

Monday Afternoon, October 15, 2007

Thin Film

Room: 613/614 - Session TF-MoA

Emerging Topics in Atomic Layer Deposition

Moderator: S.M. George, University of Colorado at Boulder

2:00pm **TF-MoA1 Atomic Layers in Nano(bio)technology**, *M. Knez, L. Zhang, S.-M. Lee*, Max-Planck-Institute of Microstructure Physics, Germany, *A.J. Patil, S. Mann*, University of Bristol, UK, *K. Nielsch, U. Gösele*, Max-Planck-Institute of Microstructure Physics, Germany **INVITED**

In nanotechnology biological systems play an increasingly important role, since some of the naturally occurring biological macromolecules show perfect order on the nanoscale. The perfection of the natural organization of molecules is, in particular for the nanotechnology, often a target for imitation, but can almost never be obtained in a similar quality. An alternative way to obtain nano- or microstructures in close similarity to natural ones is their structural replication from inorganic materials or the modification of the chemical or physical properties of such systems by attachment of inorganic materials. Some of the methods applied recently rely on wet-chemistry which frequently leads to non-uniformity or bad quality of the attached materials. The ALD is one method-of-choice for performing such replication and modification experiments, since it offers the unique possibility to cover biological structures with inorganic films as thin as few Angstroms or nanometers. In this way a number of novel nanostructures with interesting properties can be synthesized, however, limited with the deposition processes which can be performed at temperatures below the stability limit of the biological or organic molecular units.

2:40pm **TF-MoA3 Al_2O_3 and W/ Al_2O_3 Atomic Layer Deposition on Quantities of Multiwalled Carbon Nanotubes**, *A.S. Cavanagh, C.A. Wilson, S.M. George*, University of Colorado at Boulder

Atomic layer deposition (ALD) can be employed to coat individual single-walled (SW) and multi-walled (MW) carbon nanotubes (CNTs). We have performed Al_2O_3 and W/ Al_2O_3 ALD on quantities of multiwalled carbon nanotubes (MWCNTs) in a rotary reactor designed for ALD on high surface area nanoparticles. Al_2O_3 ALD was performed using trimethylaluminum (TMA) and H_2O . W ALD was performed using WF_6 and Si_2H_6 . Al_2O_3 ALD on MWCNTs yielded nanospheres that grew with the number of trimethylaluminum and H_2O reaction cycles. Al_2O_3 ALD is believed to nucleate only at defect sites on the surface because the graphene surface of MWCNTs is unreactive. The NO_2 /TMA nucleation procedure developed by Farmer and Gordon [Nano Letters 6, 699 (2006)] for ALD on SWCNTs was used to obtain very conformal Al_2O_3 ALD films on gram quantities of MWCNTs. The Al_2O_3 ALD films grew linearly with the number of TMA/ H_2O reaction cycles. This Al_2O_3 ALD film is not covalently attached to the MWCNTs. Evidence for only a physisorption interaction was provided by ALD-coated MWCNTs where the Al_2O_3 ALD coating had broken to yield "ALD macaroni on a CNT string". W ALD also grew on the conformal Al_2O_3 ALD coating to create W/ Al_2O_3 bilayers. X-ray photoelectron spectroscopy indicated that the surface of the metallic W was oxidized to form WO_3 upon exposure to atmosphere. The W ALD oxidation should be avoided by passivation with Al_2O_3 ALD. Calculations show that a metallic W ALD coating significantly enhances the CNT conductivity.

