Thin Film
Room 2022 - Session TF-MoA
ALD and Applications II

Moderator: S.M. Rossnagel, IBM T.J.Watson Research Center

2:00pm **TF-MoA1 Molecular Layer Controlled Deposition of Polymer Thin Films***, **A.A. Dameron**, Y. Du, N.M. Adamczyk, S.M. George,* University of Colorado at Boulder

Conformal polymeric thin films can be fabricated using sequential, self-limiting surface chemistries that are similar to atomic layer deposition (ALD). The simplest repetitive surface chemistry for this molecular layer controlled polymer growth is based on the reaction of two bifunctional monomer reactants. This type of polymer film growth was originally demonstrated in the 1990s in various Japanese laboratories. Subsequently, little work has been done to understand or to utilize this polymer growth method. To further develop this important technique, we have explored the condensation reaction of 1,6-hexanediamine (H@sub 2@N-(CH@sub 2@)@sub 6@-NH2) with adipoyl chloride (ClOC-(CH@sub 2@)@sub 4@-COCl) to fabricate Nylon 66 (polyamide) films. By monitoring the infrared absorbance for the C-H, N-H and C=O stretching vibrations using Fourier transform infrared spectroscopy, we have observed the linear growth of the Nylon 66 films versus number of AB reaction cycles. Polymeric condensation reactions provide a wide spectrum of other possible reactant candidates. Currently, we are exploring surface chemistries for the molecular layer controlled deposition of other polymers such as polyester. In addition, polymeric materials can be combined together with inorganic materials to form laminate structures. We have demonstrated the growth of Nylon 66/Al@sub 2@O@sub 3@ nanolaminate films. Other polymeric/inorganic films can be fabricated to create new multifunctional materials.

2:20pm **TF-MoA2 Gas Diffusion Barriers on Polymers Using Al@sub2@O@sub3@ Atomic Layer Deposition***, M.D. Groner, A.A. Dameron,* University of Colorado*; R.S. McLean, P.F. Carcia,* DuPont Central Research & Development*; **S.M. George**,* University of Colorado

Diffusion barriers are required to protect thin film devices from the corrosive effects of various gases. One example is flexible organic light-emitting diode (OLED) devices that are susceptible to degradation because of facile permeation of O@sub2@ and H@sub2@O through the plastic substrates. Our recent work has utilized quantitative Ca-tests to measure water vapor transmission rates (WVTRs) through polymers coated with Al@sub2@O@sub3@ ALD films. These Ca-tests have measured WVTRs of 1.4 x 10@super-5@ g/m@super2@/day at 38°C and 5.5 x 10@super-5@ g/m@super2@/day at 60°C for an Al@sub2@O@sub3@ ALD film thickness of ~25 nm on polyethylene naphthalate (PEN). Based on the apparent activation energy, the WVTR at 23°C is estimated to be only 6 x 10@super-6@ g/m@super2@/day. These WVTR values are excellent and close to the targeted WVTRs required for OLEDs. Our earlier measurements used radioactive tracer tests based on HTO permeability to measure WVTRs. These radioactive tracer tests measured higher WVTRs of ~1 x 10@super-3@ g/m@super2@/day at room temperature for an Al@sub2@O@sub3@ ALD film thickness of ~26nm on Kapton polyimide and PEN. The difference between the Ca-test results and the HTO radioactive tracer test results suggests that the HTO test may be influenced by tritium diffusion in addition to HTO diffusion. Additional work is focusing on improvements in diffusion barrier performance using multilayer films composed of Al@sub2@O@sub3@ ALD and other materials.

