Thin Films
Room 115 - Session TF-WeM

Vapor Synthesis of Hybrid, Organic, and Polymeric Materials (VSHOP II)

Moderators: Trisha Andrew, University of Massachusetts - Amherst, **Siamak Nejati**, University of Nebraska-Lincoln

8:00am **TF-WeM-1 Chemical Vapor Deposition of Metalloporphyrins: Engineering and Integration of Advanced Conjugated Polymers for Catalysis and Sensing**, ***Nicolas Boscher,*** Luxembourg Institute of Science and Technology (LIST), Luxembourg **INVITED**

Porphyrins have been intensively investigated as catalysts and sensing materials. The properties of porphyrin-based catalysts and sensors can be tailored from the careful selection of the central metal ion chelated at the centre of the macrocycleand its peripheral substituents. Beyond, several studies have highlighted the cooperative effect promoted by conjugated covalent links between porphyrins on both their catalytic and sensing properties. However, in spite of the many synthetic approaches developed towards the synthesis of porphyrin-based conjugated assemblies, the engineering and integration of porphyrin-based conjugated assemblies has been limited by their weak solubility.

Oxidative chemical vapor deposition (oCVD) was recently demonstrated as a convenient method for the simultaneous synthesis and deposition of porphyrin-based conjugated polymers.[1] Porphyrins possessing free *meso*-positions[1-4] and/or free *beta*-positions[5] and porphyrins bearing thienyl or aminophenyl substituents[6] have both been successfully polymerised using oCVD to yield the formation of formation fused porphyrin tapes and bridged porphyrins covalent organic frameworks, respectively. Importantly in the perspective of practical application, including heterogeneous electrocatalysis and gas sensing, the porphyrin-based conjugated polymers are readily deposited on virtualy any substrate in the form of smooth and thickness-controlled thin films.

Up-to-date, porphyrin-based conjugated polymer thin films prepared by oCVD have been successfully investigated for the electrochemical hydrogen evolution reaction,[2] nitrate reduction reaction,[6] oxygen reduction reaction,[6] oxygen evolution reactions.[3] In addition, porphyrin-based conjugated polymer thin films prepared by oCVD have also been successfully investigated as chemiresistive sensors for ammonia detection.[4] Experimental and theoretical data demonstrate the impact of both the central metal cations and substituents on the catalytic activitiesand sensing properties of the porphyrin conjugated polymer thin films.[2-6] The approach reported in this work circumvents many limitations of solution-based approaches and pave the way to the facile engineering and integration of efficient electrocatalysts and selective sensing materials from porphyrins.

[1] Bengasi *et al.*, *Angew. Chem., Int. Ed.* **2019**. [2] Huerta-Flores *et al.*, *ACS Appl. Energy Mater.* **2020**. [3] Bansal *et al.*, *J. Mater. Chem. A* **2023**. [4] Bengasi *et al.*, *Adv. Elect. Mat.* **2020**. [5] Bansal *et al.*, *Chem. Eur. J.* **2024**. [6] Mohamed *et al.*, *Adv. Mater.* **2024**.

8:30am **TF-WeM-3 Introducing Non-Covalent Interactions during initiated Chemical Vapor Deposition (iCVD)**, ***Rong Yang***, Cornell University

Initiated Chemical Vapor Deposition (iCVD) has been increasingly studied in the solvent-free synthesis and manufacturing of polymeric thin films. It eliminates bulk solvents, thus improving the environmental sustainability of polymer synthesis. Its scalability points to a new pathway for accelerating the development and environmentally friendly manufacturing of polymeric nanomaterials. While prior research has predominantly leveraged the all-dry and low-pressure reaction environment to achieve ideal gas behavior and thereby controlled synthesis conditions, recent advances in iCVD synthesis have unlocked an opportunity to depart from the ideal gas regime. In this talk, I will discuss our results on introducing non-covalent interactions to preorganize molecules and access new chemical synthesis pathways to broaden the palette of attainable polymer chemistry and morphologies. Leveraging hydrogen bonding, we demonstrated that complexing 4-vinylpyridine with hexafluoroisopropanol could increase the polymer molar mass by 700%, which in turn led to unprecedented material hardness and surface morphologies. Building from this demonstration, we tackled the challenge of undesirable chain transfer (e.g., to the imidazole group during the polymerization of 1-vinylimidazole), which has limited the synthesis of an important class of amine/imidazole-containing polymers using iCVD polymerization. Using 1-vinylimidazole as an example, we protonated the transfer-to location via a vapor complexation with acetic acid, rendering the chain transfer energetically unfavorable and enabling synthesis of poly(1-vinylimidazole) films with unprecedented purity, molar mass, and highly controllable polymerization kinetics. This new synthetic capability, in turn, led to the discovery of a novel bioactive material.

