Thin Films
Room 206 B W - Session TF-TuA
VSHOP II - Infiltration Synthesis of Hybrid Materials

Moderators: Jolien Dendooven, Ghent University, Belgium, **Mark Losego**, Georgia Institute of Technology

2:15pm **TF-TuA-1 Ruthenium Tetroxide as a Versatile and Selective Precursor for Sequential Infiltration Synthesis of Ru and RuO_2**, *Nithin Poonkottil, Matthias Minjauw, Brent Van Neste,* Ghent University, Belgium; *Eduardo Solano,* ALBA Synchrotron, Spain; *Arbresha Muriqi,* Tyndall National Institute, University College Cork, Ireland; *Matthias Filez,* Ghent University, Belgium; *Michael Nolan,* Tyndall National Institute, University College Cork, Ireland; *Christophe Detavernier,* ***Jolien Dendooven,*** Ghent University, Belgium **INVITED**

This presentation explores the use of ruthenium tetroxide (RuO_4) as a powerful and versatile precursor for atomic layer deposition (ALD) and sequential infiltration synthesis (SIS) of Ru-containing materials. Due to its strong oxidizing character, RuO_4 exhibits unique surface reactivity compared to conventional metalorganic precursors. It readily reacts with oxidizable surfaces and polymers, while showing negligible interaction with already oxidized materials [1]. This inherent chemical selectivity is particularly advantageous for nanopatterning applications, such as area-selective ALD and selective vapor-phase infiltration.

ALD or SIS of metallic Ru is achieved by alternating RuO_4 and H_2 at low temperatures, optimally around 100°C, enabling efficient reduction reaction without decomposition of the RuO_4 precursor, which occurs above 125°C. Replacing H_2 with a milder reducing agent like methanol results in the deposition or infiltration of RuO_2 instead of metallic Ru [2]. Furthermore, alternating RuO_4 with metalorganic precursors enables growth of ternary ruthenates [3]. For example, a RuO_4–trimethylaluminum (TMA) process yields an aluminum ruthenate with a 1:1 Al:Ru ratio.

RuO_4 has long been used in liquid-phase staining of (block co)polymers to enhance contrast in electron microscopy. We demonstrate that its selective reactivity is preserved in the vapor phase: RuO_4 reacts with polystyrene (PS) but not with poly(methyl methacrylate) (PMMA) [4]. This selectivity enables targeted SIS within PS-b-PMMA templates. Alternating RuO_4 and H_2 exposures in such templates, followed by plasma removal of the polymer, yields well-defined Ru nanostructures. Similarly, RuO_2 nanopatterns are obtained using RuO_4/methanol chemistry in the same template.

Mechanistic insights were obtained using in situ FTIR and DFT calculations, revealing that RuO_4 preferentially oxidizes the aromatic CH and C=C bonds in PS, while PMMA remains unaffected. Grazing-incidence wide-angle X-ray scattering (GIWAXS) confirmed the formation of crystalline Ru in the infiltrated PS domains. Microscopy and synchrotron-based X-ray analysis further corroborated the morphological fidelity of the Ru and RuO_2 nanostructures to the original PS template, as well as the evolution of contrast with increasing SIS cycles.

1. M. M. Minjauw et al. Chem. Mater. 2019, 31, 1491–1499.
2. N. Poonkottil et al. Chem. Mater. 2022, 34, 8946–8958.
3. M. M. Minjauw et al. Dalton Trans., 2022, 51, 10721–10727.
4. N. Poonkottil et al. Chem. Mater. 2022, 34, 10347-10360.

