

# Wednesday Afternoon, October 20, 2010

## Thin Film

Room: Pecos - Session TF-WeA

## Thin Films: Growth and Characterization

Moderator: N.P. Guisinger, Argonne National Laboratory

2:00pm **TF-WeA1 Growth and Characterization of Thin Films for Organic Electronics Applications**, *D.J. Gaspar, L. Wang, Z.H. Zhu, M.H. Engelhard, B.J. Tarasevich, J.S. Swensen, R.E. Williford, M.E. Gross, W.D. Bennett, D.W. Matson*, Pacific Northwest National Laboratory **INVITED**

There are two basic ways of generating organic thin films for electronics applications – vacuum-based processes and solution processes (each with many variations). Each has advantages and disadvantages in film purity, morphology, deposition rate, process control, molecular design and materials choices. This presentation will describe the deposition, characterization and performance of organic thin films deposited using variants of both methods for organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs), and other applications utilizing electroactive organic thin films. Specific advantages in film purity and access to different classes of materials are discussed. Surface characterization using time of flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM and conductive AFM), ellipsometry and Fourier transform infrared spectroscopy (FTIR) are used to characterize thin films, highlighting the challenges in characterizing these often sensitive and usually amorphous films, as well as need to develop a solid experimental understanding of the composition and structure of thin films deposited for organic electronics applications to understand performance.

2:40pm **TF-WeA3 Bio Modification of Titanium Surfaces with Grafted Sodium Styrene Sulfonate Thin Films**, *G. Zorn, D.G. Castner*, University of Washington

Ti and its alloys are commonly used as biomaterials due to their unique mechanical properties and good corrosion resistance. Still, Ti implants can induce the formation of a fibrous layer that can compromise bonding at the interface with the living tissue. The lack of proper integration of Ti with tissue can lead to implant failure. Since the biological response to implanted biomaterials is initiated at their surfaces, the performance of Ti and Ti alloys can be improved by modifying their surfaces. A promising approach for surface bio-modification is grafting a bioactive polymer onto Ti implant surfaces. For optimal grafting, it is important to fully understand the nature of the bio-modified surfaces since it has a pivotal role in the biomaterial performance. The main thrust of this work is to graft bioactive sodium styrene sulfonate (NaSS) onto Ti surfaces to control and improve their response in biological environment.

Smooth Ti films evaporated onto silicon wafers were used as substrates. XPS showed that the surfaces of these films are covered with a layer of TiO<sub>2</sub>. The roughness of these surfaces, as measured by AFM, was 0.7nm. Methacryloxypropyltrimethoxysilane (MPS) was used as a cross linker between the Ti and the NaSS; the substrates were soaked in a solution of MPS in chloroform (5%v/v) for 1 hr at room temperature and then removed from the solution and heated at 140°C for 4 hrs. After attaching the MPS molecules, XPS surface composition and high resolution XPS data suggested that the Ti substrates were covered with a uniform thin film. Additional evidence for the MPS attachment to the Ti surfaces was the appearance of the C<sub>1</sub>H<sub>1.5</sub>O<sub>2</sub> fragments from the methacrylate group along with the decrease of the Ti and TiO<sub>x</sub> fragments in the ToF-SIMS data. The NaSS grafting was then done at 90°C in an oxygen free environment for 15hrs using a 0.7M solution of NaSS monomer in dimethyl sulfoxide (DMSO). After NaSS grafting the XPS composition showed an increase of the C/Ti ratio and an appearance of sulfur and sodium. ToF-SIMS successfully detected the sulfonate group, C<sub>8</sub>H<sub>7</sub>SO<sub>3</sub>, and a decrease of the Ti containing fragments. Fourier transform infrared spectroscopy (FTIR) and near edge absorption fine structure (NEXAFS) indicated an ordered array of the grafted NaSS layer on the Ti surfaces and AFM showed a uniform coverage with a roughness of 1.11nm.

Currently the mechanism of competitive protein adsorption on titanium surfaces before and after NaSS grafting is being studied. The XPS nitrogen signal indicates a higher amount of bovine serum albumin (BSA) or fibrinogen is adsorbed onto the titanium surfaces after modifying them with the NaSS layer.