8:45am **TF-WeM-4 oCVD PEDOT Thin Film as the Hole Transport Layer in Perovskite Solar Cellto Enhance Device Stability and Performance**, ***Meysam Heydari Gharahcheshmeh,*** San Diego State University/ Department of Mechanical Engineering

Stability concerns have hindered the practical use of perovskite solar cell (PSC) devices. One significant factor contributing to this issue is the inherent acidity of the commonly used hole transport layer, poly(3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS), potentially jeopardizing the stability of PSC devices. To address this challenge, this study explores employing oxidative chemical vapor deposition (oCVD) with antimony pentachloride (SbCl5) as a liquid oxidant for fabricating PEDOT-Cl thin film. This technique is utilized to create stable and ultrathin PEDOT films with high conformity, presenting a promising alternative as a hole transport layer in PSCs. The resulting oCVD-grown PEDOT-Cl thin films, showcase exceptional optoelectronic properties, precise nanostructure control, stability, and integration capabilities. These attributes establish them as a robust and effective choice to be used as the hole transport layer in PSC device. Integration of oCVD PEDOT-Cl thin films as the hole transport layer in PSCs yields a remarkable power conversion efficiency (PCE) of 20.74%, surpassing the 16.53% PCE achieved by spin-coated PEDOT:PSS thin films treated with dimethyl sulfoxide (DMSO) as a polar solvent. Additionally, PSCs incorporating oCVD PEDOT-Cl thin films exhibit a noteworthy 2.5× improvement in stability compared to their PEDOT:PSS-DMSO counterparts.

Keywords: Oxidative Chemical Vapor Deposition, PEDOT, $SbCl_5$ Oxidant, Perovskite Solar Cells

9:00am **TF-WeM-5 Networking Density Effects on the Patterning Performance of Metal-Organic Resists Deposited via Hybrid Molecular Layer Deposition**, ***Long Viet Than,*** *G. D'Acunto, S. Bent,* Stanford University

The implementation of extreme ultraviolet (EUV) lithography in semiconductor manufacturing promises to extend Moore's Law by enabling the patterning of sub-20 nm feature sizes. However, further device scaling is dependent on the implementation of EUV-tailored photoresists that meet requirements in sensitivity, resolution, and line edge roughness. With feature sizes approaching the nanometer scale, stochastic variation in the photoresist molecular structure also affects pattern quality, resulting in the need for new resist chemistries with uniform chemical distribution.

Metal-organic thin films deposited via hybrid molecular layer deposition (MLD) are a promising class of materials to address the challenges of designing new EUV-compatible resist chemistries, by incorporating EUV-absorbing metal centers into the polymer network while exhibiting Å-level thickness control and atomic-scale homogeneity. In this work, we investigated a series of hybrid MLD-derived aluminum alkoxide (alucone) resists, deposited via trimethylaluminum (TMA) and a series of alcohol counter-reactants (glycerol, ethylene glycol, and sequential dosing of methanol/ethylene glycol). This process yielded thin films that are chemically akin, as demonstrated by x-ray photoelectron spectroscopy (XPS), but exhibit notable differences in networking/crosslinking density. The resist performance was evaluated via electron beam lithography, a well-established proxy for EUV. The alucone resists exhibited negative-tone patterning, attributed to the loss of organic ligands and alumina formation resulting from electron-induced reactions. Decreasing the crosslinking density enhanced the resist contrast, thus improving the resolution. On the other hand, increasing the crosslinking density resulted in drastically reduced developer solubility. The variation observed between these hybrid materials underscores the importance of structure-property relationships for the rational design of metal-organic EUV resists.

9:15am **TF-WeM-6 Synthesis of Disulfide Polymer by Oxidative Molecular Layer Deposition (oMLD)**, ***Amit K. Datta,*** University of Missouri, Columbia*; N. Paranamana, P. Kinlen, M. Young,* University of Missouri-Columbia

