

Thin Film

Room: Pecos - Session TF-MoA

Organic ALD

Moderator: G.N. Parsons, North Carolina State University

2:00pm **TF-MoA1 Inorganic/Organic Interface Structure on ALD Modified Polymer Fibers**, *J.S. Jur, J.C. Spagnola, W.J. Sweet, B. Gong, Q. Peng, G.N. Parsons*, North Carolina State University

Inorganic thin film growth by atomic layer deposition (ALD) on polymer fibers is shown to be significantly affected by the process conditions and materials. Transmission electron microscopy in combination with *in situ* quartz crystal microbalance analysis shows a strong influence on processing temperature and polymer backbone structure that can lead to varying types of interface modifications between the inorganic and organic polymer. Deposition on cellulose cotton shows conformal surface growth due to the presence of hydroxyl sites, resulting in conformal thin film growth. Polypropylene, which has no reactive sites, does allow for vapor phase diffusion of the ALD precursors, resulting in subsurface growth. The subsurface growth on polypropylene is significantly impeded at lower processing temperatures. The strong temperature dependence of interface modification is ascribed to a relatively large increase in bulk species diffusivity that occurs upon the temperature-driven free volume expansion of the polymer. The interface structure can significantly modify the physical properties of resulting inorganic-coated polymer fibers. For example, we measured the electrical properties of ALD ZnO coatings on polypropylene fiber mesh, and we find that modifying the polymer inorganic interface using low temperature ALD Al₂O₃ before ZnO ALD produces fibers with conductance that is increased by a factor >100x as compared to ZnO coated polypropylene without the interface pretreatment. For a range of polymer materials studied, we find distinct trends between polymer structure, ALD process conditions and resulting interface structure, and these results will be presented and discussed.

2:20pm **TF-MoA2 Molecular Layer Deposition of Hybrid Siloxane/Alumina Polymer Films**, *A.I. Abdulagatov, B. Yoon, V.R. Anderson, Z.M. Gibbs, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Polydimethylsiloxane (PDMS) is an important polymer with excellent flexibility and low elastic modulus. The properties of PDMS are also tunable based on varying the cross-linking between the polymer chains. PDMS MLD was initially attempted using the sequential dosing of bis(dimethylamino)dimethylsilane or dimethylmethoxychlorosilane (DMMCS) and water at different temperatures. Unfortunately, the surface reactions appeared to terminate and no mass gain was measured after about 20 MLD cycles. After precursor dosing was stopped, the deposited film was observed to decrease in mass. This loss of mass is believed to be related to desorption of cyclic siloxanes from the PDMS MLD film. Cyclic siloxane desorption is entropically favored at longer PDMS chain lengths and higher temperatures and is facilitated by the high flexibility of the PDMS chains. To prevent desorption of the cyclic siloxanes, hybrid siloxane/alumina films were grown by mixing aluminum into the siloxane film using trimethylaluminum (TMA). The new hybrid MLD films contain [-Si(CH₃)₂-O-] units that are separated by [-Al-O-] linkages. The hybrid siloxane/alumina polymer films were grown using the precursor sequence: DMMCS; H₂O, TMA; and H₂O. Quartz crystal microbalance studies revealed linear growth with growth rates of ~22 ng/cm² at 200°C. FTIR vibrational studies revealed -Si(CH₃)₂OCH₃, -Si(CH₃)₂OH, -AlCH₃, and -AlOH surface species after the DMMCS; H₂O, TMA; and H₂O exposures, respectively. FTIR studies also observed self-limiting adsorption during the individual precursor exposures. X-ray reflectivity (XRR) measurements revealed a hybrid siloxane/alumina growth rate of ~1.0 Å/cycle at 200°C and a film density of ~2.3 g/cm³. Elemental analysis of films using X-ray photoelectron spectroscopy (XPS) indicated that the films were chlorine-free. Hybrid siloxane/alumina polymer films could be grown at temperatures as low as 120°C, and these films showed some chlorine impurities.