2:45pm **TF-TuA-3 Extrinsic Cation Incorporation in the Magic Size Indium Sulfide Cluster via Vapor Phase Infiltration**, ***Kihoon Kim,*** *Taylor Harville, Donghyeon Kang, Nuwanthaka Jayaweera, Karen Mulfort, Jeffrey Elam, Cong Liu, Alex Martinson,* Argonne National Laboratory

The intentional introduction of impurities into a material is essential for controlling the properties of semiconductor materials from the bulk to the nanoscale. Here, we report the extrinsic cation incorporation into molecular-level semiconductor clusters via vapor phase infiltration synthesis. Exposure of magic-size $In_6S_6(CH_3)_6$ clusters to a conventional volatile organometallic precursor, i.e., dimethyl cadmium, induces the substitutional incorporation of Cd, modifying their optical properties. The extent of cation incorporation can be controlled by adjusting the exposure cycle, reaction temperature, and precursor dosage. Unlike conventional cation incorporation processes, this phenomenon is limited to specific organometallic precursors. The underlying reaction mechanisms are further investigated using density functional theory.

3:00pm **TF-TuA-4 Vapor Phase Infiltration of $VOCl_3$ into P3HT: The Interplay of Doping, Dedoping, and Hybridization**, ***Li Zhang***[1,2], *Shawn Gregory, Mark Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) of metal halide precursors has been shown effective in the doping of conjugated polymers. Previous publications have found that the conductivity follows a predictable pattern with metal halide exposure time: an initial increase followed by an eventual decrease. The conductivity initially increases due to doping that increases the number of charge carriers. The eventual decrease has been attributed to an increase in the number of scattering sites created by the infiltrated metal oxide clusters. Herein, we explore VPI of the conjugated polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) with $VOCl_3$ + H_2O to modify the conductivity and optical absorbances. Conductivity initially increases with $VOCl_3$ exposure time, peaks around 20 mins to 1 h, and eventually begins to decrease. UV-Vis and XPS measurements at varying hold times confirm that the increased conductivity is due to an increase in the number of charge carriers, as expected. However, at extended exposure times of > 1 h, UV-Vis measurements show an increase in the pi-pi* absorbance and decreasing polaronic absorbance, indicating a decrease in the concentration of charge carriers, not just an increase in the concentration of scattering sites. Furthermore, EDX measurements show a plateauing of the vanadium concentration in the films at ~1 h, meaning no further scattering sites should be created. In situ conductivity and in situ UV-Vis spectroscopy measurements during VPI confirm decreasing conductivity and charge carrier concentrations during the $VOCl_3$ exposure step. From these observations, we postulate that as exposure time increases, $VOCl_3$ can no longer diffuse into the bulk of the film, causing the thermal de-doping rate to exceed the VPI doping rate. This hypothesis is depicted in the attached Figure 1, where between t_2 and t_3 the effects of thermal dedoping take place starting at the bottom of the film. XPS of the films shows relatively constant doping concentration on the surface regardless of exposure time, but through careful experimentation, we have been able to use XPS to observe a decrease in dopant concentration at the film/substrate interface at times > 1 h, consistent with this proposed bulk de-doping mechanism. Additionally, tests including a vacuum hold step inserted after a 1 h $VOCl_3$ exposure show decreasing conductivity with increasing vacuum hold times, showing that thermal dedoping can occur under vacuum and at the operating temperatures used for this specific process. This work shows the importance of thermal de-doping in designing conductivity of VPI doped conjugated polymer films.

3:15pm **TF-TuA-5 Approaches to Elucidate the Chemical Mechanisms of Atomic Layer Infiltration Processes and Final Hybrid Structures**, ***Mark Losego,*** Georgia Tech

Further advancing the fundamental understanding of atomic layer infiltration (ALI) processes (also known as vapor phase infiltration, VPI, and sequential infiltration synthesis, SIS) is essential to advancing process development, chemical design, material properties, and application spaces. Fundamentals include both the thermodynamics and kinetics of the process as well as the chemical mechanisms of reaction and inorganic cluster development. Over the past few years, our group has focused on elucidating the latter for several systems, and this talk will discuss what we have learned about approaches to take to understand chemical mechanisms of ALI processes and the physicochemical structure of ALI hybrid materials. An interesting case is the dramatic difference in reaction mechanism between trimethylaluminum and titanium tetrachloride with ester groups in, for example, PMMA. While the TMA reacts directly with and consumes the carbonyl to form a M-O bond, $TiCl_4$ attacks the ether oxygen to form its M-O bond, cleaving the alkyl group and leaving the carbonyl unreacted. These differences elucidate approaches to do purely additive or additive and subtractive chemistry during ALI, opening new application spaces. Moreover, it appears that the bound $-TiCl_3$ moiety remains reactive toward the polymer, forming multiple cross-links which reduces the residual hydroxide concentration (making it less hydrophilic) and increases the connectivity of the polymer. To understand the structural development of the inorganic clusters requires clarifying the oxidation state, coordination number, and chemical state, (e.g., fraction of oxide versus hydroxide). This approach usually requires multiple spectroscopies, whose selection may be limited by the spectroscopic activity or absorption edge of the metal center. A set of deductive processes – applying the constraints of charge state and coordination number – can then be used to develop a model structure and test against additional spectroscopic

