Tuesday Afternoon, October 20, 2015

Thin Film
Room: 111 - Session TF-TuA

ALD for Emerging Applications

Moderator: Robert Grubbs, Micron Technology, Erwin Kessels, Eindhoven University of Technology, Netherlands

2:20pm TF-TuA1 ALD ZnO for Rapid Synthesis of Cu-BTC MOF Thin Films and Patterns, *Junjie Zhao**, *W.T. Nunn, P.C. Lemaire, Y. Lin, M.D. Dickey,* North Carolina State University, *G.W. Peterson,* Edgewood Chemical Biological Center, *M.D. Losego,* Georgia Institute of Technology, *G.N. Parsons*, North Carolina State University

Metal-organic frameworks (MOFs) are crystalline porous materials that consist of metal ions/clusters and organic linkers. MOFs typically exhibit high surface area, good adsorption capacity and opportunity for post-synthetic modification. However, the insoluble MOF powders typically synthesized through conventional solvothermal methods may not be the ideal configuration for gas filters, chemical sensors and smart membranes etc. Growing MOF thin films onto various functional substrates, especially in a high-throughput process with low energy input, is therefore highly desired for MOF industrial implementation and new applications.

Here we report a rapid room-temperature synthesis route for Cu-BTC (Cu$_3$(BTC)$_2$) MOF thin films using ZnO nucleation layers deposited via atomic layer deposition (ALD). We find in just 1 minute of exposure to the Cu-BTC precursor solution, dense Cu-BTC thin films can be integrated onto various ALD ZnO coated substrates including silicon wafers, polymer spheres, and fibrous materials. MOF patterns can also be obtained on pre-patterned ZnO surfaces. The space-time-yield of the Cu-BTC production reaches up to 2.9×10^4 kg·m^{-3}·d^{-1}, which is over 10× higher than previous reports. We further investigated the surface reactions between ALD ZnO and MOF precursor solutions using high-resolution EDX, XRD and FTIR. The results suggest hydroxyl double salt ((Zn,Cu)(OH)$_3$NO$_3$) is an important intermediate to drive the rapid formation of Cu-BTC thin films. Breakthrough tests were performed to demonstrate the high adsorption capacity of these MOF-functionalized materials for toxic industrial chemicals. This rapid room-temperature approach is also promising for new MOF-based composite materials for membrane separation, gas storage, chemical sensing and other applications.

2:40pm TF-TuA2 Reactions During Atomic Layer Deposition on and in UiO-66-NH$_2$ Metal Organic Framework Crystals, *Paul Lemaire*, *J. Zhao, C. Oldham, G.N. Parsons*, North Carolina State University

Metal organic frameworks (MOFs) are microporous materials with chemically functionalized high surface areas. MOFs are attractive for multiple applications including filtration, gas storage, and catalysis. Post-synthetic modification (PSM) is a way to impart additional functionality into these materials and most PSM techniques reported are solution based processes. Vapor-phase PSM methods are highly desired due to the advantageous efficiency in reagent and solvent reagent removal.

In this work we report on a fundamental study on the functionalization of the UiO-66-NH$_2$ MOF through atomic layer deposition (ALD). ALD is a vapor phase self-limiting process that enables the controlled deposition of thin films. The UiO-66-NH$_2$ MOF is of particular interest for its high thermal and chemical stability and catalytic activity. We investigated how UiO-66-NH$_2$ interact with ALD precursors, including titanium tetrachloride (TiCl$_4$), titanium isopropoxide (TTIP), and trimthylaluminum (TMA).

QCM analysis shows that the UiO-66-NH$_2$ consumes a relatively large amount of precursor in the first exposure, with a ~16% and ~20% for TiCl$_4$/TTIP and TMA respectively. It is likely that the majority of the MOF pore volume is filled within the first cycle. For the first ALD cycle, purge time ranging 0.5-2.5 hours are necessary to completely remove excess unreacted precursor and byproducts. Following the first cycle, the mass loading per cycle decreases and becomes relatively linear.

