Wednesday Morning, November 12, 2014

Thin Film
Room: 307 - Session TF+MS+PS-WeM

Applied ALD: Nanoelectronics and Emerging Applications
Moderator: Jesse Jur, North Carolina State University

8:00am TF+MS+PS-WeM1 ALD and Beyond CMOS Materials, *Robert Wallace*, University of Texas at Dallas **INVITED**
Two-dimensional layered materials, such as graphene and transition metal dichalcogenides (TMDs), have been recently proposed for a number of novel device concepts due to their interesting materials properties. For example, the possibility of low surface defect densities due to an anticipated dearth of surface defects and dangling bonds raises the prospect of improved performance for low power tunnel field effect logic devices that switch on and off very rapidly due to the anticipated steep subthreshold slope characteristic. However, for ALD processes, such surfaces present significant challenges for nucleation and growth. This talk will review our recent work on in-situ characterization of 2D materials for such device applications. This research is supported in part by the STARNet Center for Low Energy Systems Technology, sponsored by the Semiconductor Research Corporation (SRC) and DARPA, the SWAN Center sponsored by the SRC Nanoelectronics Research Initiative and NIST, and by an IBM Faculty Award.

9:00am TF+MS+PS-WeM4 Combining Gas Phase Aerosol Deposition with Atomic Layer Deposition for Fast Thin Film Deposition: A Case Study of Transparent Conducting ZnO, *Elijah Thimsen*, Washington University, St. Louis, *M. Johnson, A. Wagner, A. Mkhoyan, U.R. Kortshagen, E.S. Aydil*, University of Minnesota
Atomic layer deposition (ALD) has emerged as a powerful and scalable technique for a variety of applications where layer-by-layer control over film properties and conformal deposition in tight geometries are needed. One common criticism of ALD is that it is slow and may become uneconomical when thick films and high deposition rates are needed. In fact, deposition rate is often an issue even with physical vapor deposition methods such as sputtering and also chemical vapor deposition. One way to deliver material onto a substrate at high rates is through deposition of nanoparticles. Gas phase aerosol deposition is particularly attractive because rates as high as 100 nm/s are possible even at low temperatures. However, aerosol deposition often yields porous films unsuitable for optoelectronic applications. In this talk, we describe a new two-step strategy for depositing dense thin films at high rates. Our strategy combines the high rates of aerosol deposition with advantages of ALD. In the first step nanoparticles are synthesized in the gas-phase and deposited onto suitable substrates by aerosol deposition. In the second step, the space between the nanoparticles is infilled by ALD. This is a versatile approach since there are many material options for forming both the nanoparticle network and the ALD coating. In the specific example that will be discussed in this talk, the crystalline nanoparticles are synthesized in a nonthermal plasma containing the precursors that lead to nucleation and growth of the desired material. These nanocrystals are deposited on suitable substrates through supersonic expansion and inertial impaction. Using this approach, we demonstrate fast deposition of nanocrystalline ZnO films, an earth-abundant, nontoxic, low cost material that can be used as a transparent conducting oxide (TCO), from a plasma containing Ar, O_2 and diethylzinc. The space between the particles is filled either by Al_2O_3 or Al-doped ZnO (AZO) to give continuous TCO films. After annealing in H_2 and coating with Al_2O_3, the ZnO nanocrystal network becomes conductive with Hall effect electron mobilities as high as 3.0 cm^2 V^{-1} s^{-1}. Depending on the combination of the nanocrystals, ALD coating, and post processing, we have obtained transparent films with resistivity values as low as 3.8 x10^{-3} Ohm cm. The lowest resistivity films were obtained with undoped ZnO nanoparticles coated with AZO. The resistivity can be improved by doping the nanocrystals, which has proven to be challenging. We will discuss the effects of nanocrystal size, doping of nanocrystals in the gas phase, and film porosity on electrical conductivity.

9:20am TF+MS+PS-WeM5 Detecting Order in the Molecular Layer Deposition of Polymer Films by X-Ray Diffraction, *David Bergsman*, *R.W. Johnson, R. Britto, S.F. Bent*, Stanford University
The deposition of highly ordered, thin, organic films is of great importance to a variety of fields. The development of biological sensors, organic solar cells, and optical devices relies on the ability to grow thin layers of organic material with various thicknesses, compositions, functionalities, and levels of crystallinity. One promising method of creating such films is molecular layer deposition (MLD), which uses an alternating sequence of self-saturating reactions by vapor-phase organic precursors at the substrate to grow films in a layer-by-layer fashion. This technique has been demonstrated with a variety of precursor chemistries and has been shown capable of growing films on high aspect ratio features with low surface roughness and high conformality. But despite the growing use of MLD, many questions still remain as to the orientation of the molecular chains within the deposited films and the packing of these chains. Many different factors may contribute to varying degrees of crystallinity during growth, such as chain-chain steric repulsion, Van der Waals forces, chain growth angle, and inter-chain hydrogen bonding. Here, we demonstrate that some MLD chemistries can form nanoscale organic films that exhibit well-ordered packing. Polyurea MLD films with different thicknesses and backbone chemistries were grown in an MLD reactor and then examined with x-ray diffraction (XRD) using synchrotron radiation at the Stanford Synchrotron Radiation Lightsource (SSRL). Spectroscopic ellipsometry was used to observe film thickness, while x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy monitored for film degradation. XRD results for the polyurea MLD films show peaks at q-values of 1.5/Å, corresponding to a d-spacing around 4.2 Å. Changing the precursor from a more rigid to a more flexible backbone leads to variations in d-spacing and diffraction intensity. Growth on substrates with different surface chemistries and roughness, as well as the effect of heating and re-cooling the films, is also explored. These results suggest that thin organic films with varying levels of packing order can be grown using MLD by tuning the precursor chemistry.