Poly-2,5-dimercapto-1,3,4-thiadiazole (pDMCT) is a redox-active polymer consisting of heterocyclic monomer units connected by disulfide bonds. pDMCT has been used as a battery material, biocide, and corrosion inhibitor. Upon electrochemical reduction, the disulfide bonds in pDMCT break to form thiolate anions that readily coordinate with cations, providing lithium ion conductivity for battery applications and allowing for capture of heavy metal cations. In this work, our goal is to study the vapor-phase formation of thin films of pDMCT using oxidative molecular layer deposition (oMLD) for use as a protective coating in solid state lithium-ion batteries. We employ alternating vapor exposures of the 2,5-dimercapto-1,3,4-thiadiazole (DMCT) monomer and a molybdenum pentachloride ($MoCl_5$) chemical oxidant to perform oMLD growth in a custom viscous-flow reactor at 150 °C and ~1 Torr. We employ *in situ* quartz crystal microbalance (QCM) studies during growth to understand the film growth chemistry, as well as *ex situ* spectroscopic and electrochemical characterization to confirm formation of pDMCT. QCM studies and *ex situ* thickness measurements indicate controlled linear growth. We examine the effect of precursor dose times on polymer chain length, and the effect of polymer chain length and film thickness on electrochemical properties. The controlled growth of ultrathin films of pDMCT shows promise for the application of this chemistry as a protective coating for lithium-ion battery applications and for passive uptake of heavy metal ions. More broadly, these studies establish that oMLD can be used to create polymers connected by disulfide linkages, opening a new class of polymers accessible by oMLD synthesis.

9:30am **TF-WeM-7 High-Throughput MLD for Advanced EUV Photoresists: Stability and Performance of Organic-Inorganic Hybrid Films***, **Duncan Reece,*** University of Washington, UK*; E. Crum, A. Dao, J. Keth, D. Bergsman,* University of Washington

The development of sub-5nm semiconductor architectures requires photoresists that efficiently absorb Extreme Ultraviolet (EUV) light, maintain structural integrity under high-energy exposure, and are sufficiently thin for precise patterning while being robust enough to withstand the processing environment. Molecular Layer Deposition (MLD) is exceptionally well-suited for this purpose due to its precise control over film composition and thickness, which is crucial for tailoring photoresist properties to meet the stringent specifications of next-generation lithography.Using our previously published high-throughput multi-chamber MLD system, we investigated the stability and mechanical properties of organic-inorganic hybrid thin films designed for EUV lithography applications. MLD's capability to layer angstrom-thick films precisely enables the creation of photoresists that are both thin enough for advanced lithographic detail and durable against developers and etchants.We synthesized 18 different film chemistries using combinations of three organometallic precursors—diethyl zinc, trimethylaluminum, and tin(IV) t-butoxide—and six organic precursors: ethylene glycol, 1,2,4-trihydroxybenzene, 1,5-hexadiene-3,4-diol, 2-butyne-1,4-diol, cis-2-butene-1,4-diol, and 2-methylenepropane-1,3-diol. These films were evaluated for stability in air, developer compatibility, and etchant resistance, both before and after UV exposure. Candidates exhibiting enhanced properties post-exposure were further assessed for mechanical robustness using Atomic Force Microscopy and nanoindentation.Further characterization involved Fourier Transform Infrared Spectroscopy and X-ray Photoelectron Spectroscopy to elucidate degradation pathways and confirm structural integrity. Understanding these pathways is essential for assessing film stability and performance. Selected materials demonstrating optimal performance profiles underwent patterning tests using an electron beam source, with results visualized via Scanning Electron Microscopy.Our findings reveal that specific combinations of organic and inorganic components yield films with significantly improved mechanical properties and stability in air and potential developers. This research primarily aims to understand why certain combinations result in superior film properties, providing valuable insights into the development of advanced EUV photoresists. By emphasizing the fundamental aspects of material behavior, we highlight the efficacy of high-throughput MLD in the rapid screening and optimization of photoresist materials, advancing semiconductor technology.

9:45am **TF-WeM-8 Development of a 300mm Wafer Scale Molecular Layer Deposition Process***, C. Vallee,* ***Van Long Nguyen,*** University at Albany-SUNY*; O. Sathoud, D. Newman, J. Sathoud, J. McAdams, C. Wajda, K. Tapily, G. Leusink,* TEL Technology Center America