3:00pm **TF-WeA4 Probing Stability of the Molecule-Substrate Interface in Self-Assembled Monolayers by Ion-Beam-Induced Desorption**, *P. Cyganik*, Jagiellonian University, Poland, *S. Wyczawska, F. Vervaecke, E. Vandeweert, P. Lievens*, Catholic University Leuven, Belgium

Due to the ease of preparation and their relatively high stability, self-assembled monolayers (SAMs) are very promising candidates to be used in the development of micro- and nano-structured materials. With numerous detailed studies available nowadays for SAMs, the identification of SAMs adsorption geometry and stability of molecule-substrate interface still remains controversial and rather difficult to access experimentally. In this presentation we report experiments on ion-induced desorption and resonance enhanced ionization mass spectrometry of SAMs on Au(111) substrate.<sup>1</sup> Although ion-induced desorption is commonly considered as a very invasive process when used for probing monomolecular films, our experiments demonstrate that this method can be successfully applied to monitor fine changes in the molecule-substrate interface stability of model SAMs systems based on thiols (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-S-Au(111), n = 2-6) and selenols (BPnSe, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-Se-Au(111), n = 2-6). Current desorption experiments will be discussed together with recent microscopic<sup>2</sup> and spectroscopic<sup>3</sup> analysis of the molecular structure and stability of these SAMs. We demonstrate that lower or higher ion-induced bond scission efficiency can be correlated with, respectively, higher or lower chemical stability of particular chemical bonds. Thus, a new method for probing the stability of the substrate-SAM interface can be proposed.

### References

- (1) S. Wyczawska, F. Vervaecke, et al. *in preparation*.
- (2) P. Cyganik, K. Szelagowska-Kunstman, et al. *J. Phys. Chem. C* **2008**, *112*, 15466.
- (3) K. Szelagowska-Kunstman, P. Cyganik, et al. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400.

4:00pm **TF-WeA7 Benzene Adsorption on Self-Assembled Monolayers**, *S.J. Sibener, H. Yuan, D.R. Killelea, K.D. Gibson*, The University of Chicago

Non-dissociative deposition of gas-phase species onto surfaces of alkanethiol self-assembled monolayers (SAMs) allows creation of new types of multi-component nanoscale materials. Systems such as these have garnered much attention due to their central role as model systems for studies of orientation-controlled adsorption and non-dissociative attachment of functional molecules on organic surfaces of technological importance, including molecular electronics.

Benzene (C<sub>6</sub>H<sub>6</sub>), perdeuterobenzene (C<sub>6</sub>D<sub>6</sub>) or a 50:50 mixture of these two isotopologues were deposited on SAM surfaces using a supersonic molecular beam. Supersonic molecular beam techniques permitted precise control over the dynamics of the deposition process by changes in the incident reagent's translational energy (E<sub>trans</sub>) and incident angle. The results presented here highlight the role these dynamical variables play in the adsorption, desorption and conformation of the resultant multilayer molecular film. A combination of *in-situ* infrared reflection absorption spectroscopy (FT-IRAS) and mass spectrometry was used to determine the surface coverage, molecular orientation and the sticking coefficient as a function of the surface coverage of the benzene molecules deposited on SAM surfaces. The interaction between adsorbates and the SAM substrate was also investigated by varying the SAM chain length and whether the SAM contains an odd or even number of carbon atoms. These results were compared to analogous results from adsorption on clean Au surfaces.

The results of these experiments uncovered the details of the adsorption process. The effects of E<sub>trans</sub> and substrate temperature on sticking show the central role dynamics plays in the physisorption of molecules on surfaces. Most significantly, the sticking of gas-phase benzene was found to have a novel dependence on surface coverage, and non-Langmuir uptake was observed.

