

Wednesday Morning, November 2, 2011

Thin Film Division

Room: 110 - Session TF1+EM-WeM

ALD/MLD: Hybrid Organic Films

Moderator: Q. Peng, Duke University

8:00am **TF1+EM-WeM1 Vapor-Phase Fabrication of Organic-Inorganic Hybrid Thin Films Using Molecular Layer Deposition with Atomic Layer Deposition**, *M.M. Sung*, Hanyang University, Korea
INVITED

We report a vapor phase deposition method of high quality organic thin films, called molecular layer deposition (MLD). MLD is a gas phase process analogous to ALD and also relies on sequential saturated surface reactions which result in the formation of a self-assembled monolayer in each sequence. In the MLD method, the high quality organic thin films can be quickly formed with monolayer precision under ALD conditions (temperature, pressure, etc). The MLD method can be combined with ALD to take advantages of the possibility of obtaining organic-inorganic hybrid thin films. The advantages of the MLD technique combined with ALD include accurate control of film thickness, large-scale uniformity, excellent conformality, good reproducibility, multilayer processing capability, sharp interfaces, and excellent film qualities at relatively low temperatures. Additionally, a vast library of materials is accessible by ALD methods, ranging from single elements to compound semiconductors to oxides, nitrides, and sulfides. Therefore, the MLD method with ALD is an ideal fabrication technique for various organic-inorganic nanohybrid superlattices.

8:40am **TF1+EM-WeM3 Metalcone and Metalcone/Metal Oxide Alloys Grown Using Atomic & Molecular Layer Deposition Techniques**, *B.H. Lee, V.R. Anderson, S.M. George*, University of Colorado, Boulder

A new class of films known as the "metalcones" can be grown using atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques. Metalcones are hybrid organic-inorganic materials derived from the sequential, self-limiting reactions of metal and organic alcohol precursors. The first metalcones were the "alucones" based on trimethylaluminum and ethylene glycol (EG) and the "zincones" based on diethylzinc and EG. Other metalcones can be fabricated with various properties using different metal precursors together with organic alcohols. This talk reports new metalcones known as the "zircones" using zirconium tert-butoxide (ZTB) and EG. In addition, this talk will discuss two new tunable ALD:MLD films based on alloys of alucone MLD/Al₂O₃ ALD and zircone MLD/ZrO₂ ALD. Zircone MLD films were grown by using zirconium tert-butoxide (ZTB) and EG. MLD growth was observed at temperatures ranging from 105 to 195°C. *In situ* quartz crystal microbalance and *ex situ* X-ray reflectivity (XRR) experiments confirmed linear growth of zircone MLD versus number of ZTB/EG reaction cycles. Zircone MLD growth rates decreased versus temperature and varied from 1.6 Å per cycle at 105°C to 0.3 Å per cycle at 195°C. A constant density of ~2.3 g/cm³ was measured for all growth temperatures. XRR measurement also showed that zircone MLD films were very stable under ambient conditions. The metalcones will have useful mechanical, optical and electrical properties that can be tuned by growing alloys of the metalcones and their parent metal oxides. For example, this tuning allows the density of alucone MLD/Al₂O₃ ALD alloys to be varied from 1.6 g/cm³ to 3.0 g/cm³. The density of zircone MLD/ZrO₂ ALD alloys could also be varied from 2.3 g/cm³ to 4.0 g/cm³. The reflective index of zircone MLD/ZrO₂ MLD alloys was also tuned continuously between 1.63 and 1.86. These new metalcone materials provide a tool set for engineering the functional properties of thin films. These materials can be grown with atomic control of thickness and excellent conformality. The metalcones and metalcone alloys can also be thermally annealed to remove the organic constituent and create porous metal oxide films.

9:00am **TF1+EM-WeM4 Sequential Vapor Infiltration and Atomic Layer Deposition on Surfactant Films for Mesoporous Metal Oxide**, *B. Gong, D. Kim, G.N. Parsons*, North Carolina State University

Mesoporous materials are critical for applications such as catalyst support, energy storage and conversion, and chemical separations. Conventionally, solution based approaches are employed for the preparation of these materials, and amphiphilic molecules are widely used as templates to form well defined pore size and surface area. In these methods, the interaction between the hydrophilic block of the surfactant molecules and the metal oxide precursors direct the self-assembly of ordered micelles/metal oxide

hybrid materials, and porous inorganic structures were recovered after removal of the organic template. Recently, this selective interaction was also discovered during vapor phase sequential vapor infiltration and atomic layer deposition (ALD) of metal oxide onto polymers, where precursor infusion and reaction depends strongly on the interaction between the precursor and polymer starting substrate. We therefore believe that sequential vapor infiltration or ALD on amphiphilic surfactant molecule films could also yield ordered inorganic/organic hybrid materials and porous metal oxides.