Molecular layer deposition (MLD) is an advanced technique for depositing polymeric thin film at the molecular level control. In comparison to the well-known sister method for depositing inorganic thin film, the atomic layer deposition (ALD), research on MLD is still relatively limited in applications, especially in the semiconductor industry, due to the difficulty in finding suitable precursors. Organic precursors for MLD processes are typically low volatility, stability, and reactivity, which is a critical bottleneck limiting its utilization in high-volume semiconductor manufacturing that is based on 300mm wafer process platforms. In this paper, we report the development of a MLD process using a 300mm wafer process tool. MLD of polyamide, nylon 2,6, was first developed at 85°C using two precursors which are ethylene diamine (ED) and adipoyl chloride (AC). While ED has high vapor pressure providing growth saturation easily, low volatility AC precursor requires longer dosing times to reach the growth saturation and is the critical one for optimizing the growth per cycle (GPC) of our MLD process on the 300mm wafer tool (**Figure 1a**). Furthermore, the bubbling dosing mode is more effective in delivering AC to the chamber in comparison to the vapor-draw dosing mode. Our optimized MLD process shows linear growth of 0.12 nm/cycle with 15 cycles of nucleation delays on the Si wafer (**Figure 1b**). The uniformity of the deposition until 120 cycles was less than 4.8% across a 300mm Si wafer. The process is undergoing further optimization to improve GPC, uniformity, and processing time. Ellipsometry, AFM, ATR-FTIR, and XPS are key techniques for the characterization of the film growth for our MLD process.

11:00am **TF-WeM-13 Area Selective Deposition of Ferrocene-Functionalized Thin Films***, J. Lomax,* The University of Western Ontario, Canada*; E. Goodwin,* Carleton University, Canada*; J. Bentley,* The University of Western Ontario, Canada*; M. Aloisio, C. Crudden,* Queen's University, Canada*; S. Barry,* Carleton University, Canada*;* ***Paul Ragogna,*** The University of Western Ontario, Canada **INVITED**

Ferrocene is a stable molecule with well understood redox activity, and has been utilized extensively in areas such as bio-sensing, organometallic chemistry, and materials science.[1–3] This work leverages the utility of ferrocene precursors for solution and vapour phase depositions that prepare ferrocene-based thin films. There was an affinity for the deposition to occur selectively on metallic substrates, and therefore the area-selective deposition of ferrocene-containing precursors was demonstrated, which has potential applications for onwards application in nanoscale device fabrication.[4] Preparation of the small molecule precursors will be discussed as well as the analysis of the fabricated thin film/monolayers via X-ray photoelectron spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Atomic Force Microscopy (AFM), surface Raman spectroscopy, and X-ray Reflectivity (XRR)

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(2) van Staveren, D. R.; Metzler-Nolte, N. Bioorganometallic Chemistry of Ferrocene. *Chem. Rev.* **2004**, *104* (12), 5931–5986. https://doi.org/10.1021/cr0101510.

(3) Hauquier, F.; Ghilane, J.; Fabre, B.; Hapiot, P. Conducting Ferrocene Monolayers on Nonconducting Surfaces. *J. Am. Chem. Soc.* **2008**, *130* (9), 2748–2749. https://doi.org/10.1021/ja711147f.

(4) Parsons, G. N.; Clark, R. D. Area-Selective Deposition: Fundamentals, Applications, and Future Outlook. *Chem. Mater.* **2020**. https://doi.org/10.1021/acs.chemmater.0c00722.

11:30am **TF-WeM-15 Infiltration of Methanol Vapor Induces Lattice Flexibility in Microporous $Ni_2(BDC)_2DABCO$ Thin Films***,* ***Greg Szulczewski,*** The University of Alabama

Thin films of $Ni_2(BDC)_2DABCO$, where BDC is benzendicarboxylic acid and DABCO is 1,4-diazabicyclo[2.2.2]octane, were made by a hot vapor-assisted conversion technique. The thin films were characterized by x-ray diffraction, vibrational spectroscopy and scanning electron microscopy. The polycrystalline films were determined to be phase pure by powder x-ray diffraction. Infrared and Raman spectroscopy reveals the carboxylic acid ligands were converted into carboxylates. The films were activated by heating under high vacuum and adsorption/desorption isotherms were measured for several volatile organic compounds, including alcohols, nitrobenzene, toluene, and methyl iodide vapors at room temperature. The isotherms revealed a Type I behavior for ethanol, isopropanol, toluene nitrobenzene, and methyl iodide vapors. In contrast, the isotherm for methanol has a characteristic S-shape, which is characteristic of a flexible lattice. The adsorption isotherm for methanol has distinct steps, which is attributed to lattice expansion. Upon removal of methanol from the thin film, the lattice relaxes back to the original structure. The results are compared to other pillared microporous coordination compounds.

