

Thin Films Division

Room A122-123 - Session TF1-WeM

Vapor Deposition of Functional Polymer Thin Films and Composites

Moderators: Adrienne Stiff-Roberts, Duke University, John (Jack) Lyons, U.S. Naval Research Laboratory

8:00am TF1-WeM1 Durable Surface Energy Control with Initiated Chemical Vapor Deposited (iCVD) Polymers, *Karen Gleason*, Massachusetts Institute of Technology **INVITED**

Multiple iCVD homopolymer and co-polymer compositions have been employed for the tuning of surface energy from ultrahydrophobic to ultrahydrophilic and for fine-tuning the surface energy over much narrow ranges as well. The iCVD approach is particularly valuable for insoluble materials, including low-surface energy fluoropolymers and durable crosslinked networks. The iCVD surface modification layers can be ultrathin (<20 nm) and are able to conformally cover geometric features in the substrate. For iCVD poly(divinylbenzene) (PDVB), this combination of features enabled the controlled wetting and directed self-assembly of block co-polymers inside of confined features. Ultrathin and conformal iCVD fluoropolymers on aligned carbon nanotube stamps prevent densification of the stamp upon drying, enabling high-speed flexographic printing with nanoparticle inks.

Since film growth proceeds upwards from the substrate, iCVD offers the opportunity for interfacial engineering prior to beginning iCVD synthesis. Indeed, linker-free grafting can be achieved in situ immediately prior to the iCVD growth on substrates from which hydrogen atoms can be abstracted. Linker-free grafted cross-linked PDVB layers display outstanding robustness and have served as a base layer for a covalent attached top layer of iCVD fluoropolymers. The grafted PDVB/fluoropolymer bilayers provide resistance against the attachment of ice and natural gas hydrates and even proved durable when sandblasted. Grafting is essential for tethering swellable hydrophilic surface modification layers. Indeed the durability of iCVD hydrogels and zwitterionic layers is greatly enhanced by grafting for the prevention of delamination.

8:40am TF1-WeM3 Initiated Chemical Vapor Deposition of poly(N-vinylcaprolactam)-based Cross-linked Smart Hydrogel Thin Films with Tunable Temperature-responsive Swelling Behavior, *Fabian Muralter*, A. Perrotta, A.M. Coclite, Graz University of Technology, Austria

Initiated Chemical Vapor Deposition (iCVD) makes it possible to deposit smart hydrogel thin films conformally into 3D-nanostructures for sensor applications. For this contribution, cross-linked p(N-vinylcaprolactam)-based (pNVCL) thin films were synthesized by iCVD for the first time. In aqueous environment, the phase transition of these polymeric systems between a "hydrophilic" swollen state below to a "hydrophobic" shrunken state above their lower critical solution temperature (LCST) was investigated via spectroscopic ellipsometry. As previously shown for other polymers, the amount of cross-linking has been used to tune the temperature-responsive behavior of the deposited pNVCL-based systems. Interestingly, pNVCL is also reported to show decreased transition temperatures for higher molecular weight systems. Thus, by changing the filament temperature during iCVD, it was possible to lower the LCST by almost 20°C, without changing the (nominal) composition. Overall, degrees of maximum swelling of the polymer below the transition temperature of up to 250% of the dry thickness could be achieved and the LCST could be tuned in the range of 16-40°C. For probing the applicability in sensor setups, these systems were also investigated in terms of swelling in humid environment (relative humidity, RH). There, three regions could be identified: First, in rather dry environment, the systems respond by mainly filling porosity, but not showing a temperature-responsive behavior. Second, up to ~80% RH, the response in swelling is close to linear to the measured RH. Third, in very humid environment, the swelling is highly non-linear and temperature-dependent. Moreover, the film thickness approaches the value that can be observed also when the polymer is immersed in water at the respective temperature. Furthermore, the response of the polymer in water as well as in humid environment has been shown to be very fast, as, for example, it responds faster than the commercial sensor used for monitoring the RH in the measurement cell. Together with the biocompatibility reported for pNVCL, the knobs of filament-temperature and cross-linking to tune the described features of

the temperature-responsive swelling behavior of these systems make them highly promising for biomedical or environmental (sensor) applications.