2:40pm **TF-MoA3 Atomic Layer Deposition of In@sub 2@O@sub 3@ Using Cyclopentadienyl Indium: A New Synthetic Route to Transparent Conducting Oxide Films***, **J.W. Elam**,* Argonne National Laboratory*; A.B.F. Martinson,* Northwestern University*; M.J. Pellin,* Argonne National Laboratory*; J.T. Hupp,* Northwestern University **INVITED**

Indium Oxide (In@sub 2@O@sub 3@) forms the basis for an important class of transparent conducting oxides (TCO) that see wide use in optoelectronic devices, flat-panel displays and photovoltaics. Here we present a new method for depositing In@sub 2@O@sub 3@ thin films by atomic layer deposition (ALD) using alternating exposures to cyclopendadienyl indium and ozone. Using a precursor vaporization temperature of 40°C and deposition temperatures of 200-450°C, we measure growth rates of 1.3-2.0 Å/cycle. A significant advantage of this synthesis route over previous techniques is the ability to conformally coat porous materials such as anodic aluminum oxide membranes. The deposited films are nanocrystalline, cubic phase In@sub 2@O@sub 3@ and are highly transparent and conducting. In situ quadrupole mass spectrometry and quartz crystal microbalance measurements reveal a mechanism in which approximately 1 in 6 of the initial Cp ligands remain on the surface following each InCp exposure, and the remaining Cp ligand is burned off during the subsequent O@sub 3@ exposure to form CO@sub 2@. Using this method, we demonstrate for the first time the conformal coating of very high aspect ratio porous membranes with ALD In@sub 2@O@sub 3@. This technique will enable the functionalization of porous materials with In-based TCO films for the fabrication of novel photovoltaic devices.

3:20pm **TF-MoA5 Fabrication of Integrated Scanning Electrochemical-Atomic Force Microscopy Probes by Atomic Layer Deposition of Aluminum Oxide***, **D.J. Comstock**, M.C. Hersam,* Northwestern University*; J.W. Elam, M.J. Pellin,* Argonne National Laboratory

Integrated scanning electrochemical-atomic force microscopy (SECM-AFM) is a powerful tool for characterizing electrochemical and biological processes ranging from corrosion to membrane transport. SECM-AFM utilizes probes consisting of a tip electrode integrated onto a conventional atomic force microscopy cantilever, allowing for simultaneous but independent topographic and electrochemical imaging. In this study, we describe a novel process for fabricating integrated SECM-AFM probes using atomic layer deposition (ALD) techniques. ALD allows for the deposition of highly conformal, continuous insulating films with precise thickness control and is thus well suited for this project. Fabrication starts with commercially available conductive AFM probes, onto which a 50 nm thick aluminum oxide film is deposited by ALD. This insulating film serves to encapsulate the probe body, cantilever, and tip and eliminate electrical leakage currents when operating in an electrochemical environment. The tip nanoelectrode is fabricated using focused ion beam milling to selectively remove aluminum oxide from the tip apex and expose the underlying conductive film. The integrated probes are characterized by scanning electron microscopy (SEM) throughout fabrication to determine both the quality and morphology of the insulating film and the dimensions of the electrode. The films and fabricated probes are electrochemically characterized by cyclic voltammetry, in which the diffusion-limited redox current is used to determine the area of the exposed nanoelectrode. In addition, silver electrodeposition is used to visually confirm that the electrochemical activity of the probe is limited solely to the nanoelectrode at the tip apex. Both SEM imaging and electrochemical characterization have revealed tip electrodes with diameters as small as 50 nm. Finally, we demonstrate the application of these probes to SECM-AFM by acquiring topographic and electrochemical images of a model substrate.

3:40pm **TF-MoA6 Stand-Alone TiO@sub2@ Nanotubes for Nano-Sensors using Atomic Layer Deposition and Focused Ion Beam***, **D.K. Cha**, B.K. Lee, M.J. Kim,* University of Texas at Dallas*; J. Kim,* University of Texas at Dallas, U.S