In-situ FTIR analysis of the ALD functionalization of UiO-66-NH$_2$ at 150°C shows that the MOF structure is maintained during the ALD process. Dosing each of the ALD precursors results in a loss of the hydroxyl bands at ~3650, 735, and 675 cm^{-1}, but also a loss of the asymmetric and symmetric carboxylate stretching bands at ~1565 and 1375 cm^{-1} respectively. Upon water exposure, these bands reappear. These changes in the carboxylate stretching bands was consistent with shifting between the hydroxylated and non-hydroxylated UiO-66-NH$_2$ structure. Finally, the

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dehydroxylated UiO-66-NH$_2$ at 250°C was significantly less reactive towards the ALD precursors, suggesting that hydroxyl sites in UiO-66-NH$_2$ play a large role in ALD functionalization of the MOF. The ability to deposit metal oxide thin films or nanoparticles within UiO-66-NH$_2$ pores could help improve the MOF catalytic activity.

3:00pm TF-TuA3 Selective ALD Growth of Pd@Pt Core Shell Nanoparticles and its Application in PROX Reactions, *K. Cao, Q.Q. Zhu, B. Shan,* State Key Laboratory of Material Processing and Die & Mould Technology, China, ***Rong Chen***, State Key Laboratory of Digital Manufacturing Equipment and Technology, China

Bimetallic nanoparticles (NPs) have attracted great attention due to their unique properties for catalytic applications. Compared with the physical mixture of monometallic NPs or the alloyed bimetallic NPs, the formation of core shell NPs could further enhance the activity, selectivity and stability. The enhanced properties of core shell structure may originate from the lattice strain, bonding interaction and electron transfer due to the core shell interface. Synthesizing core shell nanoparticles (NPs) with well controlled shell thickness and composition is of great importance in optimizing their reactivity.

Here we report the successful synthesis of core shell NPs using an area-selective ALD technique. The selective ALD approach utilizes pinholes on the unsaturated ODTS SAMs layer to achieve selective core shell structure growth. The size, shell thickness, and composition of the NPs can be precisely controlled by varying the ALD cycles. The catalytic performance of Pd@Pt core shell NPs with different Pt shell thickness have been tested towards preferential oxidation of CO under excess H$_2$ (PROX) reaction. The results show that the core shell structured NPs exhibit both great selectivity and enhanced activity. Core shell NPs with a completely covered monolayer of Pt shell shows optimized selectivity and activity. Density functional theory simulations have been carried out to explain such behavior of the core shell NPs system towards PROX reactions.

3:20pm TF-TuA4 Thermal and Plasma ALD on Semiconductor Nanowires, *Lachlan Black*, Eindhoven University of Technology, Netherlands, *M.A. Verheijen, A.J. Standing, E.P.A.M. Bakkers,* Eindhoven University of Technology, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Semiconductor nanowires represent a novel class of materials structure with a number of interesting properties that give them potential applications in optoelectronic devices, including light-emitting diodes (LEDs), photoelectrochemical systems, and solar cells. Because of the unusually high surface-to-volume ratio of nanowires, the electrical performance of nanowire devices is especially sensitive to the condition of the semiconductor surface. It is well known that the application of thin-film dielectric and conductive layers to semiconductor surfaces can be an effective means of controlling surface properties. Such layers can provide chemical and electrical passivation, functionalisation, and contacting of semiconductor device surfaces. However, most conventional thin-film deposition techniques face severe challenges when confronted by the high-aspect-ratio features represented by nanowire geometry.

Atomic layer deposition (ALD), on the other hand, is ideally suited to thin film deposition on small-dimensioned, high-aspect-ratio structures due to its uniquely self-limiting nature, which results in outstanding uniformity and conformality, and thickness control on the sub-nm level. The application of thin films deposited by ALD to nanowire devices, in order to improve device properties, has previously been reported by a number of authors. However, there has been relatively little effort to systematically study the ALD process on nanowire surfaces in its own right. Nanowires represent an interesting test platform with which to study ALD processes and thin film properties because of the relative ease with which they can be characterised by transmission electron microscopy (TEM).

In this paper we present a fundamental experimental study of ALD on semiconductor nanowires. ALD thin films of various dielectric and conductive materials, including Al$_2$O$_3$, TiO$_2$, ZnO, and HfO$_2$, are deposited on Si and III-V semiconductor (GaP and InP) nanowire arrays grown by the vapour-liquid-solid (VLS) mechanism, and characterised by high-resolution TEM. Film thickness measured as a function of the number of deposition cycles is used to determine the linearity of the deposition rate and the growth-per-cycle, and these values are compared to those measured on co-deposited planar samples using in-situ and ex-situ ellipsometry. It is shown that both thermal and plasma-assisted ALD processes are capable of depositing films with excellent conformality and thickness uniformity along the length of the nanowires, although differences are observed for different materials. Moreover, TEM images reveal the presence of clearly defined interfacial layers in some samples.