9:00am TF1-WeM4 Promotion of Crystalline Polyfluorene Domains in Thin Films Deposited by RIR-MAPLE, *Spencer Ferguson*, B. Zhang, A.D. Stiff-Roberts, Duke University

An important goal for functional polymer thin film deposition is to selectively deposit semi-crystalline phases to enable unique properties. As a specific example, semi-crystalline β -polyfluorene (β -PFO) could improve the performance of blue polymer light emitting diodes (LEDs) due to better color purity and enhanced charge conduction. However, it has been challenging to directly investigate the impact of this crystalline phase on the performance of PFO-based LEDs films deposited by spin-casting due to poor surface quality with prominent pinholes resulting from the poor solvents or additives used to promote β -PFO[1,2]. Previous work[3] has shown that emulsion-based, resonant infrared matrix-assisted pulsed laser evaporation (RIR- MAPLE) enables deposition of pinhole-free thin films containing β -PFO.

In order to further study the ability of the emulsion target used in RIR-MAPLE to promote the deposition of β -PFO, the emulsion surfactant will be investigated to study the impact of the polarity difference between the primary PFO solvent (trichlorobenzene) and the water within the emulsion. The standard surfactant used in RIR-MAPLE is sodium dodecyl sulfate, and it has a single hydrophobic tail. In a reported study on PFO, phospholipids were used to form a lamellar structure within an emulsion to drop cast films with high concentrations of β -PFO[4]. In contrast to SDS, the phospholipid surfactant has multiple hydrophobic tails, which could significantly impact the formation of β -PFO by RIR-MAPLE. In addition, sodium alkyl aryl sulfonate will be investigated as a surfactant to determine the impact of aromatic rings on the promotion of β -PFO. As a second study, the annealing of deposited films below the glass transition temperature of PFO will be investigated to determine the impact on β -PFO concentration and the overall film morphology.

For each study, UV-Vis absorbance, photoluminescence, and surface morphology will be characterized. This work will provide a path to the fabrication of thin films containing greater concentrations of β -PFO for inclusion as the active region in blue polymer LEDs.

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9:20am TF1-WeM5 Conductive Directly Fused Poly (Porphyrin) Coatings by an Oxidative Chemical Vapour Deposition Approach, *Kamal Baba*, G. Bangasi, G. Frache, D. El Assad, J. Desport, Luxembourg Institute of Science and Technology, Luxembourg; *K. Heinze*, Johannes Gutenberg University of Mainz, Germany; *N.D. Boscher*, Luxembourg Institute of Science and Technology, Luxembourg

Thanks to their remarkable functional properties, porphyrinic compound led to the development of various technological applications, including photovoltaic¹ catalysis² and sensing.³ Among this porphyrinic compounds, conjugated and directly fused porphyrins attracted strong attention.⁴ Indeed, the high conjugation of these systems provides additional interesting functional properties such as two photon absorption, near infrared absorption and enhanced electro-catalytic activity.^{5,6} However, while the solution-phase synthesis of directly fused porphyrin coatings has been successfully developed in recent years, the deposition of these promising compounds in thin film form has remained a challenge.

In this work, we report the simultaneous synthesis and deposition of conductive directly fused poly(porphyrin) coatings based on a substrate independent and up-scalable oxidative chemical vapor deposition (oCVD) approach. The direct fusion of nickel(II) 5,15-(diphenyl)porphyrin (NiDPP) is successfully achieved using different oxidants, such as iron(III) chloride (FeCl₃), copper(II) chloride (CuCl₂) and copper(II) perchlorate hexahydrate (Cu(ClO₄)₂·6H₂O). The decisive reactions and side reactions during the oCVD process are evidenced by Laser Desorption Ionization High Resolution Mass Spectroscopy (LDI-HRMS) and UV-Vis-NIR absorption. FeCl₃ is demonstrated to be the most suitable oxidant, allowing the formation of

singly-fused poly(NiDPP) or conductive doubly or triply-fused poly(NiDPP) that strongly absorb in the near-infrared spectral region. Owing to the highly conjugated structure of the fused tapes, the deposited coatings films exhibit electrical conductivity up to $7 \times 10^{-1} \text{ S cm}^{-1}$ and strong absorption in the visible to near-infrared spectral region.

The described approach is not specific to NiDPP, providing the fact that meso-position remains available, other porphyrins can be fused and deposited in thin film form. Interestingly, the developed approach is inherently scalable and readily allows the deposition and patterning of conductive fused porphyrin thin films on sensitive substrates, such as printer paper or polymer foils, paving the way to the integration of directly fused porphyrin into advanced optoelectronic devices.

