

Emerging Materials

Room Van Eyck - Session EM2-WeA

Vapor Phase Infiltration

Moderators: Anjana Devi, Ruhr University Bochum, Maarit Karppinen, Aalto University

1:30pm **EM2-WeA-1 Vapor Phase Infiltration of Polymers for the Synthesis of Organic-Inorganic Hybrid Materials: Process Kinetics, Chemical Pathways, and Final Hybrid Structure**, *Mark Losego*, Georgia Institute of Technology **INVITED**

Vapor phase infiltration (VPI) infuses polymers with inorganic atomic clusters to create unique organic-inorganic hybrid materials with novel chemical, electrical, optical, and mechanical properties. These new materials have been used in applications ranging from energy harvesting to filtration media to photolithographic hard masks. This talk will discuss our efforts to develop an appropriate phenomenological model to describe the VPI processing kinetics and our use of *in situ* gravimetry to validate this model. The talk will also explore our current understanding of the final hybrid structure and our use of electron microscopy, spectroscopy, and density functional theory (DFT) to understand the inorganic's chemical state and its bonding structure to the polymer. Finally, several example applications will be discussed, and it will be shown how an understanding of the processing kinetics and chemical structure can be used to scale the VPI process to treat macroscale objects – including plastic components and textiles – as well as the additional complications and/or opportunities that avail themselves from process scale-up.

2:00pm **EM2-WeA-3 Atomic Layer Deposition on Polymer Thin Films: On the Role of Precursor Infiltration and Reactivity**, *Robin Petit, J. Li, B. Van de Voorde, S. Van Vlierberghe, P. Smet, C. Detavernier*, Ghent University, Belgium

Polymers play a role in a variety of applications owing to their flexibility, low toxicity and ease of processing. In many cases (e.g., lighting, photovoltaics, displays), they are incorporated into devices as host materials for electro-optical components (e.g., quantum dots), which are sensitive to the environment, i.e., moisture, oxygen and temperature. Polymers do not provide adequate protection, apparent from their high water vapor and oxygen transmission rates. To improve the stability, they are coated with barrier layers. We report on the use of Al₂O₃ ALD, with TMA and H₂O, to coat polymer thin films: polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate glycol) (PET-G) [1].

Polymers being complex molecular networks encompassing a free volume, this free volume causes a growth delay during Al₂O₃ ALD on polymers, calling for an understanding of the nucleation, precursor infiltration and polymer relaxation effects that impact this growth delay. Here, the reactivity of the polymers towards TMA is investigated with FTIR and XPS, while the extent of TMA infiltration as a function of deposition temperature is probed with *in situ* ellipsometry (SE).

Our results show that the temperature and presence, location and amount of polymer functional groups (C-O, C=O) influence the growth delay. While PS showed no infiltration, TMA-induced swelling was observed for PMMA and PET-G, with a change in reversibility as a function of temperature (Fig. 1). At low temperatures, TMA mainly physisorbs, while a pericyclic reaction drives the interaction with TMA for PMMA and PET-G at elevated temperatures (Fig. 2). For PET-G, this reaction can result in chain scission, accounting for the significant TMA infiltration. Furthermore, SE is used to determine the moment of closed layer formation, halting the infiltration and indicating the onset of linear growth (Fig. 3). The better understanding of the influence of the ALD deposition conditions and polymer properties on the barrier growth enables faster, more effective barrier creation for other ALD-polymer combinations.

[1] Petit, R. R.; Li, J.; Van de Voorde, B.; Van Vlierberghe, S.; Smet, P. F.; Detavernier, C. Atomic Layer Deposition on Polymer Thin Films: On the Role of Precursor Infiltration and Reactivity. ACS Appl. Mater. Interfaces 2021, 13, 38, 46151–46163.

