

Tuesday Afternoon, October 30, 2012

Thin Film

Room: 11 - Session TF2-TuA

ALD for Hybrid Films and Bioapplications

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

2:00pm **TF2-TuA1 Characteristics of Nanomaterials Embedded in Atomic Layer Deposition Thin Films.** *J.S. Jur, P.J. Krommenhoek, J.C. Halbur*, North Carolina State University, *H.O. Everitt*, Duke University, *J.B. Tracy, G.N. Parsons*, North Carolina State University

Atomic layer deposition (ALD) is demonstrated as a method to fabricate NP embedded thin films, and provides new opportunities to alter the characteristic properties of nanomaterials. This work examines conducting and semiconducting ALD materials growth on nanoparticles and nanowires for opportunities to alter the optical behavior and conductive behaviors of nano-enabled materials. For example, gold nanoparticles (15 nm diameter) are embedded into dense inorganic zinc oxide nanofilms deposited by atomic layer deposition onto a fibrous textile template. By changing the dielectric field surrounding the nanoparticle with the ALD ZnO, the surface plasmon resonance is dampened, resulting in significant changes to the optical absorption behavior of the textile. The alteration of the surface plasmon resonance is examined with increasing nanoparticles concentration on the fiber surface and with increasing ALD coating thickness. For example, the absorption at 900 nm is enhanced by up to 4.8x for a 45 nm ZnO ALD coating. Minimal increase in absorption is observed with additional ZnO growth. Cathodoluminescence evaluation of ZnO ALD on Au nanoparticles -loaded nylon-6 produces a ~65% decrease in the defect luminescence and a corresponding ~80% increase in the band edge luminescence. In addition, an analysis of the electrical properties of nanoparticle and nanowire embedded ALD thin films are provided. Using externally fabricated nanomaterials and embedding them in ALD thin films offers the ability to study and understand near surface interactions that can alter the characteristics of the nanomaterials.

2:20pm **TF2-TuA2 ALD-Based Fabrication and Chromatographic Separations on Binder-Free, Carbon Nanotube-Templated Thin Layer Chromatography Plates.** *M.R. Linford, R.C. Davis, D.S. Jensen, S. Kanyal*, Brigham Young University, *M.A. Vail, A.E. Dadson*, Diamond Analytics

We recently reported the use of patterned carbon nanotube (CNT) forests as scaffolds for the microfabrication of silica-based thin-layer chromatography plates (TLC) (*Advanced Functional Materials* 2011, 21(6), 1132 – 1139). In this fabrication, CNTs were infiltrated by low pressure chemical vapor deposition of silicon using SiH₄, which was then oxidized and hydrated. Thorough characterization by RBS, XPS, TEM, SEM, and ToF-SIMS has been performed on these materials, which has given us a considerable understanding of them, e.g., the structure of the Si/SiO₂/Al₂O₃ (30 nm)/Fe(6 nm) stack deposited prior to CNT growth has been confirmed, multiwall CNTs are grown in our process, CNT growth is base (bottom up) and not tip (top down), the thickness of the Fe catalyst layer plays a key role in the fabrication of our plates – when the catalyst layer is too thick CNT structures are unstable, etc. Fast and efficient separations were demonstrated on these plates.

Nevertheless, the oxidation of silicon in these materials leads to a volume expansion of the support, which appears to affect the A-term of the van Deemter equation in our separations. That is, distortions in the material appear to adversely affect separations performed on them. Accordingly, we have now shown that TLC plates can be fabricated by (i) priming patterned nanotube forests with a few nanometers of amorphous carbon, followed by a layer of Al₂O₃ deposited by atomic layer deposition (ALD), (ii) deposition of SiO₂ in a fast (pseudo) ALD of this material, and (iii) oxidizing at a lower temperature (ca. 600 K) than was used previously to remove the CNTs. An amino bonded phase was created. The resulting TLC plates show 125,000 – 225,000 N/m in a baseline separation of four fluorescent dyes. An even more recent and newly developed microfabrication method in our laboratory of CNT-templated TLC plates also shows fast separations with 400,000 – 500,000 N/m in preliminary results. These separations rival (or exceed) those of HPLC/UPLC in both speed and efficiency. Separations of biological interest will be shown.

4:00pm **TF2-TuA7 Conductivity and Mechanical Stretching of Conductive ALD Coatings on Nonwoven Fiber Mats.** *W.J. Sweet, C.J. Oldham, G.N. Parsons*, North Carolina State University

Advanced sensing, responsive and protective electronic systems integrated with fibers and flexible textile media may lead to new solutions for functional device deployment and integration. A challenging aspect of conductive coatings on fibers is the observation that most good conductors, including doped metal oxides or metallic films, are not readily flexible when coated in thin film form onto polymer fibers. For this work, we use atomic layer deposition (ALD) to produce conformal coatings of conductive ZnO, Al:ZnO and others on complex nonwoven polypropylene and nylon fibers. We measured conductivity of the as-formed coated fibers as a function of deposition temperature and other process parameters. We also measured the mechanical response of the coated and uncoated fiber mats, including measuring the change in conductivity upon fiber mat stretching. We find that in all materials measured to date, the conductivity of the fiber mat decreases with increasing applied tensile stress. For example, for Al-doped ZnO on nylon deposited at 115°C, we obtained fiber mats with conductivity of 33 S/cm, and after a 10% strain, the conductivity drops to ~3.3 S/cm. Generally, the largest conductivity decrease occurs for the materials that are most conductive to start. However, results indicate a correlation between some process parameters, such as deposition temperature, and conductivity resiliency, showing possible directions to attain highly flexible and reliable conductive material integration. In this presentation we will summarize our results regarding mechanical resiliency and conductivity and identify key parameters needed to achieve stretchable fibers that are also highly conductive.