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[1] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

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

evidence or to compare with simulated spectra. Often, spectroscopies that provide next-nearest neighbor and beyond information can help to further elucidate and verify these proposed structures.

4:00pm **TF-TuA-8 Functionalization of Polymer Membranes for Water Treatment using Chemical Vapors***, **Jeffrey Elam**, Seth Darling, Anil Mane, Rajesh Pathak, Bratin Sengupta, Rahul Shevate, Vepa Rozyyev,* Argonne National Laboratory **INVITED**

Polymer membranes are used extensively in water purification to filter and remove particulate and molecular contaminants.Ideally, these membranes should exhibit high permeance, selectivity, and fouling resistance, but these attributes are rarely achieved simultaneously.One approach to improve membrane performance is to modify the polymer using reactive chemical vapors to impart the desired physiochemical properties.In this presentation, I will describe recent work at Argonne using atomic layer deposition (ALD), sequential infiltration synthesis (SIS), and vapor-phase grafting to modify polymer membranes used for ultra- and nano-filtration in water treatment.These techniques rely on self-limiting chemical reactions between gaseous precursors and a solid surface to grow material in an atomically controlled fashion. We have used ALD to produce ultrathin and conformal inorganic layers allowing the membrane pore size and pore wall composition to be precisely tuned, SIS for the bulk modification of polymers by creating an organic-inorganic hybrid material, and vapor-phase grafting of small molecules to achieve additional control over the membrane surface properties.We have also developed methods to accelerate the nucleation and growth of metal oxide layers on polymers to create superhydrophilic, anti-fouling surfaces using only a few ALD cycles.Our studies employ a suite of in-situ and in-operando measurements to elucidate the surface chemistry for these processes and extensive ex-situ characterization and testing to understand the effects of chemical vapor treatment on polymers and how they impact membrane performance.

4:30pm **TF-TuA-10 Resolving Surface Effects and Bulk Properties for VPI-Modified Polymers***, **Seancarlos Gonzalez**, Yuri Choe, Joelle Scott, Agni Biswal, Cecilia Osburn, David Bergsman,* University of Washington

When applying vapor phase synthetic techniques to a porous substrate like a polymer, sometimes there is not a clear delineation between vapor phase infiltration (VPI) and atomic layer deposition (ALD). In ALD, while the objective is often to deposit onto a surface, some diffusion into the subsurface layer is expected. In contrast, VPI can also cause the formation of a surface layer in addition to the components infiltrated throughout the bulk substrate. In some cases, such as for materials for membrane separations, this distinction can have a pronounced impact on device performance. However, the potential presence of a surface layer can complicate material characterization by making it unclear which properties are attributable to the bulk versus the surface.

In this work, we highlight the challenges associated with characterizing the differences between surface and bulk growth in VPI, using an example system based on the infiltration of inorganic and organic reactants into acrylonitrile butadiene styrene (ABS) substrates. First, ABS is infiltrated with diethyl zinc (DEZ) and water to form zinc oxide. It is then infiltrated with 2-methylimidazole (2-HmIM), which can react with zinc oxide to form a metal-organic framework (MOF) known as ZIF-8. Select samples were then exposed to water, which can etch away surface ZIF-8, and then compared against non-etched samples. Successful reactant infiltration was confirmed using secondary ion mass spectrometry (SIMS) to measure reactant infiltration depth, along with thermogravimetric analysis (TGA) to measure reactant loading. Substrates were then examined using x-ray diffraction (XRD) to determine ZIF-8 crystallinity and scanning electron microscopy (SEM) to measure surface morphology, with samples compared with and without surface etching. Results suggest that confinement within the polymer matrix may serve to restrict the crystallization of MOF particles, as opposed to surface deposition where crystallization can proceed unhindered. This distinction can be challenging to characterize due to the limitations of many characterization techniques, and suggests that careful consideration must be given to surface phenomenon, even when using bulk modification techniques like VPI.