11:45am **TF-WeM-16 Nanomolecularly-Induced Kinetic, Chemical, and Morphological Effects During Thin Film Synthesis of Hybrid Inorganic/Organic Nanolaminate Multilayers***, **Collin Rowe**, G. Sharma,* Materials Science and Engineering Department, Rensselaer Polytechnic Institute*; A. Devos,* Institute of Electronics, Microelectronics and Nanotechnology, CNRS UMR 8250, France*; H. Pedersen,* Department of Physics, Chemistry, and Biology, Linköping University, Sweden*; G. Ramanath,* Materials Science and Engineering Department, Rensselaer Polytechnic Institute

Molecular nanolayers (MNLs) at inorganic thin film interfaces are known to improve chemical stability, and stimulate completely unexpected mechanical responses and electrical and thermal transport behaviors[1]. Stacking inorganic/organic thin film interfaces with nanoscale proximity, e.g., in high-interface-fraction multilayers, offers promise to access emergent properties via superposition of nanomolecular effects. Synthesizing such structures requires low-temperature depositions of high-quality ultrathin inorganic nanolayers to preserve the integrity of the MNLs. Here, we will demonstrate the synthesis of titania/organo-diphosphonate[2] and AlO_xN_y/hydroquinone multilayers with sharp interfaces by sequential atomic- and molecular-layer deposition (ALD/MLD) cycles. Our results from electron microscopy, X-ray diffraction, and ion beam and photoelectron spectroscopy measurements show that MNLs can significantly alter the inorganic nanolayer growth rate, composition, surface roughness, and phase stability. Examples include up to ~50% decrease in titania growth rates by diphosphonate MNLs, and near complete aluminum nitride to oxide conversion by hydroquinone MNLs. Atomistic mechanisms underpinning these changes will be discussed in terms of the impact of the MNL backbone structure and terminal chemistry on the surface reaction pathways. Acoustic pump-probe spectroscopy measurements on our hybrid multilayers reveal unusual acoustic damping responses which will be described in terms of the MNL interface chemistry and nanolayer periodicity. Further understanding and harnessing such MNL-induced effects and their correlations with emergent properties is crucial for designing high-interface-fraction hybrid nanolaminates for applications.

[1] *Engineering inorganic interfaces using molecular nanolayers*, G. Ramanath, C. Rowe, G. Sharma, V. Venkataramani, J. G. Alauzun, R. Sundararaman, P. Keblinski, D. G. Sangiovanni, P. Eklund, H. Pedersen, **Appl. Phys. Lett.** 122, 260502 (2023).

[2] *Nanomolecularly-induced effects at titania/organo-diphosphonate interfaces for stable hybrid multilayers with emergent properties*, C. Rowe, A. Kashyap, G. Sharma, N. Goyal, J. G. Alauzun, S. T. Barry, N. Ravishankar, A. Soni, P. Eklund, H. Pedersen, G. Ramanath, **ACS Appl. Nano Mater.** (2024).

12:00pm **TF-WeM-17 The Impact of Copolymer Molecular Sequence on Electronic Transport***, **Mahya Mehregan**,* University of Missouri-Columbia*; J. Schultz, M. Maschman, M. Young,* University of Missouri, Columbia

Conjugated polymers (CPs) have garnered significant attention for application in electronics and electrochemical devices, including supercapacitors, solar cells, electrochromics, batteries, microelectronics, and sensors.Blending different conjugated monomers together into copolymersprovides a powerful platform for controlling CP properties.However, torationally improve the performance of conjugated copolymers in these electronic and electrochemical applications, a fundamental understanding of how copolymer structure influences electronic transport is necessary. Conventional synthesis methods for CPs provide poor control over the short-range molecular structure, or sequence, of copolymers, making it difficult to understand the role of short-range molecular structure on electronic transport.Here, we employ vapor-phase oxidative molecular layer deposition (oMLD) at 150°C and ~1 Torr to deposit thin films of conjugated copolymers one monomer at a time, providing control over the copolymer molecular sequence. Because oMLD is a vapor deposition technique, these polymers are also chemically pure with no side-chains or additives.In this study, we specifically control the molecular sequence of copolymers of 3,4-ethylenedioxythiophene (EDOT) and pyrrole (Py) by adjusting the dosing scheme of EDOT and Pymonomers during oMLD growth. Using this synthesis approach, we establishnew insights into how short-range molecular structureinfluences electronic transport through these copolymers. Specifically, we find:(1)a departure from the rule of mixtures, where the block length of each homopolymer within the copolymer influences the overall electronic conductivity even at a constant overall composition; and (2) evidence for a critical hopping distance (or quasi-Debye length) between conductive domains, where electronic conductivity decreases by multiple orders of magnitudewhen the spacing between conductive domains is greater than this critical distance. The fundamental insights into the electronic conductivity through conjugated copolymers we describewill inform the design of conjugated copolymers for electronic and electrochemical devices. More broadly, this study demonstrates thatoMLDcan be used as a platform for polymer materials discovery by synthesizing copolymers with precise control of molecular sequence.

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