# Monday Morning, October 20, 2008

**Thin Film**
**Room: 302 - Session TF+NC-MoM**

**ALD of Hybrid Materials and ALD on 3D Nanostructures**
**Moderator:** S.M. Rossnagel, IBM T. J. Watson Research Center

8:20am **TF+NC-MoM1 Interfacial Organic Layers: Tailored Nucleation and Growth of Inorganic Thin Films for Applications in Molecular Electronics and Barrier Layers**, *J.R. Engstrom*, Cornell University **INVITED**
Interfacial organic layers, including self-assembled monolayers, have long been recognized for their potential to modify the chemical and physical properties of surfaces. One particularly exciting concept is to use interfacial organic layers to promote thin film deposition of inorganic materials, particularly in situations where nucleation is problematic. Another interesting concept involves making use of the organic layer itself as an active component in molecular-based electronics. Here, a challenge is to make electrical (top) contact with the organic layer, whilst not degrading its properties, nor forming electrical shorts due to penetration of the organic layer. Key to the realization of both of these concepts is developing an understanding of the interactions between thin film precursors, and interfacial organic layers possessing a variety of terminal organic functional groups and also microstructures. In this talk we will summarize our work in this area concerning: (i) the formation of the interfacial organic layers and their characterization; (ii) the reactions of these layers with Ti- and Ta-amido coordination complexes; and (iii) the formation of inorganic thin films on these layers using atomic layer deposition. Here we make use of supersonic molecular beam scattering techniques, atomic force microscopy, scanning transmission electron microscopy, and x-ray photoelectron spectroscopy. We will find that (undesired) penetration of the organic layers by the coordination complexes can be avoided and/or minimized by proper design of the organic layer. Concerning growth on the layers using atomic layer deposition, we find that the chemical termination and microstructure of the organic layers play an important role in terms of the kinetics of nucleation and growth, and the evolution of thin film morphology.

9:00am **TF+NC-MoM3 New Approaches to Molecular Layer Deposition Using Ring-Opening and Heterobifunctional Reactants**, *D. Seghete, B. Yoon, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder
Molecular layer deposition (MLD) can produce organic or hybrid organic-inorganic films. Current MLD schemes usually employ two homobifunctional monomers as reactants. This approach presents practical difficulties because the homobifunctional monomer can react with two chemical functional groups on the surface. These "double" reactions can remove the active surface species and reduce the MLD growth rate. Homobifunctional reactants can be avoided by using ring-opening and heterobifunctional reactants. The ring-opening reactants prevent double reactions by containing a concealed functionality that only expresses itself upon reaction. The heterobifunctional reactants have two chemical functional groups that are different. These precursors react only monofunctionally with the surface to avert double reactions and growth termination. In this study, we report a three-step MLD process that involves trimethylaluminum (an inorganic trifunctional reactant), ethanolamine (a heterobifunctional reactant), and maleic anhydride (a ring-opening reactant). The extension to three-step ABC MLD processes expands the variety of reactants and compositional diversity that can be achieved for MLD. In this three-step process, trimethylaluminum (TMA) reacts with carboxylic acid species (-COOH) to deposit -AlCH$_3$ species. The -AlCH$_3$ species then react preferentially with the hydroxyl end of ethanolamine (EA) to form a surface terminated with -NH$_2$ species. Maleic anhydride (MA) then reacts with these amine species and undergoes a ring-opening reaction to produce carboxylic acid (-COOH) species. The TMA can then react again with the carboxylic acid species to repeat the ABC cycle. In situ Fourier transform infrared spectroscopy and quartz crystal microbalance measurements were employed to monitor the surface reactions and measure the mass changes at temperatures from 80-150 ºC. Ex situ x-ray reflectivity (XRR) confirmed the linear growth of the MLD films versus number of ABC cycles. The growth rates decreased with increasing temperature from 23 Å per ABC cycle at 90 ºC to 8 Å per ABC cycle at 150 ºC. The XRR scans also established the low surface roughness, uniform composition and low density of the MLD films.