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* TFD James Harper Award Finalist

5:00pm TF-TuA9 Capacitive Deionization for Water Desalination Using Charge Storage in Manganese Oxide Films Grown by Atomic Layer Deposition, *Jasmine Wallas, M.J. Young, C.B. Musgrave, S.M. George*, University of Colorado, Boulder

Capacitive deionization (CDI) is a promising water desalination technique based on the reversible electrosorption of anions (Cl^-) and cations (Na^+). Traditional CDI relies on ion storage in the electric double layer (EDL) on the surface of carbon electrodes. Additional ion storage can be achieved through charge storage in thin films of various materials, such as manganese oxide, that are deposited on the electrodes. In this work, we have demonstrated a dramatic improvement in reversible Na^+ ion storage using MnO_2 films on electrodes prepared using atomic layer deposition (ALD).

The MnO_2 films were prepared by first growing MnO ALD films using bis(ethylcyclopentadienyl) manganese and H_2O on flat Ti electrodes. These MnO films were then electrochemically oxidized to MnO_2. Conversion of MnO to MnO_2 was monitored during electrochemical oxidation with cyclic voltammetry. A large increase in capacitance occurred concurrently with the conversion to MnO_2. The reversible adsorption of Na^+ under applied potential in NaCl solutions was then confirmed with electrochemical quartz crystal microbalance (E-QCM) analysis. Adsorption of Na^+ and an elemental composition of $Na_{0.25}MnO_2$ after Na^+ adsorption was further verified with x-ray photoelectron spectroscopy (XPS) studies.

MnO_2 films on flat Ti electrodes dramatically increased the ion storage from NaCl solutions. A maximum areal capacitance of 5.6 mF/cm^2 was observed from MnO_2 films prepared from MnO ALD films with an initial thickness of 447 Å. This areal capacitance is >170 times larger than the areal capacitance of an uncoated Ti electrode. MnO_2 films were also prepared on electrodes composed of high surface area carbon nanotubes (CNTs) using 200 cycles of MnO ALD and electrochemical oxidation. These MnO_2-coated CNT electrodes also displayed a significant increase in areal capacitance compared with uncoated CNT electrodes. These results indicate that MnO_2 coatings on electrodes could substantially enhance the charge storage for CDI and water desalination.

5:20pm TF-TuA10 Magnetoelectric Effect in Multiferroic Nanocomposites of Atomic Layer Deposition Pb(Zr,Ti)O₃ Coupled with Templated Mesoporous CoFe₂O₄, *Diana Chien, A. Buditama, L. Schelhas, S.H. Tolbert, J.P. Chang*, University of California at Los Angeles

Ultra-thin, uniform, and conformal PZT films are needed to engineer nanoscale multiferroic composites with complex architectures. By coupling the piezoelectric PZT film with a magnetostrictive material (e.g. CFO), a magnetization (polarization) can be induced by an applied electric (magnetic) field via the strain-mediated magnetoelectric coupling effect, in which strain is transferred at the interface between the piezoelectric and magnetostrictive layers. Using atomic layer deposition (ALD), a surface-reaction controlled process based on alternating self-limiting surface reactions, an ultra-thin film of PZT can be synthesized with precise control of the film thickness and elemental composition (Zr/Ti = 52/48). ALD provides superior uniformity and conformality over complex surface structures with high aspect ratios.

ALD PZT thin films were synthesized by depositing alternating layers of PbO, ZrO_2, and TiO_2 layers using Pb(TMHD)₂, Zr(TMHD)₄, and Ti(Oi-Pr)₂(TMHD)₂ as metal precursors and H_2O as the oxidant. The number of local cycles and global cycles were regulated to achieve the desired stoichiometry and thickness, respectively. ALD of PZT was studied to obtain (100) oriented $Pb(Zr_{0.52}Ti_{0.48})O_3$ on Pt (111) oriented silicon substrates. In order to attain a highly oriented PZT thin film, a (100) textured $PbTiO_3$ seed layer was required because PZT orientation is generally governed by nucleation. The stoichiometry and crystallinity of PZT films were confirmed by XPS and XRD measurements. The conformality was confirmed over high aspect ratio structures.

