenzene-4, 4'-dicarboxylic

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acid as the organic precursor we use diethyl zinc (DEZ) as the inorganic precursor for our hybrid thin films of the $(\text{Zn-O-C}_{14}\text{H}_9\text{N}_2\text{-O}_4)_k$ type. The fabrication route developed for the hybrid films was then combined with the diethylzinc/ H_2O ALD process for ZnO in order to grow $[(\text{ZnO})_m(\text{Zn-O-C}_{14}\text{H}_9\text{N}_2\text{-O}_4)_k]_n$ superlattice structures where single azobenzene layers are sandwiched between thin crystalline zinc oxide blocks. The ratio of the ALD-ZnO and MLD- $(\text{Zn-O-C}_{14}\text{H}_9\text{N}_2\text{-O}_4)$ cycles was varied between 199:1 and 1:1. The kinetics of the trans-cis-trans photoisomerization were studied by alternate exposures to UV radiation and visible light ($\lambda > 450$ nm). Our inorganic-organic hybrid and superlattice structures were found to be photoreactive upon 360 nm irradiation. This observation confirms that switching processes with photochromic compounds, such as azobenzene, can be implemented in inorganic-organic thin films prepared by the ALD/MLD technique. This underlines the exciting new possibilities provided by the ALD/MLD technique for preparing novel light-sensitive materials.

2:45pm EM-TuA-6 Organic/Inorganic Nanocomposite Synthesis through Sequential Infiltration of 3D Printed Polymer Parts: A Microstructural Study, David J. Mandia, Argonne National Laboratory; R Waldman, University of Chicago; P Kozak, Argonne National Laboratory; S Letourneau, Boise State University; G Sterbinsky, D Gosztola, L Ocola, A Yanguas-Gil, J Elam, Argonne National Laboratory

The modification of polymer 3D printed parts using chemical vapor infiltration methods, such as sequential infiltration synthesis, can be used to impart novel functional properties to 3D printed parts. In this work, we describe the infiltration and characterization of 3D printed parts composed of polymers including poly(lactic acid) (PLA), poly(methyl methacrylate) (PMMA) and acrylonitrile butadiene styrene (ABS), with ZnO using diethyl zinc and water. This results in the formation of a hybrid organic/inorganic composite in the sub-surface region of the polymer whose thickness depends on processing conditions. Through a combination of X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and photoluminescence, we have studied the bonding environment, medium range order, and electronic properties of the resulting material. We discovered that through control of the purging step, growth can proceed in two different regimes, one in which the growth seems to be dictated by precursor molecules coordinating with reactive sites within the polymer, and another that is consistent with infused precursors reacting within the polymer itself. This results in a higher incorporation of inorganic material and a change in microstructure from a coordination environment characteristic of atomic-size inorganic cluster to denser, wurzite-like domains.

3:00pm EM-TuA-7 Reactivity of Common ALD Precursors with OH/H₂O-containing Metal Organic Framework Materials, Kui Tan, University of Texas at Dallas; S Jensen, Wake Forest University; L Feng, Texas A&M University; H Wang, Rutgers University; J Klesko, R Rahman, J Cure, K Wei, University of Texas at Dallas; H Zhou, Texas A&M University; J Li, Rutgers University; T Thonhauser, Wake Forest University; Y Chabal, University of Texas at Dallas

The ability to incorporate metal atoms into nanoporous materials such as metal organic frameworks (MOFs) in a well-controlled fashion provides new opportunities to prepare functionalized and modified materials for potential applications such as catalysis and gas separation. There are however new challenges that need to be overcome such as understanding the reaction mechanisms in order to develop structural and process optimization. MOFs possess three-dimensional structures, with complex pore architecture, leading to a number of possible processes (gas transport, adsorption and reaction) that are much more complex than on flat surfaces. To address these issues, we have combined *in-situ* infrared spectroscopy, X-ray-photoelectron spectroscopy and *ab initio* calculation to study the reaction of a number of common ALD precursors -- trimethylaluminum (TMA), diethylzinc (DEZ), titanium tetrachloride (TiCl_4) - with in several Zr-MOFs containing hydroxyl (OH) and water (H_2O) groups. Differentiating reaction with OH and H_2O groups is particularly interesting since their reactivity highly depends on both the chemical and structural (i.e. sterics) environments. We find that the OH groups in the $\text{Zr}_6(\mu_3\text{-OH})_4(\mu_3\text{-O})_4(\text{OH})_x(\text{H}_2\text{O})_y$ cluster node do not all react at similar rates (i.e., the reaction pathway and energetics are highly dependent on their location, accessibility and chemical environment). For different OH-containing MOFs without H_2O groups, the activation temperatures for the TMA reaction with bridge OH of Zr_6 clusters decrease with their node connectivity, and are 250°C, 150°C and 24°C for UiO-66-NH₂, Zr-abtc and MOF-808, respectively. Interestingly, the amine group in UiO-66-NH₂ is found to act as a catalytic active site by anchoring TMA molecules and facilitating their reaction with nearby hydroxyl groups, which is not

observed in un-functionalized UiO-66. This synergistic effect between -NH₂ and -OH is fully elucidated by first-principles calculations. In addition, we find that TMA easily reacts with water adsorbed on the external surfaces of wet MOFs crystals at room temperature, forming a thick Al_2O_3 blocking layer on the periphery of MOFs crystals. These findings provide a basis for the design and synthesis of new MOFs structures requiring ALD for new applications.

3:15pm EM-TuA-8 Atomic/Molecular Layer Deposition of Inorganic-Organic Carboxylate Network Thin Films for Possible Sensing Applications, Jenna Penttinen, M Nisula, M Karppinen, Aalto University, Finland

We introduce novel atomic/molecular layer deposition (ALD/MLD) processes for the fabrication of crystalline inorganic-organic coordination network thin films with different s-block elements and different aromatic polycarboxylates. The deposition processes fulfill the basic principles of ALD/MLD-type growth including the sequential self-saturated gas-surface reactions and atomic/molecular-level control of the film thickness, and yield crystalline thin films in a wide deposition temperature range. We have investigated the stability of the films in heat and humidity treatments to verify that some of the films reversibly absorb water molecules forming well-defined crystalline water-derivative phases. This suggests that the materials could be utilized e.g. for gas storage and sensing applications. Also interestingly, for some of our as-deposited crystalline thin-film materials there are no bulk structures reported in literature. Our work thus underlines the strength of the ALD/MLD technique in discovering new exciting coordination network thin-film materials that may ultimately be potential material candidates for the next-generation application in, e.g., electronics, sensors, and other high-technology products.

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