Emerging Materials
Room Hall 3E - Session EM-TuA

Vapor Phase Infiltration

Moderators: Jolien Dendooven, Ghent University, Belgium, **Sang In Lee**, Synos Foundation

4:00pm **EM-TuA-11 Selective Deposition of Al_2O_3 on Patterned Polymer Substrates using Vapor Phase Infiltration***, **Maggy Harake**, Y. Lee,* Stanford University*; B. Yu,* Lawrence Berkeley National Laboratory*; G. D'Acunto,* Stanford University*; R. Ruiz,* Lawrence Berkeley National Laboratory*; S. Bent,* Stanford University

As semiconductor lithography nears sub-10 nm feature sizes with the upcoming adoption of high numerical aperture extreme ultra-violet lithography, patterning materials that enable these small dimensions are not the only challenge. Lithographic materials must facilitate high-precision pattern transfer and ensure uniform feature sizes with minimal placement errors thereby mitigating the stochastic variations that limit density scaling. We have recently introduced a concept of area-selective deposition (ASD) with vapor phase infiltration (VPI) akin to atomic layer deposition, which is a promising tool for high-precision patterning.

Our approach involves utilizing a patterned *two-color* surface modification monolayer, where regions of the *first color* serve as non-growth surfaces resembling conventional ASD schemes, while regions of the *second color* act as growth promoters through enhanced VPI. We engineer the *two-color* surface modification layers by leveraging the versatility and lithographic compatibility of graft-to-polymer brushes.

This work reports on the selective infiltration of Al_2O_3 using VPI on patterned substrates coated with growth-promoting sequence-defined polypeptoid (PP) polymers and polystyrene brushes (PS) (non-growth surface). We investigate PP side-chain chemistry to determine which monomer combinations are most receptive to ALD precursors and gain insight into how to tune the thickness of the oxide film. Furthermore, we consider how three Al precursors (triethylaluminium, trimethylaluminum (TMA), and dimethyl aluminum isopropoxide (DMAI)), which vary in ligand type and size, interact with and influence growth within the polymers and lead to different oxide film densities.

We confirm successful growth of the oxide film on the PP surface of the substrate using atomic force microscopy (AFM). Additionally, blanket substrates covered with PP or PS polymer brushes show large variations in Al uptake and selectivity, as determined by x-ray photoelectron spectroscopy (XPS) and angle-resolved XPS, depending on the ALD precursor-PP interaction. From XPS we determine that TMA creates a thick oxide film within PP and not in PS. DMAI, the larger molecule of the three and the only one containing an Al-O bond, is shown to not be selective between the two types of polymer brushes. In-vacuo infrared spectroscopy measurements provide mechanistic insight into the reactions with the various precursors. Finally, upon reactive ion etching, we demonstrate successful pattern transfer from the VPI-hardened polymer pattern onto the substrate, providing a bridge for existing patterning technologies to be paired with this selective process.

4:15pm **EM-TuA-12 Sequential Infiltration Synthesis of Al_2O_3 in PMMA and PLA Thin Films: Convergence of Results Across Experimental Data and Theoretical Studies***, **Michele Perego**,* CNR-IMM, Agrate unit, Italy*; A. Motta, G. Seguini, C. Wiemer,* CNR-IMM, Agrate Unit, Italy*; K. Ronnby, M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Sequential infiltration synthesis (SIS) is a vapor phase infiltration technique for the creation of organic-inorganic hybrid materials and/or inorganic nanostructures from a suitable polymer template. So far, the number of inorganic materials that can be grown by SIS is quite limited. To expand the materials library and widen the application fields, studies on kinetics, diffusivity, reaction energy and mechanism are necessary.

In this work, Al_2O_3 is infiltrated in poly (methyl methacrylate) (PMMA) and poly (lactic acid) (PLA) thin films by means of a standard ALD reactor, operating at 70°C in quasi-static mode, using trimethyl aluminium (TMA) and water. Selected polymers are characterized by the presence of ester groups that are expected to act as reactive sites for TMA. In situ spectroscopic ellipsometry reveals that significant swelling and deswelling of PMMA occur during TMA exposure and purging, respectively, due to sorption and subsequent desorption of TMA molecules that are not stably incorporated into the PMMA matrix. PLA exhibits a much larger swelling than PMMA during TMA exposure, but no significant deswelling is observed during purging, suggesting that a large amount of infiltrated TMA molecules is effectively trapped into the polymer matrix by a stable chemical bond. Accordingly, ex-situ XPS analysis demonstrates that much more Al_2O_3 is grown in PLA than in PMMA. Additionally, ex-situ XPS analysis indicates that, in both cases, TMA incorporation occurs through the formation of an Al-O covalent bond at the C-O-C group, as already observed in other biopolymers.

