Thin Films
Room 115 - Session TF2-TuA

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

Moderators: Mark Losego, Georgia Institute of Technology, **Adriana Creatore**, Eindhoven University of Technology

4:00pm **TF2-TuA-8 Roll-to-Roll Photoinitiated Chemical Vapor Deposition of Polymer Films for Liquid-Repellent Textiles*, Trisha Andrew,*** University of Massachusetts - Amherst*; W. Viola, E. Chalouhi,* Soliyarn **INVITED**

Textile manufacturers currently use fluorocarbon based coatings/finishes to produce the liquid repellency that is now expected of fabrics in many contexts, including sporting apparel, upholstery, wall/floor covering, and personal protective equipment. However, it is increasingly apparent that these fluorocarbon chemicals spread throughout the global environment and bioaccumulate in groundwater and aquatic ecosystems because they cannot be chemically degraded by either naturally occurring microorganisms or prevalent atmospheric/oceanic/aquatic reactions. Selected vacuum-based coating processes, such as sputter coating and plasma-enhanced chemical vapor deposition, have been periodically explored over the past three decades to produce fluorine-free liquid repellent textile finishes. To date, the capital equipment and maintenance costs of continuous-process sputter coaters and similar plasma-based coaters, which require ultrahigh vacuum levels ($<10^{-6}$ Torr) to function, is too prohibitive for the textile industry to feasibly adopt. Further, historic experience has revealed that ultrahigh vacuum dependent processes have limited applicability in high-throughput textile finishing due to the microfibers and lint generated by most commodity textiles as they travel through a continuous process coater, which contaminate the process chamber and prevent pump down.

Recently, research spun-out from the University of Massachusetts Amherst and matured by Soliyarn Inc. has validated the concept and manufacturing readiness of photoinitiated chemical vapor deposition (piCVD) as a sustainable process for textile finishing. piCVD is a low-vacuum process during which a photoinitiated chain growth polymerization reaction is enacted within a custom-designed reactor to produce surface-grafted, functional polymer coatings on a diverse selection of substrates, including synthetic and naturally-derived woven or knit fabrics. Informed monomer choice has lead to the development of fluorine-free polymer coatings that match or outcompete commercial water-repellent finishes. With informed selection of high quantum yield molecular photoinitiators and coupled mechanical engineering design to optimize vapor delivery to the fabric surface(s), piCVD can be executed over large areas in a continuous, roll-to-roll format under mild vacuum (<1 torr). During this talk, we will survey the major design features of our roll-to-roll piCVD coater, detail the learning milestones that lead to the conception, improvement and optimization of this system and highlight the properties of the liquid-repellent finishes created via piCVD.

4:30pm **TF2-TuA-10 Battery Separators with Ultrathin iCVD-Polymer Coatings Mitigate Polysulfide Crossover in Lithium-Sulfur Batteries*, Ramsay Nuwayhid,*** *H. Ford, J. Yeom, C. Love, J. Long, R. Carter,* U.S. Naval Research Laboratory

Lithium-ion batteries are approaching theoretical energy limits, necessitating development of advanced battery chemistries for critical applications. Lithium-sulfur (Li-S) batteries are an attractive alternative, due to the high abundance of sulfur in the earth's crust and high capacity of sulfur cathodes based on the conversion reaction of sulfur (S_8) to Li_2S. A major challenge in the practical implementation of Li-S batteries is the dissolution of intermediate lithium polysulfides formed during the conversion reaction, which react with the Li anode and sulfur cathode to form impeding interphases leading to loss of active material and poor cycle life. To overcome this technical challenge, we employ initiated chemical vapor deposition (iCVD) to conformally coat porous polyethylene separators used in Li-S cells to shield polysulfide crossover from the sulfur cathode to Li anode and enhance cycling performance. A novel copolymer, poly(divinylbenzene-co-(dimethylaminomethyl)styrene) (pDVB-co-DMAMS), is synthesized by iCVD and optimized to maintain cross-linking ability through DVB while the DMAMS functions to mitigate adverse polysulfide dissolution via specific adsorption at amine moieties. We first evaluate the electrochemical properties of pDVB-co-DMAMS in Li/Li symmetric cells through electrochemical impedance spectroscopy (EIS), demonstrating that iCVD-coated separators significantly reduce cell resistivity compared to cells with bare separators. Conformal coatings from 40-400 nm are evaluated in Li-S cells, in which thicker coatings show superior shielding of polysulfide cross-over through electrochemical self-discharge tests and UV-VIS spectroscopy. Furthermore, XPS and SEM analysis of the Li metal anode post-cycling reveals less crossover of polysulfide species and a smoother surface morphology for cells with iCVD-coated separators. Ultimately, 40 nm coatings are demonstrated to be the optimal thickness, maintaining high porosity of the separator and enabling high capacity retention at high gravimetric rates based on sulfur loading. Overall, this work demonstrates iCVD as a promising technique to stabilize reactive interfaces in beyond Li-ion battery systems.