2:15pm **EM2-WeA-4 Obtaining Robust Hydrophilic Surface on Soft Polymer Through Atmospheric Pressure ALD**, *Albert Santoso, B. van der Berg, V. van Steijn, R. van Ommen*, Delft University of Technology, Netherlands

In the recent times, the use of modified soft polymer is increasing in a range of applications, such as biotechnology and medicine. Due to their flexible nature, good optical transparency, and high fidelity, soft polymers such as PDMS (polydimethylsiloxane) are known to be a good coating and microfluidics material. As a result, fields such as optical sensor, membrane separation, and bio-assays benefit tremendously. However, this polymer suffers from the lack of a hydrophilic group, limiting its application to several commercial potentials, especially in proper fluidic handling. Furthermore, research in obtaining robust hydrophilicity often involves changing the bulk material and/or extremely complicated processes. Therefore, there is a need for precise surface manipulation with relatively simple processes. Among many surface modification techniques, atomic layer deposition (ALD) is known for its atom-level control. Furthermore, its deposition on a polymer involves both surface reaction and infiltration, leading to formation of buffer layer without changing much of its bulk properties. This study focuses on the use of atmospheric pressure atomic layer deposition (APALD). Opposed to the conventional vacuum ALD, it makes the use of vacuum technology superfluous and at the same time allows convective transport to challenge the limitation in aspect ratio coverage. The results shows that deposition of 100 cycles form a 46nm layer of titanium oxide, of which the surface contact angle stays 74° over a period of 8 weeks. This is much more hydrophilic than bare PDMS (110°) and vacuum ALD (recovering back to 90°). Both scanning electron microscopy and x-ray photoelectron spectroscopy depth profiling show that uniform deposition of surface and formation of mixed layer in the range of few microns are vital for preventing diffusion of uncured monomers to the surface, leading to more stable hydrophilic surface. Furthermore, this result is confirmed by washing some PDMS in organic solvent to reduce the amount of uncured monomer, resulting in a contact angle of 65° after 8 weeks. There are also little to no changes observed in the transparency and mechanical property. This study not only provides a novel and easy method to modify soft polymer such as PDMS, but also opens up various potential in the field of microfluidic coating and commercial layer deposition.

2:30pm **EM2-WeA-5 Modified 3D Printed Architectures: Effects of Infiltration by Alumina on ABS**, *Atilla Varga, S. Barry*, Carleton University, Canada

In recent years 3D printing has gained enormous popularity thanks to its affordability, accessibility, ease of use, and the ability to easily employ a variety of polymer materials. These potential polymer substrates are highly tunable in flexibility and strength which make them the ideal for printing filaments, they can incorporate metal powders, wood fibers, carbon fibers, and other composites.[1] The integration of 3D printing and industrial nanoscale processes such as ALD will have a significant impact in the development of advanced 3D printed architectures leading to a wide array of applications as currently being investigated.

Our group has previously shown improvement of solvent stability for 3D-printed acrylonitrile-butadiene-styrene (ABS) architectures using an alumina thin film.[2] We demonstrated a 30-50% increase in solvent exposure resistance with a ~200 nm thin film. In addition we observed infiltration in the ABS polymer when no thermal pretreatment was performed on the ABS architecture, with deposition carried out above the glass transition temperature.

Infiltration requires inherently different conditions than film deposition, specifically a longer exposure to the precursors, which ideally improves infiltration depth.[3] By infiltrating ABS rather than overcoating it with alumina, we will be improving the material's glass transition temperature (T_g). Various deposition parameters such as pulse length, soak time, and temperature have varying effects on the glass transition temperature and will be discussed.

The T_g of ABS could be improved by 10° C after the infiltration of alumina. Interestingly, this improvement was effective for only one heat-cool cycle. After cooling, the plastic reverted to its normal T_g. We speculate that this is caused by the plastic flowing together, out of the infiltrated alumina matrix. Scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDX) will be used to examine the modified polymer structures (Figure 1). Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and conductivity probe measurements

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will be used to observe the physical property changes (focusing on T_g of the treated compared to the untreated polymer).