Two density functional theory (DFT) approaches were used to investigate the infiltration of TMA into PMMA and PLA polymers. Binding configurations and energies were modelled using a gas phase model of a ten-unit polymer. For both polymers, TMA was found to form an adduct with the oxygen in the C=O with an exothermic reaction energy, consistent with experiment. Furthermore, TMA was able to exothermically insert into the C-O-C bond of PLA, forming a covalent Al-O bond, aligning with the ex-situ XPS results. Infiltration modelling employed a periodic model with two eight-unit polymer chains. Both PMMA and PLA displayed swelling upon TMA infiltration, saturating with increasing TMA, consistent with experimental findings.

This combined experimental and theoretical study provides insight into SIS of Al_2O_3 in PMMA and PLA. The methodology can be extended to other precursors or polymers, unravelling of the complexities of SIS at the molecular level.

4:30pm **EM-TuA-13 Expanding the Toolbox of Vapor Phase Infiltration Processes***, **Tamar Segal-Peretz**,* Technion Israel Institute of Technology, Israel **INVITED**

Vapor phase infiltration (VPI), also named sequential infiltration synthesis (SIS), is a technique derived from ALD that enables the incorporation of inorganic species into polymeric matrices. VPI can modify the properties of polymers by creating hybrid organic-inorganic materials with enhanced mechanical, electrical, optical, or catalytic functionalities. In addition, polymer patterns can be used as templates for confined growth, enabling simple conversation of organic nanostructures into inorganic ones, upon polymer removal. With these abilities, VPI is an appealing technique for a wide range of applications- from nanopatterning and sensing to energy storage devices and water filtration membranes. To continue expanding VPI processes, key challenges need to be addressed. These include new VPI chemistries, better understanding and control over growth processes and depth gradients, as well as new polymer chemistries, morphologies, and architecture for VPI.

Here I will describe our efforts in addressing these challenges. To expand VPI chemistries, we demonstrated the use of TDMA ligands in VPI, creating SnO_2 and HfO_2 nanostructures from block copolymer templates. Despite the large volume of these precursors that reduce diffusion through the polymer, exploring the parameter space of VPI enabled us to rationally design these processes. We also explored new ways for fabricating multi-material structures via VPI by controlling either the precursors' diffusion or their ratios in a three-precursor process, leading to spatially controlled structures and doped metal oxides. We investigated ZnO nucleation and growth in an array of polymers, setting design rules for this important VPI process. Finally, we demonstrate how this knowledge can be harnessed for a new application- protecting degradable polymers from UV radiation. We show how VPI can enhance the growth of ALD on the polymer surface leading to the synergic effect of high durability of these sensitive polymers under destructive UV radiation.

5:00pm **EM-TuA-15 Organic-Inorganic Hybrid Thermoelectric Materials Through Vapor Phase Infiltration***, **Kristina Ashurbekova**,* CIC nanoGUNE, Spain*; M. Naumochkin, H. Reith, K. Nielsch,* Leibniz Institute for Solid State and Materials Research (IFW), Germany*; M. Knez,* CIC nanoGUNE, Spain