9:40am TF+MS+PS-WeM6 Native Oxide Diffusion and Removal During the Atomic Layer Deposition of Ta_2O_5 on InAs(100) Surfaces, *Alex Henegar*, *T. Gougousi*, University of Maryland, Baltimore County
The use of high-κ dielectrics on III-V semiconductors in place of Si/SiO_2 structures in metal oxide semiconductor devices has been perpetually hindered by poor quality native oxides at the substrate/film interface. A promising solution for the removal of these oxides is the atomic layer deposition (ALD) growth technique which has shown the ability to remove native oxides during deposition without additional processing for certain chemistries.[1–4]

In this work, Ta_2O_5 thin films were deposited on InAs(100) by ALD using pentakis dimethyl amino tantalum (PDMAT) and H_2O to study the effects of film deposition on the native oxides. 3 and 7 nm films were grown at 150-300 °C on InAs substrates covered with native oxides and substrates chemically etched in NH_4OH. Analysis of the film deposited on native oxide covered substrates by x-ray photoelectron spectroscopy (XPS) shows arsenic and indium oxides are readily removed during deposition of 3 nm Ta_2O_5 at 250 and 300 °C, temperatures very close to the optimal ALD temperature for the specific chemistry. At lower temperatures both oxides persist with indium oxides generally being harder to remove.

Depth profiling by argon-ion sputtering data of 7 nm films shows that indium oxides have diffused into the Ta_2O_5 film. The sharp decrease in oxide signal after the first sputter cycle indicates that the majority of the indium oxide is located near the surface suggesting the migration of indium oxides to the film surface during deposition. Arsenic oxides, however, are detected in smaller amounts and generally speaking remain at the interface. For depositions on etched InAs no arsenic oxides were detected but a small amount of indium oxides remain even at the optimal deposition temperatures. Films grown on etched substrates always contain less indium and arsenic oxides than their equivalents deposited on native oxide surfaces. Mixing of indium oxide in the films may have a significant negative effect on their insulating properties negating any gain from a sharper interface.

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[3] M.L. Huang, Y.C. Chang, C.H. Chang, Y.J. Lee, P. Chang, J. Kwo, T.B. Wu, and M. Hong, Appl. Phys. Lett. **87**, 252104 (2005).

[4] C.-H. Chang, Y.-K. Chiou, Y.-C. Chang, K.-Y. Lee, T.-D. Lin, T.-B. Wu, M. Hong, and J. Kwo, Appl. Phys. Lett. **89**, 242911 (2006).

11:00am TF+MS+PS-WeM10 ALD in High Aspect Ratio Structures and Nanoporous Materials, *C. Detavernier*, *Jolien Dendooven*, University of Ghent, Belgium **INVITED**
Atomic layer deposition (ALD) is known to be an excellent technique for the deposition of thin films with uniform thickness over micro- and

nanoscale 3D structures. The superior conformality of ALD is a direct consequence of the self-saturated surface reaction control and makes the technique increasingly useful in the rapidly growing field of nanotechnology. The successful ALD-based processing of nanostructured materials requires however a careful optimization of the growth parameters. In this work, we present an extensive study on the conformality of ALD in high aspect ratio structures and nanoporous materials.

A first experimental approach was based on the use of macroscopic, trench-like structures in combination with low precursor pressures. In this way, the transport of the precursor molecules in the test structures was governed by molecular flow, as in microscopic trenches under standard ALD conditions. This method allowed us to quantify the conformality of the trimethylaluminum (TMA)/H2O process as a function of the aspect ratio and the TMA exposure time. Our experimental data indicated that the sticking probability is a determining factor in the conformality of ALD [1]. A better understanding of the effect of this parameter on the conformality was obtained via kinetic modeling and Monte Carlo modeling.