9:20am **TF+NC-MoM4 Molecular Layer Deposition of Hybrid Organic-Inorganic Polymers Based on Metal Alkyl and Diol Reactants**, *B. Yoon*, *J.L. O'Patchen, S.D. Davidson, D. Seghete, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder
Hybrid organic-inorganic polymers can be deposited by molecular layer deposition (MLD) using metal alkyl and diol reactants. Our earlier work studied the deposition of alucone MLD films using trimethyl aluminum (TMA) and ethylene glycol (EG). In this work, we extend the possible metal alkyl reactants to diethyl zinc (DEZ) and the diols to 1,4-butanediol (BD), and 1,4-hydroquinone (HQ). Our studies were performed using in situ Fourier transform infrared (FTIR) spectroscopy to identify the surface species, in situ quartz crystal microbalance (QCM) measurements to quantify the mass gains with each surface reaction, x-ray reflectivity (XRR) studies to measure the film thicknesses and densities and transmission electron microscopy (TEM) to image the MLD films on nanoparticles. The reaction of TMA and EG results in a poly(aluminum ethylene glycol) film that can be described approximately as (Al-O-CH$_2$CH$_2$-O)$_n$. These (Al-O-R-O)$_n$ polymer films are known as alucones. The reaction of DEZ with organic diols produces zinc-containing (Zn-O-R-O)$_n$ polymer films that can be called "zincones". FTIR spectroscopy studies revealed that the surface chemistry for zincone MLD was similar to alucone MLD. QCM measurements showed linear growth for zincone MLD versus number of reaction cycles. Corresponding XRR and TEM studies revealed zincone MLD growth rates of 2.0 Å per AB reaction cycle. Different organic constituents can be incorporated into alucone MLD films using other organic diols. Alucone MLD was studied using TMA + BD and TMA + HQ. QCM measurements showed linear growth with total mass gains of 30 ng/cm$^2$ for TMA + BD and 89 ng/cm$^2$ Using film densities obtained from XRR studies, these total mass gains represent growth rates of 2.3 Å and 5.4 Å per AB reaction cycle for TMA + BD and TMA + HQ, respectively. The larger growth rates for TMA + HQ may be explained by the greater rigidity of HQ that could prevent "double" reactions from reducing the number of active surface sites and lowering the growth rate per AB reaction cycle.

9:40am **TF+NC-MoM5 Infrared Analysis of Conformality of Al$_2$O$_3$ and ZnO Atomic Layer Deposition on 3D Fibrous Structures**, *G. Scarel*, *G.K. Hyde, J.C. Spagnola, J.-S. Na, B. Gong, Q. Peng, G.N. Parsons*, North Carolina State University
Conformally coated 3D natural fibers are becoming important in various areas of catalysis, bio-scaffolds, drug delivery, energy storage and conversion applications. In this work we report on growth and characterization of inorganic coatings (Al$_2$O$_3$ and ZnO) on fibers including cotton and polypropylene. The coatings were prepared using low temperature (about 100 degree centigrade) ALD. We used tri-methyl aluminum and H$_2$O for Al$_2$O$_3$ and di-ethyl zinc and H$_2$O for ZnO. ALD is well known to produce conformal coatings on planar surfaces and deep trenches. However it is more difficult to establish and to characterize linear growth and conformality in complex 3D fibrous systems. We have developed a new method to evaluate linear growth and conformality on complex nano- and micro 3D structures. The method uses infrared spectroscopy to detect longitudinal optical (LO) modes in off-normal configurations (Berreman effect). These features pertain to ionic oxides and are sensitive to film thickness because they are generated by vibrations normal to the ionic oxide layer surface. We show that the height of a peak related to an LO mode grows linearly with the number of ALD cycles and that this linear behavior is related to the linearity of the growth on a planar Si(100) substrate. In addition, the angular behavior of the height of peaks related to LO modes in transmission infrared spectra can be related to the degree of coating conformality. In addition the data show that on 3D structures, especially on fibers, the number of incubation cycles needed before linear growth starts is even higher than on planar substrates. We investigate this phenomenon considering the structural, compositional, and the surface energy properties of the coated structures. The method we propose offers an easy non-local method to ascertain linear growth and conformality on complex 3D samples coated using ALD.

10:20am **TF+NC-MoM7 Ferromagnetic Nanostructures by Atomic Layer Deposition: From Thin Films to Ferrofluids and Core-Shell Nanotubes**, *K. Nielsch*, Hamburg University, Germany, *J. Bachmann*, Hamburg University and Max Planck Institute of Microstructure Physics, Germany **INVITED**
Magnetic nanostructures have a broad range of applications, most prominently in the areas of data storage, microelectronics, biosensing, and cell separation. For the preparation of such structures, we use atomic layer deposition (ALD), a thin film technique with the unique ability to coat pore structures of high aspect ratio conformally and uniformly while accurately

tuning the layer thickness. We approach the preparation of the magnetic materials $Fe_3O_4$, Co, and Ni in two steps. ALD is first used to deposit $Fe_2O_3$,[1] CoO or NiO,[2] either from the reaction of the corresponding metallocene with ozone or from that between the metal alkoxide and water. The oxide is subsequently reduced to the desired ferromagnetic phase by hydrogen gas. By conformal coating of self-ordered porous anodic alumina membranes, arrays of magnetic nanotubes with diameters down to 20 nm and wall thicknesses of less than 5 nm have been achieved. The magnetic properties of the nanotube arrays, studied by SQUID magnetometry, strongly depend on the geometric parameters. The effects of tube wall thickness and tube diameter have been studied systematically,[1] and the experimental data match the results of our theoretical simulations.[3] Dissolution of the alumina matrix yields ferrofluidic suspensions, made out of widely tunable magnetic particles. Finally, ALD also enables us to create core-shell nanoobjects combining different magnetic materials in various, accurately controlled geometries.