The fabrication of a multiplicity of hybrid thermoelectric (TE) materials is limited by the fabrication methodologies and incompatibilities of the involved materials classes. We present a new set of hybrid materials with covalently bound organic/inorganic interfaces by growing Sb_2Te_3, Sb_2Se_3, Bi_2Te_3, Bi_2Se_3 inside the bulk of the semi-conducting polymer Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) by vapor phase infiltration (VPI). In this work, we focus on the p-type Sb_2Te_3-PEDOT:PSS. $SbCl_3$ and $(Me_3Si)_2Te$ were used for the VPI growth of Sb_2Te_3 inside the bulk of the spin-coated polymer. SEM, SIMS and XPS results showed Sb_2Te_3 infiltration throughout the whole 200 nm polymer depth. TEM showed the rhombohedral phase of Sb_2Te_3 grown in the bulk and on top of the polymer. TE characterization of the hybrids over a temperature range of 293–433 *K*was performed with a lab-on-chip ZT test platform which allowed simultaneous characterization of all in-plane parameters of the films, including the electrical conductivity (σ), Seebeck coefficient (*S*), thermal conductivity (λ_{total}), Hall coefficient R_H, and the thus derived Power Factor (PF) and ZT. TE characterization was performed over several heating-cooling cycles (293–433 K), until equilibrium of the measured parameters was reached. Interestingly, during the first three heating-cooling cycles, the difference in σ between each measurement increased to values of more than 80 S cm^{-1}, changing from semiconducting behavior to metallic. This likely originates from migration and crystallization of the inorganic phase in the polymer that leads to formation of additional conductive paths. The thermal transport behavior supports this idea, showing a delta λ_{total}decrease by 0.3 W m^{-1} K^{-1} with thermal cycling. This indicates that the degree of disorder increases through formation of out-of-plane Sb_2Te_3 crystals. Decoupling of σ from $\lambda_{total}$is related to suppression of the lattice λ by enhancing the boundary-scattering events for heat-carrying phonons. At the same time the chemical bonds in Sb_2Te_3-PEDOT:PSS are promoting the direct electronic interaction between the inorganic and organic phases, facilitating electron transport. Finally, a great increase in *S* to a value of 135 μV K^{-1} at 293 K was achieved, much higher than the intrinsic *S* of PEDOT:PSS (20 μV K^{-1}). A remarkable PF of 610 μW m^{-1} K^{-2} was obtained at 433 K, corresponding to σ of 250 S cm^{-1}. The results offer new solutions for energy harvesting technologies with high flexibility. *K.A. acknowledges MSCA IF fundings, No:101032113.*

5:15pm **EM-TuA-16 Surprising, Simultaneously Enhanced H_2/CO_2 Selectivity and H_2 Permeability in Polymer Gas Separation Membranes by 1-Cycle Alumina Atomic Layer Deposition: The Effects of Inadvertent Vapor-Phase Infiltration***, L. Hu,* University at Buffalo*; W. Lee, A. Subramanian,* Stony Brook University*; E. Deng,* University at Buffalo*; K. Kisslinger,* Brookhaven National Laboratory*; S. Fan,* University of Colorado Boulder*; V. Bui,* University at Buffalo*; Y. Ding,* University of Colorado Boulder*; H. Lin,* University at Buffalo*;* ***Chang-Yong Nam****,* Brookhaven National Laboratory

For polymer gas separation membranes that typically rely on the molecular sieving effect, an improved selectivity typically accompanies a lowered permeability, thus limiting a simultaneous improvement of the two parameters (i.e., Robeson upper bound). Here, we discover that polybenzimidazole (PBI), one of the leading membrane materials for H_2/CO_2 separation, can exhibit simultaneously increased H_2 permeability and H_2/CO_2 selectivity, surpassing the Robeson upper bound, once treated by simple, low-temperature (85 °C) 1-cycle alumina atomic layer deposition (ALD).[1] We find that the normal 1-cycle alumina ALD (i.e., not using an intentional exposure-mode protocol), comprising 15 msec sequential dosing of trimethylaluminum (TMA) and water with 10 sec intermediate purging, leads to a surprising vapor-phase infiltration (VPI) of alumina into PBI matrix, penetrating over several micrometers deep into the film. The resulting AlO_x-doped PBI hybrid membrane features remarkably increased H_2 permeability by 120% - 270% and H_2/CO_2 selectivity by 30% at 35 - 200 °C, compared to the untreated control. This unusual, simultaneously enhanced H_2 permeability and H_2/CO_2 selectivity were attributed to the disrupted PBI polymer chain packing by the AlO_x infiltration, which was found to be mediated by the reaction between infiltrating TMA and amine groups available in PBI. The suggested mechanism was further supported by the TMA-only-infiltrated PBI membrane that displayed a similarly increased H_2 permeability. Given the simple and fast treatment protocol, this demonstration showcases a facile and scalable way of utilizing ALD and VPI for engineering and improving polymeric membranes important for CO_2 capture and future H_2 economy.

[1] L. Hu et al., "Few-cycle atomic layer deposition to nanoengineer polybenzimidazole for H_2/CO_2 separation", *Chem. Eng. J.* **479**, 147401 (2024)

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