As a second substrate, porous titania thin films with pore sizes in the low mesoporous regime (< 10 nm) were considered in order to get insights on the minimum pore diameter that can be achieved by ALD. Novel in situ characterization techniques were developed to monitor the pore filling by ALD. Synchrotron-based x-ray fluorescence and scattering techniques provided cycle-per-cycle information on the material uptake and densification of the porous film, while ellipsometric porosimetry was used to quantify the pore size reduction. This study nicely demonstrated the ability of ALD to tune the diameter of nanopores down to the molecular level [2].

Finally, we performed ALD of TiO2 into a 3D ordered silica powder with two types of mesopores [3]. By varying the Ti-precursor exposure time, we investigated the introduction of TiO2 into the differently sized mesopores. A TEM study revealed the diffusion limited nature of the TiO2 ALD process, leading to anisotropic penetration profiles in this specific pore structure. We observed a systematic deeper penetration of the deposition front along the main channels compared to the narrower mesopores. These results were corroborated by modeling work.

[1] J. Dendooven et al., J. Electrochem. Soc. 156, P63, 2009. [2] J. Dendooven et al., Chem. Mater. 24, 1992, 2012. [3] S. P. Sree et al., Chem. Mater. 24, 2775, 2012.

11:40am **TF+MS+PS-WeM12 Pyrolysis of Alucone MLD Films to Form Electrically Conducting and Nanodomained Al$_2$O$_3$/C Composite Films**, *J.J. Travis, J.W. DuMont, **Steven George***, University of Colorado, Boulder

Alucone is an aluminum alkoxide polymer grown using molecular layer deposition (MLD) techniques with trimethylaluminum and organic diols or triols as the reactants. Alucone films can be pyrolyzed under inert atmosphere or vacuum to yield electrically conductive Al$_2$O$_3$/C composite films. This pyrolysis provides a pathway to deposit ultrathin, conformal and conducting Al$_2$O$_3$/C films on high surface area substrates. Our recent results have shown that the electrical conductance of the Al$_2$O$_3$/C films is dependent upon the amount of carbon in the film. The initial alucone films are non-conducting. After pyrolysis to 850°C, alucone films grown using glycerol, with three carbons, or hydroquinone, with six carbons, display high electrical conductivity of ~1-3 S/cm. In contrast, pyrolyzed alucone films grown using ethylene glycol, with only two carbons, remain non-conducting. In situ transmission Fourier transform infrared (FTIR) spectroscopy was used to monitor the pyrolysis of the alucone films. The C-H, C-O and C-C vibrational features were lost from the alucone films between 300-450°C. The vibrational spectra also showed prominent carboxylate features at 400-450°C. Carboxylate features are consistent with COO$^-$ – Al^{3+} complexes at the interfaces between the Al$_2$O$_3$ and carbon regions of the composite. High resolution transmission electron microscopy (HRTEM) images are consistent with a highly interfacial nanodomained Al$_2$O$_3$/C composite. These Al$_2$O$_3$/C composite films may provide electrical conductivity and oxidation resistance during electrochemical processes on metal and carbon electrodes.

12:00pm **TF+MS+PS-WeM13 Atomic Layer Deposition of Metal Oxides on Ultra-High Aspect Ratio, Vertically Aligned Carbon Nanotube Arrays**, *Kelly Stano, M. Carroll, R.P. Padbury, J.S. Jur, P. Bradford*, North Carolina State University

Atomic layer deposition (ALD) is commonly used to coat high aspect ratio structures, including vertically aligned carbon nanotube arrays (VACNTs). Previous studies, however, have demonstrated precursor diffusion depths of only 60 μm for long exposure times, leading to a "canopy effect" where preferential coating takes place at the top of arrays. In this research we report the first example of conformal Al$_2$O$_3$ ALD on 1.5 mm tall VACNTs with uniform coating distribution from CNT base to tip. Large-scale CNT arrays with free volume aspect ratios ~15,000 were able to be uniformly coated by manipulating sample orientation and mounting techniques, as confirmed by cross-sectional energy dispersive x-ray spectroscopy. Conformal coating was achieved through modification of CNT surface chemistry via vapor phase techniques including pyrolytic carbon deposition and atmospheric pressure oxygen plasma functionalization. Thermogravimetric analysis revealed that arrays which were functionalized prior to ALD coating were more stable to thermal degradation compared to untreated, ALD coated arrays. Interestingly, CNTs could be easily removed during thermal oxidation to yield arrays of continuous, high surface area, vertically aligned Al$_2$O$_3$ nanotubes. Additionally, functionalized and ALD coated arrays exhibited compressive moduli two times greater than pristine arrays coated for the same number of cycles. Al$_2$O$_3$ coated arrays exhibited hydrophilic wetting behavior as well as foam-like recovery following compressive strain. These processing techniques have been successfully applied to other ALD precursors to yield CNT arrays uniformly coated with ZnO and TiO$_2$ as well.

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