4:20pm **TF-WeA8 Ex and In Situ Analysis of the Growth of Ultrathin Organic Films from Ethanol Solutions**, *T. Hauffman, E. Tourwé, A. Hubin, H. Terryn*, Vrije Universiteit Brussel, Belgium

In order to form stable self-assembling organic monolayers on numerous substrates, dipping deposition from organic solvents is a widespread technique. However, it is rarely investigated what is the influence of the solvent on the substrate and the molecules which are supposed to be deposited. In this study we present the self assembly of phosphonic acids from an ethanolic solution on aqueous based pretreated aluminium oxides. Following the deposition behavior with XPS and AFM throughout

deposition time, it was concluded that the nature of the deposition is random and fluctuating. In order to understand better what is going on, the deposition was followed in situ with odd random phase multisine impedance spectroscopy. This technique gives the opportunity to follow the behavior of the organic molecules as well as the behavior of the buried substrate. It was observed that ethanol adheres on the surfaces, changing the water based chemistry which was obtained through the pretreatment. Furthermore, a competition between the adsorption of the phosphonic acids and ethanol was seen, explaining the non-stable behavior previously analysed with XPS and AFM.

This statement was proven by characterizing ethanol-stabilised aluminium oxide samples during different immersion times. Although here no monolayer was formed, the trend observed corresponded with continuous organic layer growth.

**4:40pm TF-WeA9 Effect of Deposition Pressure on the Structural, Optical and Electrical Characteristics of  $Y_2O_3$  Thin Films by Reactive Magnetron Sputtering.** *V.H. Mudavakkat, K.B. Karuppanan, C.V. Ramana*, University of Texas at El Paso

Significant research efforts have been directed in recent years on the growth of  $Y_2O_3$  films because of their interesting physical, electronic, and optical properties. The diverse range of potential applications of  $Y_2O_3$  films includes storage capacitors, random access memory (RAM) and metal-insulator-semiconductor (MIS) devices, protective and antireflective coatings for IR detectors, and optical filters. In the present work,  $Y_2O_3$  films have been produced by the magnetron sputter-deposition. The effect of pressure on the structure, optical and electrical properties of  $Y_2O_3$  films has been investigated. The rate of deposition found to be significantly influenced by the overall pressure during deposition. Optical characterization carried out using transmittance analysis indicate that the samples at lower deposition rates showed weaker absorption in comparison to the samples with higher deposition rates. X-ray diffraction (XRD) showed that the as-is deposited films at room-temperature exhibit [111] oriented cubic structure. Electrical characterization indicate that films are insulating with a very high resistivity. The capacitance-voltage characteristics are also obtained for  $Y_2O_3$  films. The results will be presented and discussed.

**5:00pm TF-WeA10**, *R.S. Vemuri, S.K. Gullapalli, R.V. Chintalapalle*, University of Texas at El Paso

Tungsten oxide ( $WO_3$ ) is a wide band gap semiconductor ( $\sim 3.2$  eV), which exhibits excellent properties suitable for the development of integrated chemical sensors and electrochromics. N-type conductivity coupled with selectivity and sensitivity to certain type of chemicals make  $WO_3$  thin films interesting for  $NO_x$  and  $H_2S$  sensors. The present work was performed to understand the effect of oxygen partial pressure on the microstructure, optical and electrical properties of  $WO_3$  thin films and optimize the conditions to produce materials suitable for sensor applications.  $WO_3$  thin films were produced by the reactive RF magnetron sputtering. The films were grown at various reactive gas pressures (2.3 – 5.6 mTorr) by changing the oxygen flow rate while keeping the deposition temperature fixed at 400°C. Optical spectroscopy analysis of the grown films indicates that optical properties are sensitive to the oxygen partial pressure. The spectral transmission of the films increased with the increase in oxygen concentration. The band gap of these films was found to be increasing from 2.6 eV to 3.25 eV with increasing oxygen pressure. Electrical conductivity  $\{\sim 10^{-2} (\Omega\text{-cm})^{-1}\}$  measurements indicate that there is a correlation between the growth conditions, optical and electrical properties.