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9:40am **TF1-WeM6 Molecular Design and Vapor Phase Synthesis of Crown-Ether-Based Thin Film Materials**, *Darrin Liao, G.W. Rubloff, S.B. Lee, K. Gregorczyk*, University of Maryland, College Park

Ion transport in materials and at their interfaces plays a profound role in a wide spectrum of applications. These include: energy generation (solar-driven water splitting and fuel cells); energy storage (batteries and capacitors); environmental management (water desalination and purification, and nuclear waste management and remediation); solid-state ionic devices (neuromorphic computing); and a variety of biological systems (ion channels). Here we present an MLD synthesis route to incorporating ion-selective moieties into a thin film, concentrating on the crown ether (CE) family of molecules for their well understood and characterized affinity to selectively bind metal cations in the electron-rich center of the molecule.

Two commercially available crown-ether materials (CE), 1,4,10-Trioxa-7,13-diazacyclopentadecane(2A15C5) and for 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (2A18C6), were measured using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to assess their suitability as precursors. The results for both molecules show that vaporization begins at $\sim 100\text{--}150\text{C}$ in both cases, leading to evaporation of essentially all the material by $\sim 200\text{--}250\text{C}$. The DSC curves for both materials show heat flow indicative of phase changes in the range of the vaporization temperatures $\sim 100\text{--}150\text{C}$. Malonyl chloride (MC) was used as an organic linker precursor. In-situ spectroscopic ellipsometry (SE) was used to probe the MLD process parameters, showing a wide temperature window between $75\text{C}\text{--}150\text{C}$ with a linear growth rate $\sim 5\text{--}6 \text{ \AA/cycle}$. Detailed cycle-by-cycle SE show step-wise growth corresponding to the discrete precursor pulses for the CE and the MC. This allows estimates of thickness added per precursor dose, which include an increase in thickness of $\sim 0.295 \text{ nm}$ during the MC pulse and $\sim 0.343 \text{ nm}$ for the 2A15C5 CE pulse, for a total thickness added of $\sim 0.622 \text{ nm}$ for a full MLD cycle.

Chemical analysis of the as-grown MLD films was conducted by in-vacuo X-ray photoelectron spectroscopy (XPS). The presumed molecular configuration of CE and MC film is confirmed by the presence of all expected elements in the expected ratios. The O 1s spectrum indicates the presence of two species, consistent with expectations based on the presence of both C-O-C oxygen in the CE ring and C=O oxygen in the MC. The N 1s spectrum shows a single species of N in the film, as predicted from the CE moiety. The C 1s spectrum is more complex but consistent with the structure: on the higher binding energy side, we see a peak associated with N-C=O at $\sim 290 \text{ eV}$, an overlapping C-N and C-O at $\sim 288 \text{ eV}$, and a C-C peaks at $\sim 285 \text{ eV}$.

11:00am **TF1-WeM10 Chemical Insolubility of Vapor Phase Infiltrated Poly(methyl methacrylate) / AlOx Hybrid Materials**, *Emily McGuinness, C.Z. Leng, M.D. Losego*, Georgia Institute of Technology

Vapor phase infiltration (VPI) is a relatively new processing technique used for transforming polymers into organic-inorganic hybrid materials. VPI has been used to improve polymer mechanical properties, protect fabrics from UV and thermal degradation, dope conducting polymers, and act as a contrasting agent in electron microscopy for imaging phases of polymer blends. Recently, our group has explored a new application for VPI, the