In this work, mesoporous aluminum oxide and titanium oxide materials were prepared by the vapor phase infiltration and ALD on two kinds of surfactants: the ionic cetyltrimethylammonium bromide (CTAB) and poly ethylene oxide based nonionic surfactant F127 (PEO-PPO-PEO). The nitrogen adsorption and desorption measurement was employed to measure the specific surface area and the pore size distribution of the resulted material. In-situ FTIR was used to monitor the chemistry change during the vapor infiltration, SEM TEM and XRD were used to characterize the structure and the morphology of the porous material.

We find that both sequential vapor infiltration and ALD produced mesoporous materials. However, the vapor phase infiltrated films show a relative higher specific surface area and narrower pore size distribution. This can be explained by the more uniform distribution of metal oxide into the surfactant layer compared to ALD. These results demonstrate a new vapor phase approach for well defined mesoporous materials, which would potentially important for many advanced applications.

9:20am **TF1+EM-WeM5 Flexibility and Water Vapor Transmission Rates for Al-, Hf-, and Zr-based ALD Films and Nanolaminates Utilizing Water and Glycerol Co-Reactants**, *M.J. Sowa, E.W. Deguns*, Cambridge NanoTech, Inc.

Organic electronics constructed on flexible substrates stand to revolutionize the display and lighting markets due to the low potential cost of manufacturing inherent to roll-to-roll manufacturing. A significant downside to organic electronics is their sensitivity to atmospheric oxygen and moisture. Various encapsulation techniques have been demonstrated, some of which have achieved Water Vapor Transmission Rates (WVTR) better than 1e-6 g/m²/d, which has been suggested to be the maximum allowable rate to give a minimum usable lifetime of 10,000 hours for Organic Light Emitting Diodes (OLEDs). However, most of the encapsulation technologies that provide these low WVTRs lack the flexibility of the underlying plastic substrate or the organic electronics, limiting the actual flexibility of the final product.

Here we will report on the flexibility of aluminum-, hafnium-, and zirconium-based ALD films deposited on representative substrate material samples of polyethylene naphthalate (PEN) at 115°C. Metal precursors used were trimethyl aluminum (TMA), tetrakis(dimethylamino)hafnium (TDMAH), and tetrakis(dimethylamino)zirconium (TDMAZ). Water was used as the ALD co-reactant for producing inorganic films while glycerol was utilized as the co-reactant for depositing hybrid organic films. Various nanolaminate combinations of the inorganic/organic materials were also investigated for their response to various levels of strain. Inorganic Al₂O₃ films subjected to 2% strain were observed to begin cracking at thicknesses below 27nm. A 2% strain did not cause any cracking on organic films deposited with TMA and glycerol to the thickest film studied at 245nm. Organic films were always observed to be more flexible than inorganic films of the same thickness. Nanolaminates were observed to have flexibility intermediate to their pure inorganic and organic constituents.

WVTR measurements were performed on inorganic, organic, and nanolaminate aluminum films. A WVTR of 6.1e-6 g/m²/day was obtained for a 100nm inorganic Al₂O₃ film. A substantially more flexible 100nm TMA + glycerol film gave a WVTR of 9.2e-6 g/m²/day.

The technical issues associated with uniformly delivering glycerol to a 115°C ALD reactor will also be discussed.

9:40am **TF1+EM-WeM6 Polymer Wires Containing Quantum Dots with Different Lengths Grown by Molecular Layer Deposition: Potential Applications to Sensitization in Photovoltaics**, *T. Yoshimura, R. Ebihara, A. Oshima*, Tokyo University of Technology, Japan

[Introduction] Molecular layer deposition (MLD) grows tailored polymer wires with designated molecular arrangements by connecting different kinds of molecules with monomolecular steps. We grew polymer wires with quantum dots (QDs), called as "polymer multiple quantum dot (polymer

MQD),” by MLD using three kinds of molecules, terephthalaldehyde (TPA), *p*-phenylenediamine (PPDA) and oxalic dihydrazide (ODH), and proposed their potential applications to sensitized photovoltaic devices.

[Polymer MQDs] As a preliminary work, polymer MQDs of OTPTPT, OTPT and OT were grown. In OTPTPT, molecules are connected in a sequence of -ODH-TPA-PPDA-TPA-PPDA-TPA-ODH---. The region between two ODHs is a QD of ~3-nm long. In OTPT, ~2-nm-long QDs are constructed with a molecular sequence of -ODH-TPA-PPDA-TPA-ODH---. In OT, ~0.8-nm-long QDs are constructed by connecting ODH and TPA alternately. A polymer MQD with three kinds of QDs, “3QD-MQD,” in which OT-like QD [OT], OTPT-like QD [OTPT] and OTPTPT-like QD [OTPTPT] are formed in one polymer wire, was grown with a sequence of -ODH-TPA-ODH-TPA-PPDA-TPA-ODH-TPA-PPDA-TPA-PPDA-TPA-ODH---. For polymer MQD growth, we used the carrier-gas type MLD, where carrier gas of nitrogen was employed to give molecular gas blows onto substrates through valves for molecular gas switching.