[1] J. Bachmann, J. Jing, M. Knez, S. Barth, H. Shen, S. Mathur, U. Gösele, K. Nielsch, J. Am. Chem. Soc. 2007, 129, 9554-9555.

[2] M. Daub, M. Knez, U. Gösele, K. Nielsch, J. Appl. Phys. 2007, 101, 09J111.

[3] J. Escrig, J. Bachmann, J. Jing, M. Daub, K. Nielsch, D. Altbir, Phys. Rev. B 2008, accepted.

**11:00am** **TF+NC-MoM9 Tube-in-Tube Nanostructures Formed from the Kirkendall Effect using Atomic Layer Deposition on Three Dimensional Electrospun Fiber Templates**, *Q. Peng, X.Y. Sun, J.C. Spagnola, R.J. Spontak, C. Saquing, S.A. Khan, G.N. Parsons*, North Carolina State University

Three-dimensional (3D) macrostructures consisting of well-defined nanoscale elements with controlled properties have attracted significant interest for a range of fields. To date, large-scale fabrication of these 3D macrostructures remains an important outstanding challenge. We are currently exploring atomic layer deposition on a variety of nano- and micro-scale fiber systems for fabrication of macro size 3D structures with molecular-scale control. Recently, we have applied low temperature (< 80 degree C) Al2O3 and ZnO ALD processes onto 3D polyvinyl alcohol electrospun fiber matrix templates to form Al2O3, ZnO and Al2O3/ZnO/Al2O3 multilayer nanotubes with controlled tube wall thickness. SEM, TEM and XRD have been used to probe the structure and crystal structure of the materials as a function of deposition parameters and post-deposition calcination and annealing. We find that upon annealing at 700 degree C, the ZnO and Al2O3 layers in the Al2O3/ZnO/Al2O3 coaxial structures can react with each other, due to the solid-state reaction and diffusion process between ZnO/Al2O3 (Kirkendall effect), to form pairs of coaxial ZnAl2O4 hollow nanotubes separated by a nanoscale gap. Moreover, by controlling the thickness of the individual Al2O3 and ZnO layers and the ZnO/Al2O3 thickness ratio, the final thickness of the nanotubes and the separation nanogap can be tuned to form a variety of well-defined tube-in-tube nanosystems. Under some conditions, unreacted ZnO layers can remain after annealing, resulting in multi-compositional structures with segregated voids. These results show the feasibility of extending reactivity of ALD thin films and Kirkendall effect to form a range of quasi-one-dimensional nanostructures for a variety of potential applications.

**11:20am** **TF+NC-MoM10 Structured Photoanodes for Enhanced Electron Transport in Dye Sensitized Solar Cells (DSSC) with Atomic Layer Deposition (ALD)Functionalization**, *M.J. Pellin, A.B.F. Martinson, J.W. Elam,* Argonne National Laboratory, *J.T. Hupp*, Northwestern University **INVITED**

Inexpensive, efficient solar energy conversion requires synthetic methodology capable of creating structures that resolve the conflict between the long lengths required for efficient photon absorption with the short photoelectron diffusion lengths found for all but the most perfect crystalline materials. DSSC's photoanodes utilize titania nanocrystals sensitized with monolayers of dye to achieve efficient photon absorption. However, DSSC conversion efficiencies have been limited to ~10% by a charge collection time of milliseconds at the maximum power point. Thus efficient charge extraction is only possible with an iodide/triiodide ($I^-/I_3^-$) redox shuttle with both the high driving force needed to regenerate dyes at acceptable rates (and the consequent >500 mV energy cost/photon)and a remarkably inefficient $I_3^-$ electron interception rate. We have been addressing this problem using the ability of ALD to conformally grow nm thick, pin-hole free layers on nanoporous, high surface area supports. The charge collection times can be improved either by reducing the dimensionality of the photoanode or by reducing the electron collection distances. We address the former with precision films grown on nanoporous substrates such as anodic aluminum oxide (AAO) or silica aerogel supports. The AAO, for instance, has a regular array of 200 nm straight channels that traverse its 60 @smicron@ thick membrane. ALD is used to conformally coat with either ZnO or $TiO_2$ (achieving peak efficiencies at ~ 4-5 nm thickness) the membrane channels. One side of the membrane is coated with a thick transparent conducting oxide such as ITO. The pore walls are then sensitized with a dye and the resulting photoanode is assembled into a photocell. The linear tubes thus created form a one-dimensional network of 60 m long tubes with excellent charge collection times. Dramatically reduced electron collection distances can be tested with a more complex structure grown by first coating the AAO substrate with a transparent conducting oxide such as ITO, then adding a wide band gap oxide ($TiO_2$), before completing the cell with dye attachment and assembly. In these cells, electron diffusion occurs radially through the thin (~5 nm) $TiO_2$ layer into the TCO, rather than along the pore. Again the electron diffusion times are dramatically reduced. The wide palate, precision composition, and conformal nature of ALD synthesized films enable the exploration of these complex structures improving our understanding of the factors limiting solar energy conversion.

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