Various tubular metal oxide nanomaterials such as TiO@sub2@ nanotubes have attracted considerable interest due to their excellent properties for nano-sensors and integrated circuits. In this study, we focus on the characteristic of single TiO@sub2@ nanotubes which are grown by atomic layer deposition (ALD) on nano porous membranes with self-assembled monolayers (SAMs) treatments. The TiO@sub2@ nanotubes are 20-200 nm in diameter with a wall thickness of 5-20 nm. For the electrical characterization of single TiO@sub2@ nanotubes, electrical test structure devices are fabricated on SiO@sub2@/Si wafer patterned with Au/Cr electrodes by focused ion beam (FIB), which has site-specific platinum deposition capability. A single TiO@sub2@ nanotube with a diameter of 200nm shows that the current increases linearly with the applied voltage (-3V to 3V) and resistivity is calculated to be approximately 100 @ohm@ cm. It is also found that the conductance of a single TiO@sub2@ nanotube is affected by the ambient, indicating the surface of TiO@sub2@ nanotube is sensitive to the presence of absorbed species such as water molecular. This conductance changing suggests that individual TiO@sub2@ nanotubes can be used for nano-sensor application. In addition, photo-conduction behaviors of single TiO@sub2@ nanotubes will also be discussed for photovoltaic nano-device applications. This research was supported by a grant (code #: M105KO010026-05K1501-02611) from Center for Nanostructured Materials Technology under 21st Century Frontier R&D programs of the Ministry of Science and Technology, Korea and The State of Texas.

4:00pm **TF-MoA7 Atomic Layer Deposition of Electrocatalytic Platinum for Solid Oxide Fuel Cells*, X. Jiang*,** *S.F. Bent,* Stanford University

Atomic layer deposition (ALD) has been actively explored for a number of applications. It is currently being investigated as an enabling technology to fabricate thin film solid oxide fuel cells (SOFCs). ALD can potentially be used to grow several fuel cell components, including electrolyte, catalyst, and electrode materials, at ultrathin, nanometer-scale thickness. Here we explore the use of ALD for the deposition of the Pt electrocatalyst for an SOFC. We have successfully carried out the Pt ALD process using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe@sub3@) and O@sub2@ as precursors and N@sub2@ as a carrier and purging gas. Ex situ analysis has been carried out on the as-deposited Pt films using a variety of analytical techniques, including atomic force microscopy (AFM),scanning electron microscopy (SEM), X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS), and four-point probe method. The analysis on native oxide-coated silicon wafers shows that the as-deposited platinum film is of excellent uniformity, with no measurable impurities and low electrical resistivity. We have also shown that Pt films of high quality can be deposited by ALD on RF-sputtered yttria stabilized zirconia (YSZ), a good candidate for the SOFC electrolyte. Deposition on YSZ is found to occur with a shorter incubation period than that on SiO@sub2@. The expected operating temperature of the SOFC ranges from 300°C to 1000°C. Post-ALD annealing studies of the morphology and resistivity of the Pt film as a function of temperature and film thickness show that for temperatures up to at least 550°C, resistivity remains relatively constant. However, film roughness, which is desirable for catalytic activity, increases with temperature. In addition, we have carried out area selective ALD of Pt on YSZ using microcontact printing for fabrication of the electrode and current collector for the SOFC. Results of these studies will be presented.

4:20pm **TF-MoA8 Co and CoSi@sub 2@ Films Prepared by Plasma-Enhanced Atomic Layer Deposition for Contact Applications*, H.-B.-R. Lee,*** *H. Kim,* POSTECH, Korea

The CoSi@sub 2@ has been studied as an alternative contact material to TiSi@sub 2@ in microelectrtonics technology since the CoSi@sub 2@ has immunity to shrinkage of line width, low resistivity, and thermal stability. However, typical process consisting of Co sputtering followed by a post annealing has several problems such as poor conformality and Si consumption in nanoscale regime. Therefore we investigated plasma-enhanced atomic layer deposition (PE-ALD) of Co thin films using several metal organic precursors and NH@sub 3@ plasma. The Co PE-ALD processes were studied as a function of key growth parameters including precursors and reactant exposure times and growth temperatures. Rutherford backscattering and X-ray photoemission spectroscopy results indicate that the impurity contents in PE-ALD Co thin films are low resulting in a very low resistivity down to 10µ@ohm@cm. After the deposition, the Co films were annealed to form CoSi@sub 2@ with Ti/TiN capping layers and the results were compared with physical vapor deposition (PVD) Co. In addition, direct ALD process of CoSi@sub 2@ was investigated using additional Si precursor. The microstructures of CoSi@sub 2@ films prepared by annealing and direct deposition were investigated by synchrotron radiation X-ray diffraction and transmission electron microscope.

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