4:20pm **TF2-TuA8 Molecular Layer Deposition of Alucones and Zincones Using Hydroquinone.** *Y. Lee, S.M. George*, University of Colorado, Boulder

Alucones and zircones are metal alkoxide polymer films that can be grown using molecular layer deposition (MLD) techniques. In this study, alucones and zircones were grown using trimethylaluminum (TMA) and diethylzinc (DEZ) as the metal precursors and hydroquinone (HQ) as the organic reactant. HQ is an aromatic diol that has a rigid structure with a central benzene ring. The benzene ring may lead to interesting electrical conductivity and the rigid structure may help to avoid “double reactions”. Quartz crystal microbalance measurements and X-ray reflectivity (XRR) studies were employed to examine film growth. Individual mass gains after the TMA and HQ exposures were consistent with a TMA:HQ stoichiometry of 4:3 in the MLD film. This TMA:HQ stoichiometry suggests the presence of Al₂O₂ dimeric core species. In comparison, individual mass gains after the DEZ and HQ exposures were consistent with a DEZ:HQ stoichiometry of 1:1 in the MLD film. XRR studies measured growth rates at 150°C of 2.6 Å/cycle for TMA/HQ and 2.7 Å/cycle for DEZ/HQ. The alucone and zirconone MLD films were also annealed in air at temperatures up to 350°C. There is evidence that the benzene rings polymerize after heating to 200°C. The films turn brown and a strong absorbance observed at ~320 nm is consistent with an expanded π-conjugated system. The polymerization of the benzene rings should change the mechanical properties of these annealed MLD films. Alucone and zirconone films were also grown using tetrafluorohydroquinone to observe the effect of fluorination of the benzene ring.

4:40pm **TF2-TuA9 Organic-Inorganic Hybrid Thin Films Prepared by Ozone Assisted Molecular Layer Deposition (MLD).** *J. Huang, M. Lee, A.T. Lucero, J. Kim*, The University of Texas at Dallas

Recently, organic thin films have been attracting attentions due to their flexibility and transparency which are suitable for large-scale display and flexible electronics applications. Alternatively, inorganic thin films have several benefits over organic thin films such as high functionality (e.g. high conductance, high dielectric constant or high polarization, etc). Potentially, organic-inorganic hybridization can widen the range of their applications, for both worlds, with new functionalities. A novel technique has been reported using a modified atomic layer deposition (ALD) method, named molecular layer deposition (MLD), which can be applied to build an organic and inorganic hybrid stack. Hybrid thin films by MLD minimized the formation of defects during the growth of the organic and inorganic layers because they are deposited by sequential, self-limiting surface reactions similar to ALD process.

In this study, we investigated the growth characteristics of organic-inorganic laminates. We focused on 7-octenyltrichlorosilane (7-OTS) and metal-oxide hybrid thin film, using ozone based MLD. 7-OTS is deposited by an exchanging reaction between functional group and water. The terminal vinyl group (C=C) of 7-OTS is converted into a carboxylic group

(-COOH) through in-situ ozone (O₃) modification. Metal oxide is then deposited as a linker layer in-between of each OTS layers using conventional ALD precursors, such as diethyl zinc (DEZ) and water. We found out that MLD process is kinetically control, which mean for a very limited of time, if we need organic molecules to form chemical bonding on top of certain surface, some special process would be required. In our experiment, we used repeating pulse to get a good coverage of organic molecules. Besides, effect of depositing temperature, dosing time, even in-situ UV activation with variety of time, location and power will also be discussed.

Characterization of organic-inorganic hybrid thin films have been extensively investigated using transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Electrical characteristics of the hybrid films will also be reported.

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5:00pm **TF2-TuA10 Organic-Inorganic Hybrid Structure Formation via Sequential Vapor Infiltration**, *H. Akyildiz, M. Yokus, R.P. Padbury, J.S. Jur*, North Carolina State University

Hybrid film formation onto polymer surfaces during atomic layer deposition (ALD) has inspired a number of processing schemes that promote precursor infiltration to increase the extent of hybrid reaction. These hybrid materials have shown opportunity in mechanical, electronic, biomedical and catalytic applications. In this work we utilize a sequential vapor infiltration (SVI) process, defined by subsets of consecutive precursor exposures, to understand the minimum precursor exposure required to saturate the formation of the hybrid material. As a test system, we examine consecutive exposures of trimethylaluminum followed by a H₂O exposure onto polyamide 6 (PA6). We investigate the effect of temperature, pressure, and exposure time on the mass change of high surface area PA6 fabrics (3 m²/g). A saturation in the mass increases is reached after ~10 TMA (0.2 sec dose, 30 sec hold) exposure cycles, resulting in a ~14 wt% increase at 30 °C and 1.5 wt% increase at 150 °C. Cross-sectional transmission electron microscopy shows a conformal surface modification of ~75 nm at 60 °C. The influence of water resident in the PA6 is examined by conducting a 120 °C *in situ* anneal prior to SVI processing, which results in a decreased of ~4 wt % at lower exposure temperatures. Still, the total mass increase is inversely proportional to temperature. A reaction-diffusion mechanism for the precursor penetration is proposed that considers a decrease in diffusion with an increased extent of reaction near the outer surface of the fiber. Application of these hybrid modifications to the mechanical and dielectric properties of the fabric is explored.

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