protection of thermoplastic polymers from solvent dissolution. In this study, poly(methyl methacrylate) (PMMA) thin films were infiltrated with trimethylaluminum (TMA) and water at different temperatures and to different depths of infiltration. The resultant AlO_x / PMMA hybrid films were then exposed to a variety of solvents to explore their stability. Chemical stability was found to vary non-linearly, with infiltration temperature. Films infiltrated at lower temperatures (70C and 100C) swelled or partially dissolved in good solvents for neat PMMA, such as toluene or chloroform, and partially dissolved in isopropanol and water, which are not good solvents for PMMA (Fig 1). In comparison, films infiltrated at higher temperatures (130C) showed enhanced solvent stability in most solvents, even those that dissolved neat PMMA. The increased solvent resistance is likely due to crosslinking between PMMA functional groups and TMA molecules, a reaction that has been reported to vary with temperature. Due to this variability, PMMA films infiltrated at low temperatures are only partially crosslinked while those infiltrated at high temperatures are fully crosslinked, making them more solvent resistant. The increased dissolution of hybrid films in certain alcohols and polar solvents is hypothesized to result from an interaction between the inorganic crosslinker and the solvent. We also found that complete transformation of the polymer into hybrid material was unnecessary for dissolution resistance at higher temperatures. An infiltration depth of 0.5 mm was sufficient for complete resistance to toluene dissolution at room temperature. For proof-of-concept, we applied this treatment to a quarter inch thick laser-etched PMMA sheet and then exposed it to toluene at 60C for 10 minutes. While the design on the neat PMMA version rapidly dissolved, the sheet with a 0.5 mm AlO_x / PMMA subsurface layer showed nearly complete retention of its design (Fig 2). In this talk, we will explore these findings and discuss the differences in solvent stability of AlO_x / PMMA hybrid materials as a function of temperature as well as investigate the underlying chemical and structural variations that yielded these results.

11:20am **TF1-WeM11 Atomic and Molecular Layer Deposition of Hybrid Mo-thiolate Thin Films**, *Jingwei Shi, C. Maclsaac, L. Zeng, S.F. Bent*, Stanford University

As a member of the two-dimensional transition-metal dichalcogenides (TMDs) family, MoS_2 has attracted great attention since it possesses unique and desirable properties for optical, electrical, and electrochemical applications. MoS_2 derives many of its interesting properties from its bonding structure, such as its direct band gap from the lack of interlayer interactions, and its good electrocatalytic performance from defect and edge Mo-S sites. Therefore, a material that contains Mo-S motifs while also lacking the long-range order found in MoS_2 may be an interesting system to study.

To this end, we recently reported the synthesis of a Mo-thiolate thin film utilizing a combination of atomic layer deposition (ALD) and molecular layer deposition (MLD) with molybdenum hexacarbonyl and 1,2-ethanedithiol as precursors. ALD and MLD are vapor deposition techniques that may allow engineering of thickness dependent properties through its inherent angstrom-level control. The Mo-thiolate class of materials synthesized previously contained Mo-S bonding as well as aliphatic ethyl carbon chains. In this work, we extend and compare that system with the deposition of Mo-thiolate films containing butyl and benzyl organic linkers. The new process utilizes molybdenum hexacarbonyl and 1,4-butanedithiol or 1,4-benzenedithiol as precursors. The 1,4-butanedithiol and 1,4-benzenedithiol contains the S-R linkages, and the Mo-S linkages are created during each half-cycle reaction. Ellipsometry measurements of film thickness with precursor pulse time show that this system has a saturating growth rate. The measured growth rate is 1.0 \AA per cycle for Mo-butanethiolate and 1.5 \AA per cycle for Mo-benzenethiolate, at a deposition temperature of 170 C . X-ray photoelectron spectroscopy (XPS) shows that the material is compositionally similar to the predicted elemental ratios. XPS analysis also shows the presence of Mo(VI) as well as oxygen contamination, suggesting some non-idealities to the process.

Key differences between the Mo-thiolate hybrids and MoS_2 are revealed when post-deposition annealing treatments are performed on the Mo-thiolate films. Due to the existence of carbon linkages in the Mo-thiolate films, the annealed films show signatures in Raman spectroscopy not only of crystalline MoS_2 but also of graphitic carbon. We further explore the differences in optical properties between the three compositionally distinct Mo-thiolates. Through this systematic comparison study, we aim to understand the role of different molecular linkages in the Mo-thiolate framework, which may be beneficial for the deliberate design of hybrid thin films based on their desired properties.