[1] T. Abudula et al., *Front. Bioeng. Biotechnol.*, **2020**, *8*, 586186

[2] Varga A. C., Barry, S. T., *J. Vac. Sci. Technol. A*, **2022**, accepted

[3] Robin R. P. et al., *ACS Appl. Mater. Interfaces*, **2021**, *13*, *38*, 46151–46163

2:45pm **EM2-WeA-6 Polymer-Inorganic Hybrids for Inducing Self-Healing Functionality in Metal Oxides**, *Oksana Yurkevich, E. Modin, CIC nanoGUNE, Spain; I. Šarić, M. Petravić, University of Rijeka, Croatia; M. Knez, CIC nanoGUNE, Spain*

A rapid surge of research works is the commitment to the sustainability of mankind. However, the vast majority of these works are devoted to the self-healing of organic materials. At the same time, there is a growing demand for implementing this functionality to the inorganic materials due to the rapid development in the area of flexible electronics. The few existing examples for inorganic materials rely on liquid healing agents, such as liquid metals or liquid precursors. The progress in this field remains very challenging, mainly because of a lack of feasible healing agents and suitable ways to supply them to the damaged site. In this work, we propose an approach to form self-healing metal oxides (MeO) by applying the vapor phase infiltration (VPI) method.

We used VPI as a tool to induce self-healing properties into hybrid organic-inorganic materials. This was achieved by infiltration of metal organics into the polymers which do not possess reactive oxygen-containing functional groups. Application of a typical VPI process to a functional polymeric substrate will result in the formation of dispersed metal oxide clusters and nanoparticles (NPs) inside the polymer along with an inorganic thin film of the same MeO on the surface. This hybrid polymer matrix with dispersed NPs can serve as a reservoir with healing agents for a repair of a cracked MeO film. Self-healing of inorganic materials and structures was realized also without liquid agents by making use of the mobility of inorganic NPs within polymers, as the spatial distribution of NPs can be tuned by means of harnessing both enthalpy and entropy.

After the infiltration process, samples were transferred into the microscope chamber and cut in a controllable way by a Focused Ion Beam (FIB). Usage of FIB and SEM allowed inspecting the ruptured area of the hybrid structure prior to and after its exposure to the ambient atmosphere. X-ray photoelectron spectroscopy (XPS), energy-dispersive x-ray spectroscopy (EDX), and transmission electron microscopy (TEM) were used to analyze the chemical structure and composition of the obtained hybrids. The self-healing effect after exposure of the FIB-cut sample to air was observed for zinc and indium metal oxides (Fig.1). Hereby, we introduce an alternative materials architecture and construction framework for designing inorganic materials capable to self-heal.

3:00pm **EM2-WeA-7 Tailoring the Interfacial Interactions of Porous Polymer Membranes to Accelerate Atomic Layer Deposition: The Latent Path to Antifouling Membranes**, *Rahul Shevate, V. Rozyyev, R. Pathak, A. Mane, S. Darling, J. Elam, Argonne National Laboratory, USA*

Atomic layer deposition (ALD) is a powerful strategy to engineer hybrid organic-inorganic membranes with emergent functionalities. The combination of atomic-level thickness control, wide materials palette, and unprecedented conformality allow the physiochemical properties (e.g., hydrophilicity) of mesoporous polymer membranes to be precisely tuned. The nucleation of ALD materials growth on polymer surfaces relies on chemical interactions between the ALD metalorganic precursor and functional groups in the polymer structure and these interactions dictate the number of ALD cycles required to achieve a continuous coating. Strategies to enhance these interactions could enable desirable properties such as anti-fouling behavior to be imparted on inert polymer surfaces that lack the necessary functional groups for ALD nucleation. In this study, we demonstrate that the reactivity of polyacrylonitrile (PAN) membranes towards ALD metal oxide (MO) precursors with Lewis acid characteristics is enhanced by introducing Lewis base functional groups (amidoxime: Am) on the PAN backbone. The resulting Lewis acid-base interactions accelerates the MO nucleation in Am-PAN and reduce the number of deposition cycles required to achieve hydrophilicity compared to the untreated PAN membrane. Unveiling the reaction mechanism, the in-situ FTIR intensity changes established enhanced interaction dynamics between the ALD MO precursors and the Am-PAN membrane, unlike the PAN membrane. For similar MO cycles, through both spectroscopic and thermogravimetric analysis, we observe enhanced MO loading in the Am-PAN membrane compared to the PAN membrane. Here we have verified that strong Lewis acid-base interactions led to enhanced loading for a