**5:20pm TF-WeA11 Effects of Deposition Temperature on Al doped ZnO Thin Film for Solar Cells by dc Magnetron Sputtering.** *W. Yang, J. Joo*, Kunsan National University, Republic of Korea, *S.M. Rossnagel*, IBM Research

Aluminum-doped zinc oxide films (AZO) were deposited on soda-lime glass substrates by dc magnetron sputtering for solar cell application. The resistivity and average transmittance were improved from  $2.3 \times 10^{-3} \Omega\text{-cm}$  to  $3.3 \times 10^{-4} \Omega\text{-cm}$  and from 77.3% to 86% at high deposition temperatures compared to films at room temperature. The mobility and carrier concentration increased, and the crystallinity and grain size also increased at high temperature during deposition. By post deposition annealing at 400°C for very short time duration, the resistivity and transmittance of room temperature films were improved up to  $4.8 \times 10^{-4} \Omega\text{-cm}$  and 90.5%. But we found the improved properties have no relation with the structural properties: crystallinity and grain size evaluated by XRD and SEM. The surface roughness of AZO films at high deposition temperature increased to 14 nm by larger grain size, but that by post deposition annealing needs an etching process due to no change of roughness.

**5:40pm TF-WeA12 Influence of Growth Rate on the Epitaxial Orientation and Crystalline Quality of  $CeO_2$  Thin Films Grown on  $Al_2O_3(0001)$  by Oxygen Plasma-Assisted Molecular Beam Epitaxy.** *M. Nandasiri, S. Kuchihbatla, P. Nachimuthu, T. Varga, V. Shuththanandan, W. Jiang, S. Thevuthasan*, Pacific Northwest National Laboratory, *S. Seal*, University of Central Florida, *A. Kayani*, Western Michigan University

Cerium oxide thin films were grown on  $Al_2O_3(0001)$  substrates with different growth rates (1-10 Å/min) by oxygen plasma-assisted molecular beam epitaxy (OPA-MBE). The growth rate induced epitaxial orientations and crystalline quality of  $CeO_2$  thin films were studied by in-situ reflection high-energy electron diffraction (RHEED), ex-situ atomic force microscopy (AFM), and high-resolution x-ray diffraction (HRXRD) techniques.  $CeO_2$  grows as three-dimensional (3-D) islands and two-dimensional (2-D) layers at growth-rates of 1-7 Å/min and  $\geq 9$  Å/min, respectively. The average surface roughness of 5-10 Å shows high-quality surfaces of  $CeO_2$  thin films. The formation of epitaxial  $CeO_2(100)$  and  $CeO_2(111)$  thin films occurs at growth rates of 1 Å/min and  $\geq 9$  Å/min, respectively. Glancing incidence XRD measurements have indicated that the films grown at intermediate growth rates (2-7 Å/min) consist of some polycrystalline  $CeO_2$  along with  $CeO_2(100)$ . The thin film grown at 1 Å/min showed six in-plane domains, characteristic of well-aligned  $CeO_2(100)$  crystallites. All six of the repeating rectangle units of O atoms from the oxygen sub-lattice in  $Al_2O_3(0001)$  that bind to Ce atoms are nonequivalent which produces six in-plane domains. This also minimizes the lattice mismatch between the thin film and the substrate leading to well-aligned  $CeO_2(100)$  crystallites. When increasing the growth rate from 1 Å/min to 2-7 Å/min, the lack of sufficient time to stabilize the Ce atoms on all the rectangle units of O atoms from oxygen sub-lattice in  $Al_2O_3(0001)$  results in poorly-aligned  $CeO_2(100)$  crystallites that start to coexist along with well-aligned crystallites. Furthermore, the content of the poorly-aligned  $CeO_2(100)$  crystallites increases with increasing growth rate up to 7 Å/min, and three out of six in-plane domains gradually decrease and eventually disappear. At growth rates  $\geq 9$  Å/min,  $CeO_2(111)$  film with single in-plane domain was identified. In order to accommodate the  $CeO_2(111)$  unit on top of the  $Al_2O_3(0001)$ , the cerium sub-lattice undergoes compression in all three axes by  $\sim 24\%$  resulting in poorly-aligned  $CeO_2(111)$  crystallites. The formation of  $CeO_2(100)$  3D-islands at growth rates of 1-7 Å/min is a kinetically-driven process unlike at growth rates  $\geq 9$  Å/min which result in an energetically and thermodynamically more stable  $CeO_2(111)$  surface.

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