4:45pm **TF2-TuA-11 Synthesis and Characterization of Ion Beam Nano-Engineered Metal-Polymer Nanocomposite Thin Films for SERS Application*, Jai Prakash,*** National Institute of Technology Hamirpur, India*; H. Swart,* University of the Free State, South Africa

Ion beam induced nano-engineering of thin film surfaces provides a unique way to tailor the surface properties for various functional applications. Ion beam induced sputtering and bi-layer interface mixing lead to nanopatterning of the surfaces with unique morphologies that are useful for a variety of applications. The present work deals with nanopatterning of thin noble metal films (deposited by e-beam evaporation) on polymer surfaces, deposited with different techniques, such as chemical vapour deposition or spin coating. Ion beam induced nano-engineering creates noble metal nanoparticles on surfaces or embedded nanoparticles within the polymer films. Such noble metal nanoparticles exhibit unique optical properties due to their localized surface plasmon resonance properties. Synthesis and characterizations (RBS, SIMS etc.) of such ion beam nano-engineered surfaces with unique optical properties for SERS applications will be discussed, with an emphasis on the role of ion beam synthesis and tailoring of surfaces.

5:00pm **TF2-TuA-12 In situ Analysis of Temperature Dependence During Molecular Layer Deposition of Polyurea*, Wallis Scholl,*** Colorado School of Mines*; T. Lill, H. Singh, M. Wang,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

The use of molecular layer deposition (MLD) in practical applications is hindered by the lack of a well-defined temperature window and low growth per cycle (GPC), which is often much less than one repeat unit of the polymer chain. Multiple studies report a lower GPC at higher deposition temperatures, and as a result MLD is typically conducted at room temperature.The mechanism behind this temperature dependence is not well understood; different sources attribute lower GPC at higher temperatures either to an increased rate of double reactions, where both functional groups in a bifunctional molecule react with the surface, or to a lower degree of physisorption of the growth precursors onto the film's surface.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy as well as *in situ* ellipsometry to monitor the film composition and thickness throughout MLD of polyurea film using toluene diisocyanate (TDIC) and ethylene diamine (ED) as precursors. The polyurea films were deposited at 0, 22, and 45 C. In agreement with previous literature (see Figure 1), over 25 MLD cycles, we observed a lower GPC at higher temperatures. The infrared spectra recorded during MLD reveal the temperature dependence of the chemical reactions and precursor physisorption. The amide I/II bands observed in the infrared spectra are related to the polyurea linkage, and indicate film growth. We find that the integrated absorbance for the amide I/II bands decreased with increasing temperature during both half cycles (see Figure 2). Further, we show evidence that precursor physisorption is the main cause for the temperature dependence of MLD. The two MLD precursors have different probability of double reaction and physisorption, and we typically observe a larger increase in integrated absorbance for the amide I/II modes during the TDIC half-cycles compared to the ED half-cycles. This discrepancy suggests that ED is more likely to physisorb than TDIC into the film and not form the polyurea linkages by reaction with the isocyanate groups. Additionally, the degree of physisorption of ED increases as the temperature is lowered. During the TDIC half-cycle, polyurea linkages are created due to chemical reaction between the physisorbed ED molecules. This also implies that to maintain a linear growth rate, as the temperature is lowered, site balance is achieved by a higher degree of double-reactions of TDIC.

5:15pm **TF2-TuA-13 Multi-Stimuli Responsive Sensors for Electronic Skin Applications*, Anna Maria Coclite,*** University of Bari, Italy **INVITED**

Embedding sensors in smart architectures that record the response from the environment and transform it in a measurable signal is the objective of artificial skins. In this talk, a smart skin based on a single novel multi-stimuli responsive material, combining force, temperature and humidity sensing will be presented. The new sensor concept is realized by combining a hydrogel and piezoelectric zinc oxide (ZnO) in an array of core-shell structures.[1] This architecture is achieved thanks to the use of vapor-based technologies for material processing, i.e. initiated chemical vapor deposition, atomic layer deposition and nanoimprint lithography. We demonstrate that the skin can detect the stimuli with lateral resolution below the one of human skin. While the piezoelectricity of ZnO provides sensitivity to external force, the thermoresponsiveness of the hydrogel core provides sensitivity to surrounding temperature and humidity changes. The hydrogel core exerts mechanical stress onto the ZnO shell, which is translated to a measurable piezoelectric signal. A localized force sensitivity of 364 pC N^{-1} is achieved with very low cross talk between 0.25 mm^2 pixels. Additionally, the sensor's sensitivity to humidity is demonstrated at 25 and 40 °C, i.e., above and below the hydrogel's lower critical solution temperature (LCST) of 34 °C. The largest response to temperature is obtained at high humidity and below the hydrogel's LCST.

We also demonstrate that the use of a multi-chamber reactor enables performing the ZnO and hydrogel depositions, sequentially, without breaking the vacuum.[2] The sequential deposition of uniform as well as conformal thin films responsive to force, temperature and humidity improved the deposition time and quality significantly. Proper interlayer adhesion could be achieved via in situ interface activation, a procedure easily realizable in this unique multi-chamber reactor. Beyond the fabrication method, also the mechanical properties of the template used to embed the core-shell nanorods and the crosslinker density in the hydrogel were optimized following the results of finite element models. Finally, galvanostatic electrochemical impedance spectroscopy measurements showed how temperature and humidity stimuli have different effects on the device impedance and phase and these differences can be the base for stimuli-recognition.

Possible applications stem from robotics to smart prostheses. Smart skins could monitor human breathing, pulse and temperature or detect dehydration.

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