Emerging Materials
Room Jan & Hubert Van Eyck - Session EM-WeA
Organic and Organic-Inorganic Hybrid Materials II & III

Moderators: Tero Pilvi, Picosun Oy, Ganesh Sundaram, Veeco-CNT

1:15pm **EM-WeA-2 Enhanced Stretchability in Inorganic-Organic Alucone Thin Films Deposited from Long-Chain Organic Precursors***, **Janne-Petteri Niemelä**, N Rohbeck, J Michler, I Utke,* Empa, Switzerland

Molecular layer deposited (MLD) hybrid inorganic-organic materials ("metalcones") have recently received increasing attention, largely due to their potential for applications demanding mechanical stretchability/flexibility.[1,2] Alucones (Al-based hybrids) are among the most studied metalcones owing to e.g. their promising performance as an electrode-electrolyte interface layer in Si-nanoparticle based batteries, where the charging/discharging cycles involve huge volumetric changes up to 300 %.[3] The research on mechanical (and battery) properties of metalcones is limited to the materials based on short-chain organic precursors,[4] while increasing the precursor chain length is an unexplored but rational route for enhancing mechanical performance of the metalcone thin films.

In this work we deposited alucone thin films using trimethyl aluminum (TMA) as the Al metal precursor, and 1,2-ethanediol (EG), 1,6-hexanediol (HD) and 1,10-decanediol (DD) as the organic precursors. The TMA/HD and TMA/DD processes were studied at 130 °C: they exhibit MLD-type behavior with self-saturating surface reactions, and linear film growth (studied up to 150-200 nm) with the growth-per-cycle values of 0.32 and 0.37 nm, respectively. Mechanical stretchability was studied via tensile testing coupled with in-situ optical microscopy for 100-nm alucone films deposited on the stretchable polyimide substrates. The critical strain for fracture was enhanced up to around 9 % for the alucone films deposited via the TMA/DD process. This value is more than an order-of-magnitude higher than the value for purely inorganic Al_2O_3 and represents a factor-of-four increase in comparison to the EG-based alucone material (the state-of-the-art for the metalcones). The 9-% critical strain translates to critical volume expansion of 300 % for (battery-relevant)[3] around 3-nm coating thickness on a nanoparticle surface (assuming a spherical particle and inverse-square-root thickness extrapolation for the critical strain), and to 0.25-mm critical bending radius on the 50-µm substrate. The film structure is moreover studied via the XRR, FTIR and SEM techniques, while the mechanical properties are further analyzed via nanoindentation.

The present results highlight that the potential of the MLD technique can be further enhanced by exploring a wider space of larger/longer/complex organic precursor molecules instead of the conventionally used small molecules.

(1) X. Meng, J. Mater. Chem. A, 2017, 5, 18326.; (2) J.-P. Niemelä et al., J. Mater. Chem. C, 2015, 3, 10349. (3) D. M. Piper, et al., Nano Energy, 2016 22, 202. (4) M. Ruoho, I. Utke et al., Mater. Today Chem. 10 (2018) 187.

1:45pm **EM-WeA-4 Self-Terminating Molecular Layer Deposition of Polyurea and Growth Rejuvenation via Precursor Linking Group Selection***, **Rachel A. Nye**, G Parsons,* North Carolina State University

Molecular layer deposition (MLD) has recently been explored due to the vast tunability of film properties and growth conditions. Polyurea coupling by MLD commonly proceeds by reacting molecules with diisocyanate functional groups (such as p-phenylene diisocyanate, PDIC) with other molecules containing diamine functional groups (such as ethylenediamine, ED). Under steady-growth conditions at 60°C, the PDIC/ED sequence typically leads to continuous film growth of ~0.41 nm/cycle. Recently, we discovered a modified polyurea MLD reaction that shows a growth trend very different from commonly reported processes. Specifically, we find that using 1,6-hexanediisocyanate, HDIC, in place of PDIC, causes a significantly lower film growth rate: less than 0.1 nm/cycle even at temperatures as low as 40°C.

Additionally, the low growth rate obtained from the HDIC/ED reaction continues to decrease with increasing cycle number. This significant change in polyurea growth rate is achieved simply by varying the organic linker groups, while maintaining the same urea coupling chemistry. Interestingly, the low growth rate of the flexible HDIC/ED can be increased by incorporating the aromatic PDIC compound into the overall polymer structure. Thus, the self-terminating and rejuvenating growth of aliphatic polyurea can be controlled with aromatic composition. The entirely flexible HDIC/ED polymer is very difficult to grow to a thick film, but incorporating small amounts of benzene enable deposition of a much thicker film without significantly affecting film properties. These trends are likely due to high frequency of double reactions for the entirely aliphatic HDIC and ED precursors. The rigid benzene ring in the PDIC precursor then seems to promote a more rigid structure that reduces the number of site-terminating reactions and enhances growth. This self-limiting and rejuvenating growth is of potential interest for the field of area selective deposition. Additionally, the ability to modulate polymer growth rates with the incorporation of benzene rings has significant implications to the development of new precursors and polymer thin film properties.