4:45pm **TF-TuA-11 Fundamental Studies of the Sorption, Diffusion, and Reaction Processes of Direct Vapor Phase Infiltration of Diethylzinc into PMMA for Hybrid Material Synthesis***, **Typher Yom**, Mark Losego,* Georgia Institute of Technology, USA

Vapor phase infiltration (VPI) is a process that is capable of creating hybrid organic-inorganic materials by allowing a precursor to diffuse a vapor phase inorganic material into a polymer matrix. Doing so can evenly distribute the material throughout the matrix due to the self-limiting nature of the precursor's reaction with functional groups on the polymer. Infiltration of ZnO into polymers is of interest because of ZnO's electrical semi-conductivity, UV absorption, piezoelectricity, and photoluminescence. One hybrid material of interest is zinc oxide mixed with polymethyl methacrylate (PMMA), which is created by the infiltration of diethylzinc (DEZ) into PMMA.In most prior studies, the seeding of ZnO infiltration by first infiltrating with aluminum oxide (via trimethylaluminum) was used because the sorption of DEZ appeared to be low.Here, we use quartz crystal microbalance (QCM) to directly study the sorption and diffusion processes of DEZ in PMMA without a seed cycle. Based on these measurements, we find that DEZ does infiltrate into PMMA at elevated temperatures (>100^{o}C). At 100 ^{o}C and below, the added mass from 36 hours of DEZ infiltration is about 25% or less than that of the polymer. On the other hand, at 110 ^{o}C and higher, the added mass from 36 hours of DEZ infiltration is at or above about 300% of the mass of the polymer. Additionally, the DEZ does stay inside the PMMA even with long purge times, which would normally remove weakly bound species.This talk will present the sorption rates and diffusion rates for DEZ into PMMA over a range of temperatures from 70 °C to 130 °C. This information will be used to further elucidate the mechanisms of this infiltration process and to what extent ZnO-polymer hybrids can be directly synthesized via vapor phase infiltration.

5:00pm **TF-TuA-12 Impact of Vapor Phase Infiltration on the Mechanical and Chemical Properties of Polyethersulfone Membranes***, Yuri Choe, **Alyssa Hicks**,* University of Washington*; David Bergsman,* university of washington

Vapor phase infiltration (VPI), also known as sequential infiltration synthesis (SIS), is an emerging technique for embedding inorganic materials into polymers using vapor-phase reactants, thereby tuning polymer properties. This technique has the potential to be useful in applications like membrane separations, where improved polymer properties, such as resistance to organic solvents, thermal stability, and selectivity, can substantially reduce processing costs. However, the infiltration of inorganic fillers can reduce polymer ductility, which can inhibit their use. Therefore, understanding the impact of VPI on polymer mechanical and chemical stability is critical for the rational design of robust membranes.

In this work, polyethersulfone membranes—often used as support layer—were treated with trimethylaluminum and water to introduce aluminum oxide via VPI. Exposure duration and process cycles were then modulated to control infiltration depth and inorganic loading, respectively, before measuring mechanical properties through burst pressure testing and dynamic mechanical analysis. Results showed that membranes were less resistant to pressure and more brittle when shallower infiltration depths and higher inorganic loadings were used. These trends were found to agree with theoretical models, such as the rule of mixtures and Gibson-Ashby formulations, which predict that the distribution of alumina would mitigate the loss of ductility. Additionally, the chemical stability of VPI-treated membranes in organic solvents and their separation performance were compared against the alumina infiltration depth, suggesting tradeoffs between chemical and mechanical stability in VPI-modified polymer membranes.

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