[Light Absorption Spectra] Light absorption measurements revealed that the peak energy of the absorption spectra shifts toward the high energy side with decreasing the QD length, namely, in the order of OTPTPT, OTPT, and OT. This effect is attributed to the quantum confinement. The absorption spectrum of 3QD-MQD is broad extending from ~480 nm to ~300 nm, which is a superposition of the spectra of [OTPTPT], [OTPT], and [OT]. This result indicates that the polymer MQD with different QD lengths could be an efficient sensitizer. In addition, the molecular orbital calculation confirmed that the electron density is high in the QD regions of 3QD-MQD.

[Proposal of Polymer MQD Sensitization] In the polymer MQD sensitization, polymer MQD is on a ZnO surface as a sensitizer. QDs exhibit narrow absorption bands comparing with bulk semiconductors like Si due to their zero-dimensional characteristics. The absorption peak energy can be adjusted by QD lengths. Therefore, polymer MQD containing different-length QDs enables us to divide the wavelength region for light absorption into narrow regions. Each QD absorbs lights of wavelengths matched to its own energy gap, and injects the excited electrons into ZnO. This might suppress the energy loss arising from the heat generation in the light absorption process. The structure is regarded as a molecular tandem structure.

10:40am **TF1+EM-WeM9 Hybrid Materials by Vapor Phase Infiltration**, *M. Knez*, Max-Planck-Institut für Mikrostrukturphysik, Germany **INVITED**

Atomic layer deposition (ALD) is a thin film deposition technique which was developed in the 1970s to meet the needs for processing thin film electroluminescent displays (TFEL). Technically and chemically it is similar to chemical vapor deposition (CVD). However, in contrast to CVD, ALD incorporates as a specific feature the separation of the chemical reaction into two half-reactions. The ALD is not only able to perform thin film coatings of inorganic materials, but also allows coatings with organic-inorganic hybrid materials and, due to the separated exposure of the substrate to the precursors, infiltration of soft matter.

This talk will show top-down approaches to hybrid organic-inorganic and bio-inorganic materials obtained by infiltration with metals from the vapor phase. With tiny amounts of metals infiltrated, biological materials, such as spider silk or collagen, can positively change their mechanical properties after being treated with pulsed vapors of metal-organic precursors. The improvement of mechanical properties is related to changes in the molecular structure of the protein-based materials. However, not only biopolymers undergo changes after infiltration. With the example of some synthetic polymers, analogous routes to modify their mechanical properties will be shown.

11:20am **TF1+EM-WeM11 Titanicene Molecular Layer Deposition Using TiCl₄ and Sugar Alcohols and Porous TiO₂ Films Produced by Annealing**, *R.A. Hall, A.I. Abdulagatov, S.M. George*, University of Colorado, Boulder

Metallene molecular layer deposition (MLD) can be performed using metal precursors and organic diols or triols. The first metallene MLD films were the alucones and zincones grown using trimethylaluminum and diethylzinc, respectively, with ethylene glycol (EG). In this work, we report the growth of titanicone MLD films using TiCl₄ and two sugar alcohols: EG and glycerol (GL). The titanicones may have useful photocatalytic properties and may form valuable porous TiO₂ frameworks upon annealing to remove the organic constituent. Titanicone films were grown using TiCl₄ and EG at temperatures between 90-135°C. Quartz crystal microbalance (QCM) measurements observed a growth rate of ~83 ng/cm²-cycle from 90 to 115°C before decreasing significantly at 135°C. X-ray reflectivity (XRR) studies obtained a growth rate of 4.5 Å/cycle with a density of 1.84 g/cm³ at 115°C. Titanicone films were grown using TiCl₄ and GL at higher temperatures between 130-210°C. The GL is believed to lead to more cross-

linking that stabilizes the MLD film. QCM measurements observed growth rates that varied slightly with temperature from 49 ng/cm²-cycle at 130°C to 34 ng/cm²-cycle at 210°C. XRR studies yielded a growth rate of 2.2 Å/cycle at 150°C. QCM measurements revealed that the surface chemistry for titanicone MLD was self-limiting. XRR studies indicated that the titanicone films were stable in air. The titanicone films were absorptive in the ultraviolet and consistent with an optical bandgap of ~3.5 eV. Annealing the titanicone films removed the carbon component and yielded porous TiO₂ films. Ultraviolet exposures also appear to be able to produce porous TiO₂ films. The ability to deposit conformal porous TiO₂ films on high surface area substrates could produce “super” high surface area substrates. These substrates may serve as TiO₂ scaffolds for dye-sensitized solar cells or photocatalytic membranes.

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