range of ALD MO materials including Al₂O₃, TiO₂, SnO₂, and ZnO. Most importantly, the Al₂O₃-Am-PAN hybrid membrane showed 23.3% higher antifouling capability compared to the pristine PAN membrane. Our approach expands the scope of design options for fouling-resistant porous hybrid inorganic-organic membranes and may reduce manufacturing costs of water treatment membranes.

Keywords: ALD, membranes, metal-binding functionalities, water treatment, filtration, nanoporous structures

3:15pm **EM2-WeA-8 Ruthenium Nanostructures via Sequential Infiltration Synthesis in Self-Assembled Diblock Copolymer Thin Films**, *Nithin Poonkottil, Ghent University, Belgium; E. Solano, ALBA Synchrotron, Spain; A. Muriqi, M. Nolan, Tyndall National Institute, University College Cork, Ireland; C. Detavernier, J. Dendooven, Ghent University, Belgium*

Vapor phase infiltration or sequential infiltration synthesis (SIS) is an ALD-derived technique for creating organic-inorganic hybrid materials, by allowing ALD precursors and reactants to react within the free volume of soft materials like polymers. SIS on diblock copolymer (di-BCP) films is critical in lithography, where material growth is typically achieved selectively in one block while the other remains inert. A plasma treatment can be used to remove the organic components, resulting in nanopatterns that resemble the reacted block. However, metal nanopatterns derived from SIS are still in its infancy, as most reports focus on metal oxides, mainly Al₂O₃.¹

We present SIS of Ru² without any pre-treatment, using alternating infiltration of RuO₄ and H₂ in polystyrene-block-polymethylmethacrylate (PS-*b*-PMMA) templates, followed by plasma treatment to create patterns of Ru nanostructures (Fig.1A). Experiments on blanket PS and PMMA films show that RuO₄ infiltration is selective (Fig.1B) into PS, with no significant out-diffusion of RuO₄ from PS, and thus a strong interaction between RuO₄ and PS. Density functional theory calculations corroborate that PS-RuO₄ interaction is energetically favorable, whereas the PMMA-RuO₄ interaction is not. The inertness of PMMA is attributed to its compact structure with no sufficient space between units to accommodate RuO₄ molecules. *In situ* FTIR shows that aromatic CH and C=C bonds in PS are consumed during the RuO₄ infiltration. XPS depth profiles confirm the infiltration of Ru throughout the polymer. An enhanced morphology and density contrast between the PS and PMMA domains in the di-BCP films after infiltration is evident from scanning electron and atomic force microscopy (Fig.2), elucidating that a single SIS cycle can already considerably change the nature of the PS domains. In grazing incidence wide angle X-ray scattering images, the diffraction signals of Ru become more pronounced with increasing number of SIS cycles, confirming the crystalline nature of the infiltrated Ru nanostructures. A significant increase in crystallinity of Ru is observed after the polymer is removed by plasma, with clear diffraction peaks present even after a single SIS cycle. Finally, the formation of Ru nanolines resembling the di-BCP nanostructure after the plasma treatment is confirmed in AFM images (Fig.2).

1. Waldman et al., *J. Chem. Phys.*, **2019**, *151*, 190901

2. Minjauw et al., *J. Mater. Chem C* **2015**, *3*, 132-137

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