2:40pm **TF-MoA3 Quantum Chemical Simulations of ALD and MLD; Insights from Simulations**, *C. Musgrave*, University of Colorado at Boulder

INVITED

Ab Initio simulations have become widely used tools in the materials, surface science and chemistry communities for predicting molecular and materials properties and for studying atomistic processes. In this talk we will give an overview of how these methods can be used to understand ALD

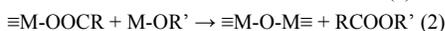
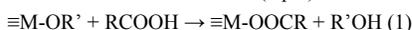
and MLD from an atomistic viewpoint and what you can learn from simulations. We will also discuss the limits of quantum chemistry and provide guidelines for those interested in using simulations to study ALD. Examples from our past and current work as well as that of others will be used to illustrate the application of these methods to surface reactions relevant to ALD and MLD. Examples include; the effect of using precursors with different ligands, including alkoxides, alkylamides and halogens, to deposit HfO₂ and Al₂O₃; the effect substrate type and functionalization on the initial ALD nucleation reactions; the ability to grow oxynitrides; and the use of simulations as a computational spectroscopy tool to compliment experiment in the determination of ALD intermediates and products.

3:40pm **TF-MoA6 Nonaqueous Sol-Gel Chemistry in Atomic Layer Deposition**, *N. Pinna*, University of Aveiro, Portugal and Seoul National University, Korea

INVITED

Nonaqueous sol-gel routes are elegant approaches for the synthesis of high quality metal oxide nanomaterials such as pure inorganic nanocrystals [1], ordered hybrid organic-inorganic materials [2] or thin films by atomic layer deposition (ALD) [3]. In this communication, after a short introduction to nonaqueous sol-gel chemistry we will focus on the ALD using nonaqueous sol-gel. In particular, the similarities and differences of the chemical processes taking place in solution and in ALD will be discussed through two examples of recent approaches of metal oxide film deposition

Our approach makes use of metal alkoxides and carboxylic acids as metal and oxygen source, respectively [4]. In the first step, it is expected that the reaction of surface alkoxide species with carboxylic acids leads to surface carboxylate species (eq. 1). In the second step an aprotic condensation reaction between surface carboxylate species and metal alkoxides leads to metal-oxide bonds formation (eq. 2).



This process enables the growth of metal oxides at temperatures as low as 50 °C on various supports.

A comparison of this nonaqueous sol-gel route to ALD approaches using ozone as oxygen source will be made. Although, from a first look it seems that the chemistry responsible for metal oxide formation is very different, this is certainly not the case. As a matter of fact it was recently reported that during the ALD of metal oxides, the exposure to ozone leads to formate, carbonate and hydroxyl groups on the surface [5-7]. According to Goldstein et al., a large amount of formate surface species were formed by the reaction of trimethylaluminum (TMA) and O₃ [5]. Therefore, the formation of surface carboxylic species upon reaction with ozone leads to similar surface states as in the case of reaction with carboxylic acids [4]. These findings will be used to discuss the chemical reactions responsible for the deposition of PbTiO_x using lead bis(3-N,N-dimethylamino-2-methyl-2-propoxide), titanium(IV) isopropoxide and a combination of water and ozone as oxygen sources as recently reported by Hyun Ju Lee et al. [8]

References:

- [1] Pinna, N. & Niederberger, M. *Angew. Chem. Int. Ed.*, **2008**, *47*, 5292
- [2] Pinna, N. *J. Mater. Chem.*, **2007**, *17*, 2769
- [3] Clavel, G. et al. *J. Mater. Chem.*, **2009**, *19*, 454
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- [6] Rai, V. R.; Agarwal, *J. Phys. Chem. C*, **2008**, *112*, 9552
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- [8] Lee, H. J. et al. *ECS Transactions*, **2009**, *19*, 829

4:20pm **TF-MoA8 Combined Atomic Layer Deposition and Molecular Layer Deposition for Encapsulation of Electrospun Nylon Nanofibers**, *C. Oldham, B. Gong, J.C. Spagnola*, North Carolina State University, *K. Senecal, T. Godfrey*, Natick Soldier RD&E Center, *J.S. Jur, G.N. Parsons*, North Carolina State University

Electrospun nanofibers are of interest for air filtration, thermal insulation, biochemical sensing, and a range of other applications. Nanofibers can be readily electrospun from polyamide-6 (PA-6) nylon, but nylon is highly susceptible to water uptake and rapid degradation when exposed to chemical reactants, including those used in ALD. The high surface area of nanofibers makes these issues more acute and difficult to manage. We have recently investigated the deposition of Al₂O₃ and ZnO on nylon nanofibers and found distinctly different results for these two material processes. Aluminum oxide ALD from trimethylaluminum and water resulted in significant fiber degradation, whereas fibers remained intact upon ALD using diethyl zinc and water. The ZnO coating was not sufficient, however,