3:00pm **EM-WeA-9 Vapor-Phase Infiltration Synthesis of Organic-Inorganic Hybrid Nanocomposite Resists for Next-Generation Nanolithography***, N Tiwale,* Brookhaven National Laboratory*; A Subramanian,* Stony Brook University*; K Kisslinger, G Freychet, M Lu,* Brookhaven National Laboratory*; J Kim,* University of Texas at Dallas*; A Stein, **Chang-Yong Nam**,* Brookhaven National Laboratory

Vapor-phase infiltration (VPI), a material hybridization technique derived from atomic layer deposition, can generate molecular-scale organic-inorganic nanocomposites with uniquely enhanced material properties by utilizing the infiltration and binding of gaseous organometallic precursors within organic media. In this study, we report the application of VPI on developing new organic-inorganic hybrid polymer resists for the next-generation nanolithography. Hybrid resists are emerging as an effective way of addressing stringent process requirements for aggressive down-scaling of semiconducting devices. However, hybrid resists generally require complex chemical synthesis while being predominantly negative-tone with high exposure dose requirement. For positive-tone processes and high-aspect-ratio pattern transfer, resist choices are limited to costly non-hybrid alternatives, whose etch resistance is still inferior compared with hybrid resists. Here, demonstrated is a novel hybrid positive-tone resist platform utilizing simple *ex-situ* VPI of inorganic components into standard resist materials. A model system based on poly(methyl methacrylate) (PMMA) thin film hybridized with AlO_x has been demonstrated for electron-beam lithography patterning, featuring fully controllable critical exposure dose, contrast, and etch resistance. The hybrid resist not only achieves exposure contrast as high as ~30, a six-fold enhancement over standard PMMA, but also enables Si nanostructures with resolution down to ~30 nm and aspect ratio up to ~17, owing to extremely high Si etch selectivity far exceeding those in known commercial positive-tone resist systems. Interrogation of the effect of varying etching protocols on etch rate reveals a surprisingly high enhancement of chemical etch resistance over the physical one with increasing amount of infiltration, which we attribute to the strong chemical biding between infiltrating Al precursor, trimethylaluminum (TMA), and carbonyl group in PMMA. Also briefly discussed is the electron-beam-induced exposure mechanism (i.e., change in solubility) in the hybrid resist probed by synchrotron X-ray absorption spectroscopy as well as other hybrid resist systems being developed for extreme ultraviolet (EUV) lithography application, where the infiltrated inorganic elements can potentially improve not the etch resistance but also EUV sensitivity and other resist performance parameters. The easy implementabilility, combined with versatile *ex-situ* control of resist characteristics, makes this hybrid resist synthesis approach uniquely suited for addressing the resist performance required for advanced next-generation nanolithography techniques.

3:45pm **EM-WeA-12 Synthesis of SiAlCO Polymer Derived Ceramics (PDC) Thin Films using Molecular Layer Deposition***, **Kristina Ashurbekova**,* Dagestan State University, Russian Federation*; E Modin, A Chuvilin, M Knez,* CIC nanoGUNE BRTA, Spain*; I Abdulagatov,* Dagestan State University, Russian Federation

Organosilicon PDC materials and its derivatives have gained interest for various important applications such as electrode material for lithium-ion batteries, ultra-high temperature composites and others [1]. Conventionally, PDC coatings are prepared by wet-chemical dip, spin, thermal-spray coating or by plasma-assisted chemical vapor deposition (CVD), followed by high temperature pyrolysis [2].

In this work, molecular layer deposited (MLD) hybrid organic-inorganic films serve as precursors for a synthesis of SiAlCO PDC composite coatings. Alumina-polysiloxane films were grown using 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V_4D_4) and trimethylaluminum (TMA) (Supplemental Figure 1). The deposition was conducted at temperatures between 120 and 220°C. An *in-situ* quartz crystal microbalance (QCM) study showed linear mass increase with the number of MLD cycles with the highest growth rate of 24 ng/cm^2/cycle occurring at 180^{o}C. QCM measurements revealed a self-limiting surface chemistry of the MLD process. FTIR analysis of deposited films showed vibrational features characteristic of organosilicon polymers: Si-CH$_3$, Si-O-Si, Si-CH=CH$_2$ and Si-O-Al peaks (Supplemental Figure 2).

Upon growth of the film, cross-linking is needed to increase the mass yield during the polymer-to-ceramic transformation. Cross-linking was achieved at 200^{o}C by introducing a third precursor, di-tert-butyl peroxide (TBP), into the MLD process, following a V$_4$D$_4$/TBP/TMA sequence. The thus obtained films were pyrolyzed at 900^{o}C in an Ar atmosphere. XRR, XRD, Raman, HRTEM, and EDX were applied for characterization of the films. After pyrolysis, the composite thin film remained amorphous. The final film contained Si, Al, O, and C uniformly distributed throughout the film. Raman spectroscopy showed presence of graphitic carbon within the film. This MLD-derived SiAlCO thin film is expected to have exceptional high temperature stability, creep, and corrosion resistance.

[1] P. Colombo, et al., *J. Am. Ceram. Soc.,***93** (7), 1805–1837 (2010)

[2] G. Borroso, et al, *J. Mater . Chem. A.,* **7**(5), 1936–1963 (2019)

Author Index

Bold page numbers indicate presenter