Wednesday Morning, October 23, 2019

11:40am **TF1-WeM12 Electroactive Thin Films of Conjugated Polymers: Energy Conversion and Storage**, *Shayan Kaviani, E. Tavakoli, S. Nejati*, University of Nebraska-Lincoln

Platinum group metals (PGM), transition metals, and metal oxides have been extensively studied as efficient catalysts in electrochemical energy conversion devices. Nonetheless, these catalysts have the drawbacks of susceptibility to poisoning and the high cost. To realize widespread application of cost-effective, clean and renewable energy conversion devices—based on electrocatalytic reactions, e.g. metal-air batteries—there is a need to develop alternative electrocatalysts. Conjugated polymers, as carbon-based metal-free materials possess electroactive properties with tunable optoelectronic properties. Here, we demonstrated a successful method to design and apply thin coats of these polymers on a high surface area gas diffusion layers to develop efficient air-cathode electrode for zinc-air batteries. We use oxidative chemical vapor deposition (oCVD), as a unique liquid-free and substrate-independent technique, and enable cross-coupling reaction of heterocyclic monomers and doping of the resulting films in a single step with high precision. We investigated the properties of a series of thiophene-based conjugated polymers. We used volatile liquid oxidants such as antimony pentachloride and gained control over dehydrocoupling polymerization reactions rate of thiophene derivatives. We showed that our oCVD processing conditions have a direct influence on the properties of the deposited films. By adjusting the oCVD settings, we deposited smooth (roughness factors < 1 nm) and conformal coatings of conjugated polymers on a variety of substrates. We showed that by tailoring the chemistry of monomers, we can tune the electrochemical properties of the oCVD-polymers. For instance, in the case of poly(thiophene) and poly(3,4-ethylenedioxythiophene) (PEDOT), the onsets of the oxygen reduction reaction (ORR) overpotential are measured to be 0.61 V and 0.76 V vs reversible hydrogen electrode (RHE) [1]. Populating the monomer structure with heteroatoms, we recorded an enhanced electroactivity—comparable to Pt/C—for polymeric domains of poly(3,4-ethylenedithiathiophene) (PEDTT). The electron transfer number for ORR in these polymers, follows the trend of electrocatalytic activity; the higher electroactivity, the higher number of electrons transferred. More interestingly, PEDTT shows high electroactivity toward oxygen evolution reaction (OER) with overpotential onset of 1.72 V vs RHE. This observation makes oCVD PEDTT, the first conjugated polymer with bifunctional electroactivity in oxygen reactions.

1. Kaviani, S., et al., *Electroactive and Conformal Coatings of oCVD Polymers for Oxygen Electroreduction*. ACS Applied Polymer Materials, 2019 1 (3), 552-560.

12:00pm **TF1-WeM13 Enhancing the Key Properties of CVD Polymer Thin Films for Device Fabrication**, *Xiaoxue Wang*, The Ohio State University; *K.K. Gleason*, Massachusetts Institute of Technology

In the last decade, the rapid development of the flexible and stretchable (soft) electronics has been largely fueled by the fundamental breakthrough in soft materials synthesis and new fabrication technologies. Among the soft electronic materials, polymers stand out due to their merits of high stretchability, biocompatibility, light weight, scalability and cost-efficiency. However, despite the great prospects of electronic polymers, several critical challenges still need to be addressed: (1) Key electrical properties, such as electrical conductivity (σ) and carrier mobility (μ) of polymers are still relatively low compared with conventional rigid semiconductors, and result in higher power consumption and lower operation speed; (2) Low thermal conductivity (κ) makes heat dissipation a critical issue; (3) Conventional solution-based processing technologies may pose wettability and compatibility issues for device fabrication on flexible substrates. Here we will present a synergistic approach to combat these challenges by using Chemical Vapor Deposition (CVD) technology as an effective tool. First, record high electrical conductivity (σ) and charge carrier mobility (μ) are achieved in poly(3,4-ethylenedioxythiophene) (PEDOT), with engineered crystallization and morphology implemented by CVD. We also build wafer-scale PEDOT-Si rectifier arrays operating at 13.56 MHz for RFID readers by direct CVD synthesis. Second, record high cross-plane thermal conductivity (>10x common polymers) is demonstrated in intrinsic poly(3-hexylthiophene) (P3HT) thin films by using a self-assembling CVD growth method. This method generates an extended chain structure with π - π stacking, and thereby significantly facilitates the thermal transport. Lastly, CVD's powerful capability in device application, with gas sensors as an example, will be presented. In summary, this work establishes an innovative method to effectively tune the key physical properties of polymers by CVD-based structure-property engineering on the molecular level. In addition, this work also has the potential to facilitate novel device

fabrication technologies and applications in artificial skin, bio-degradable sensors, stretchable photovoltaics and light emitting diodes (LEDs).

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