to impede attack and degradation during subsequent exposure to Al₂O₃ ALD using TMA. We have recently explored a new MLD process in our lab using TMA and glycidol, where the resulting film is a hybrid organic-metal oxide polymer. This MLD coating onto a ZnO-coated nylon nanofiber results in only minimal reaction with the polymer under the ZnO. After 75 MLD cycles, exposing the nylon nanofibers to 25 cycles of trimethylaluminum/water results in no visible degradation, indicating successful encapsulation by the ZnO/MLD bilayer. We will present the chemistry associated with the reaction between the TMA and PA-6. Additionally, the surface chemistry of the PA-6 nanofibers after encapsulation, and the air stability of the hybrid organic-metal oxide coatings will be discussed.

4:40pm **TF-MoA9 Structure and Properties of Ultra-High Molecular Weight PHEMA Synthesized Using Solvent-Free Initiated Chemical Vapor Deposition (iCVD), R.K. Bose, K.K.S. Lau, Drexel University**

Initiated chemical vapor deposition (iCVD) is a low temperature variant of hot-wire chemical vapor deposition (HWCVD) which has been used to produce a wide variety of free radical polymers like fluoropolymers, acrylic polymers and silicone polymers without the use of solvents. An initiator is activated in the gas phase by a resistively heated filament array. The radicals thus generated undergo surface polymerization on a cooled substrate by attaching to multiple monomer units. In this work, we produced thin films of poly(2-hydroxyethyl methacrylate) (PHEMA), an important hydrogel, for potential biomaterials applications such as skin substitutes. Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies showed that the chemistry of PHEMA obtained by iCVD synthesis matched closely to PHEMA obtained from solution synthesis. Deposition kinetics were tuned to achieve high deposition rates (~1.5 μm/min), which yielded mechanically robust ultra-high molecular weight polymer films. As a result, the films displayed a high degree of physical chain entanglement giving rise to high tensile modulus and storage modulus. This eliminates the need for chemical crosslinking, thus preserving maximum hydrophilicity for cell growth. The films showed good water transport and swellability. *In vitro* cytotoxicity studies of adult human dermal fibroblasts on PHEMA showed these films were non-cytotoxic and displayed viable cell adhesion. Non-specific protein adsorption was shown to be reduced compared to controls.

5:00pm **TF-MoA10 Molecular Layer Deposition of Alucones Using Trimethylaluminum and Glycerol or Glycidol, R.A. Hall, B. Yoon, Y. Lee, S.M. George, University of Colorado at Boulder**

Molecular layer deposition (MLD) can be used to grow hybrid organic-inorganic films using organic MLD and inorganic ALD precursors. The alucones are the most studied of these hybrid organic-inorganic films. Alucone MLD depends on the sequential, self-limiting reactions between trimethylaluminum (TMA) and various organic alcohols. In this work, alucone MLD was performed using glycerol, a sugar alcohol with three hydroxyl groups or glycidol, an alcohol molecule that contains an epoxide group. Both of these alcohols should promote cross-linking in the alucone film for enhanced film stability and film toughness.

Studies of alucone MLD using TMA and glycerol (GL) or glycidol (GLY) were performed using *in situ* quartz crystal microbalance (QCM), Fourier transform infrared (FTIR) and quadrupole mass spectrometry (QMS) techniques. The FTIR studies showed that the TMA and GL or GLY reactions were both self-limiting. For the TMA + GL reaction, the FTIR spectra observed the growth/loss of AlCH₃ and C-OH vibrations versus TMA/GL exposures. The mass gain measured by the QCM was 43 ng/cm²/cycle at 150°C. QMS confirmed the presence of TMA and GL parents and observed the CH₄ reaction products. *Ex situ* XRR measurements yielded a growth rate of 2.40 Å/cycle after 50 cycles at 150°C.

Alucone films grown using TMA and GL or GLY were more stable than alucone films grown using TMA and ethylene glycol. The instability of alucone films has been attributed to unreacted AlCH₃ species. To explore this issue, alucone films were grown using TMA, GL and H₂O exposures in an ABC sequence. QCM measurements showed that the mass gain increased to 56 ng/cm²/cycle for this ABC sequence at 150°C. In addition, the QMS observed CH₄ intensities during H₂O exposures that were ~1/4 the intensity observed during GL exposures. These results indicate that H₂O exposures can remove unreacted AlCH₃ species and increase the mass gain per cycle.

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