By controlling the composition, thickness, and conformality of ALD PZT thin films, multiferroic nanocomposites were engineered. Specifically, ALD PZT thin films were shown to uniformly coat the walls of nanoscale templated mesoporous CFO (with neck size of 6 nm in radius) to form a complex 0D-3D nanocomposite. XPS and XRD measurements confirmed the elemental analysis and crystallinity, respectively, of the PZT/CFO nanocomposites. To study the magnetoelectric coupling effect, the nanostructure was electrically poled ex-situ and the resulting magnetic moment was measured via SQUID while sweeping in-plane and out-of-plane magnetic fields. The in-plane results show that there is no change in magnetization as a function of voltage, which is due to the effect of substrate clamping. The out-of-plane results show that the magnetization changes as a function of voltage. The mesoporous CFO coated with 3 nm thick PZT film shows a greater magnetization change than the 6 nm thick PZT film, suggesting that porosity in the templated mesoporous CFO matrix is needed for a greater magnetoelectric coupling effect.

5:40pm TF-TuA11 Ultralow Density Metal Oxide Foams by Atomic Layer Deposition on Sacrificial Carbon Nanotube Matrices, *Jesse Jur, K.L. Stano, P.D. Bradford*, North Carolina State University

Ultralow density materials ($\rho \leq 10$ mg cm^{-3}) have recently gained widespread attention, and have been realized in many forms including silica, and carbon-based aerogels, as well as engineered structures such as inorganic micro- and nanolattices. Porous metal oxides, particularly alumina, are desirable due to their semiconducting and dielectric properties as well as thermal, mechanical, and chemical stability. Historically, monolithic alumina aerogels have been fabricated using sol-gel processes. Although this and other self-assembly methods can produce very high surface area aerogels, they have a moderate low density (≥ 30 mg cm^{-3}), and little to no control over pore size and structure. We present here a method by which aligned CNTFs are used as unique sacrificial templates for the formation of anisotropic, large-scale inorganic nanotube architectures that exhibit the combined characteristics of high surface area, ultralow density, and mechanical robustness. Using ALD, conformal coatings were deposited onto the CNTFs, followed by their removal via calcination in air to leave behind an interconnected network of thin-walled and aligned nanotubes of the ALD metal oxide. Analysis shows that the use of alumina ALD, one can achieve a density as low as 1.2 mg cm^3, 16x lower than previously report alumina foams. Furthermore, both CNT/alumina hybrid foams and pure alumina nanotube foams exhibit unprecedented elastic recovery following 50% compression, and possess values for strength and Young's moduli which exceed those of aerogels with similar densities. The scaling behavior of Young's modulus to foam density for pure alumina foams exhibits a power-law dependence of n≈1.9, attributed to superb ligament connectivity. As a low thermal conductivity insulation, a foam of 1 cm thickness is demonstrated to reduce a flame temperature of 1000 ° C to 45 ° C after 5 min of direct flame contact.

6:00pm TF-TuA12 The Structure and Optical Properties of ALD W:Al₂O₃ Nanocomposite Films, *Shaista Babar, A. Mane*, Argonne National Laboratory, *A. O'Mahony*, Incom, Inc., *A. Yanguas-Gil, J. W. Elam*, Argonne National Laboratory

A highly robust $W:Al_2O_3$ nanocomposite material has been reported by ALD method and used in microchannel plates (MCPs) and MEMS devices [1,2]. By adjusting the W cycle percentage during the nanocomposite synthesis, the resistivity can be tuned in the range of $10^{12} - 10^8$ Ω. Here we report a systematic study of the structure and optical properties of ALD deposited nanocomposite $W:Al_2O_3$ films using SEM, TEM, XRD, XRR, XPS, ellipsometry and UV-vis-IR spectroscopy. General oscillator and Kramers-Kronig consistent B-spline models were used to extract the optical constants of the films. We studied the impact of the composition and microstructure on the optical properties of $W:Al_2O_3$ layers as ALD cycle ratio and metal contents. We report a systematic decrease in the bandgap associated with the increase in the W content. We also discuss the high thermal stability and high absorptivity of W:Al2O3 and propose it as an ideal candidate for concentrated solar power receivers .

References:

[1] Atomic layer deposition of W:Al2O3 nano-composite films with tunable resistivity,

Anil U. Mane, Jeffrey W. Elam, Chemical Vapor Deposition, 19(4-6), (2013) 186

[2] Nanostructured composite thin films with tailored resistivity by atomic layer deposition

Anil U. Mane, Jeffrey W. Elam, SPIE 2013

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