3:00pm **TF-MoA4 Molecular Layer Deposition of Alkyl-Aromatic Polyamide Films**, *Q. Peng, R.M. VanGundy, G.K. Hyde, S.M. Stewart, G.N. Parsons*, North Carolina State University

Organic thin film materials with well controlled microstructure have significant applications in organic light-emitting devices, organic thin film transistors, organic photovoltaic cells, quantum devices, molecular electronics, biomaterial interfaces, and others. Molecular layer deposition (MLD) is a binary self-limited deposition process to form uniform and conformal polymer thin films with well controlled microstructure. We have recently investigated vapor-phase polymer MLD using (1, 4 butane diamine) and aromatic (terephthaloyl dichloride) polyamide. 1, 4 butane diamine and terephthaloyl dichloride were evaporated at room temperature and 70°C respectively. Growth on a variety of surfaces, including Au, Si-OH, Si-H, methyl-terminated Si, and amino-terminated Si, was investigated, with substrate temperature controlled between 70 and 150°C. An in-situ quartz crystal balance was used to monitor the adsorption and desorption

behavior of the monomers. Generally, the deposition rate decreased as the reaction temperature increased. At 85°C, the thickness of the polyamide film measured using ellipsometry as a function of the number of deposition cycles results in a growth rate of 0.2 nm/cycle. Transmission infrared spectroscopy verified the characteristic polyamide peaks in the films. Contact angle measurements were carried out after each monomer dosing cycle resulting in expected changes in the surface energy with each half-cycle. The thermal stability, chemical inertness and capacitance properties of the deposited polymer thin film were also characterized. Results give insight into process requirements to achieve well controlled molecular layer deposition of organic films that include aromatic elements.

3:40pm **TF-MoA6 Fabrication of Hybrid Inorganic/Organic Multilayers Using Atomic and Molecular Layer Deposition**, *D. Seghete, S.M. George*, University of Colorado at Boulder

Inorganic/organic multilayers occur in the nacreous layer of the mollusk shell and are among the strongest structures in nature. These "brick and mortar" composites are known for their high elasticity, toughness, and hardness. In this study, we report the fabrication of alternating inorganic and organic multilayers consisting of inorganic alumina (Al_2O_3) or tungsten (W) in combination with organic alucone polymer. Al_2O_3 atomic layer deposition (ALD) is performed using trimethylaluminum (TMA) and H_2O as the reactants. W ALD is accomplished using WF_6 and Si_2H_6 as the reactants. The organic alucone layer is grown using molecular layer deposition (MLD) with TMA and ethylene glycol as the reactants. The growth of the inorganic/organic multilayers was investigated using in situ quartz crystal microbalance studies. The nucleation of the inorganic Al_2O_3 or W ALD was explored on the alucone layer. The nucleation of the organic alucone MLD was also examined on the Al_2O_3 and W layers. The nucleation behavior provides information about the bonding between the inorganic and organic layers. The adhesion between the inorganic and organic layers is important for the mechanical properties of these multilayer structures. The structure and stability of the inorganic/organic multilayers were also explored using x-ray reflectivity measurements. Future mechanical property studies are planned using a nanoindenter.

4:00pm **TF-MoA7 Optimization of ALD Conformality in Ultra-High Aspect Ratio Nanopores Formed in Anodic Aluminum Oxide Templates**, *E. Robertson, I. Perez, L. Henn-Lecordier, S.J. Son, S.B. Lee, G.W. Rubloff*, University of Maryland

The very high conformality for thin film deposition in high aspect ratio structures is a major driver for broad use and adoption of atomic layer deposition (ALD) processes. ALD is particularly promising for applications coupled to anodic aluminum oxide (AAO) membranes, in which cylindrical nanopores with uniform dimensions (15-300nm dia) and spacing are formed by self-assembly during anodization. In turn these structures form templates useful for creating energy and display devices within the AAO template, or released nanotube or nanowire systems after AAO dissolution, e.g. for nanoparticle-based targeted drug delivery. We have created high-K dielectric nanotubes by HfO_2 ALD in AAO templates to investigate the relationship between ALD process parameters and the conformality of the ALD films in the nanopores as a function of nanopore dimensions and aspect ratios. SEM was used to measure pore diameters (40-80nm) before and after the ALD deposition. The HfO_2 nanotubes were then released by dissolution of the AAO template and examined via TEM imaging of the nanotubes on standard grids. TEM profiles showed HfO_2 nanotubes with lengths 1-2 microns (determined by the AAO template) and having wall thicknesses in the range 3-10 nm which vary with position along the depth of the original AAO nanopores. The AAO templates are attractive both for the applications above and for the ease with which they generate very high aspect ratio nanopores to study ALD conformality, while the nanotube release through AAO template dissolution provides a very simple means to achieve TEM analysis of ALD conformality. These advantages are particularly striking in comparison to requirements for more conventional high aspect ratio devices such as DRAM trench structures, where challenging lithography, dry etching, etc. must be combined with difficult cross-sectional TEM sample preparation to understand and optimize ultrathin conformal device layers.

4:20pm **TF-MoA8 Molecular Layer Deposition of Alucone Polymer Films Using Trimethylaluminum and Various Glycols**, *A.A. Dameron, S.D. Davidson, B.B. Burton, J.A. McCormick, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Conformal polymeric films can be grown by a sequential, self-limiting surface chemistry process known as molecular layer deposition (MLD) that is very similar to atomic layer deposition (ALD). The MLD reactants are typically monomers for step-wise condensation polymerization and can

yield completely organic or organic-inorganic alloys. Our earlier work has demonstrated polyamide growth using diamines and diacid chlorides. Alucone MLD is performed using trimethylaluminum (TMA) and various glycols as the reactants. When the glycol is ethylene glycol (EG), the alucone is poly(aluminum ethylene glycol), $[\text{Al}-(\text{OCH}_2\text{CH}_2\text{O})_n]_m$. Alucone films have been fabricated on silicon substrates at temperatures ranging from 85 °C to 175 °C. In situ quartz crystal microbalance and ex situ x-ray reflectivity experiments have confirmed linear growth of the alucone film versus number of TMA/EG reaction cycles at all temperatures. The MLD growth rates decreased at higher temperatures. Growth rates were 4 Å per cycle at 85 °C and 1.7 Å per cycle at 135 °C. In situ and ex situ Fourier transform infrared spectroscopy (FTIR) have also been used to monitor the surface reactions during alucone growth. Experiments with other glycols, such as benzene-1,4-diol (hydroquinone), demonstrate the general applicability of the alucone MLD surface chemistry to fabricate organic-inorganic films with tunable functionality.

4:40pm **TF-MoA9 Film Properties and In-Situ Optical Analysis of TiO₂ Layers Synthesized by Remote Plasma ALD**, *W. Keuning, J.L. Van Hemmen, O. Muraza, E. Rebrov, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

TiO₂ is a widely studied material due to its optical and photocatalytic properties and its hydrophilic nature after prolonged UV exposure. When synthesized by atomic layer deposition (ALD) the TiO₂ can be deposited with ultimate growth control with a high conformality on demanding topologies and even at room temperature when e.g. using a plasma based process. We report on the deposition of TiO₂ films using remote plasma ALD with titanium (IV) isopropoxide as precursor and O₂ plasma as oxidant. Stoichiometric TiO₂ films with carbon and hydrogen levels below the detection limit of Rutherford backscattering/elastic recoil detection (< 2 at.%) have been deposited within the temperature range of 25°C to 300°C. Depending on the ALD conditions and film thickness amorphous films turn anatase for temperatures higher than 200°C as revealed by X-ray diffraction. It is demonstrated that this change in crystal phase can also be observed by spectroscopic ellipsometry revealing an increase in growth rate per cycle (from typically 0.45 Å/cycle to 0.7 Å/cycle) and change in bandgap (from 3.4 eV to 3.7 eV) when the TiO₂ becomes anatase. An accompanying change in surface topology is clearly observed by atomic force microscopy. The hydrophilicity of low temperature TiO₂ films is studied by contact angle measurements for adhesion purposes revealing that the amorphous films are super-hydrophilic after UV exposure.

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