

# Thursday Morning, October 31, 2013

## Thin Film

Room: 102 C - Session TF+PS-ThM

## Advanced CVD Methods

Moderator: R.C. Davis, Brigham Young University

8:00am **TF+PS-ThM1 Non-destructive Spectroscopic Analysis of Gradient Hydrocarbon/Fluorocarbon Thin Films to Demonstrate the Formation of a Stable Gradient Structure during PECVD Film Growth.** *B.D. Tompkins, E.R. Fisher*, Colorado State University

Thin films that have a continuous change in composition in one or more dimensions have a wide variety of potential applications, including biomimetic materials, barrier films, adhesion interlayers, and optical coatings. These gradient film structures are valuable for their ability to direct processes within a film or along a surface; the ability to tailor these materials allows for unprecedented control over such a process. We have developed a plasma enhanced chemical vapor deposition (PECVD) system capable of fabricating a range of arbitrary gradient film structures using dynamic mixing of  $C_3F_8$  and  $H_2$ . We used time resolved optical emission spectroscopy (TR-OES) to characterize the PECVD process and found that the relative gas-phase density of key radical species change reproducibly based on the  $C_3F_8/H_2$  ratio at any given time. Although the  $C_3F_8/H_2$  composition can be varied continuously, verifying that a stable continuous gradient composition has been fabricated presents a more complicated analysis problem. Recently, we have adapted standard non-destructive spectroscopic analysis techniques to elucidate the structure within a gradient film. A series of homogenous films and model gradient films were examined using x-ray photoelectron spectroscopy (XPS), variable angle spectroscopic ellipsometry (VASE), and infrared spectroscopy (FTIR). By examining the shift in  $CF_2$  binding energy from XPS, dielectric constant from VASE, and the shift in  $\nu(CF_2)$  from FTIR, we demonstrate that stable confined layers with high fluorocarbon content remain incorporated into the gradient material when fabrication is complete. The ability to tailor surface composition and properties through programed deposition will also be discussed.

8:20am **TF+PS-ThM2 CVD Infiltration of Carbon into Carbon Nanotube Forests for Templated Microfabrication.** *R.R. Vanfleet, W. Fazio, J.M. Lund, K. Zufelt, T. Wood, D.D. Allred, R.C. Davis, B.D. Jensen*, Brigham Young University

Chemical Vapor Deposition (CVD) of materials into patterned frameworks of carbon nanotube forests can be used to create precise high-aspect-ratio (up to 200:1) microstructures. We call this process carbon nanotube templated microfabrication (CNT-M). The "as grown" CNT forests are very low density (at 0.009 g/cc the forest is ~1% carbon and 99% air) and not useful as mechanical materials themselves because they are extremely fragile, due to their low density and weak intratube bonding. However, when we replace the air spaces between tubes in the forest with a filler material by atomistic deposition, the infiltrated CNT framework becomes a robust microstructure consisting mostly of the filler material. We have used various deposition techniques to infiltrate the CNT framework with a range of materials. This presentation will focus on the fabrication and characterization of structures using CVD of carbon into the nanotube forest. A range of characterization has been applied to the materials and resulting structures from high resolution electron microscopies of the base materials to bending and failure tests of full structures. The materials consist of nanocrystalline graphitic carbon coated on multiwalled carbon nanotubes. The complete structures exhibit fairly low Young's modulus (5-15 GPa), and ultimate strength (100-200 MPa) with a resulting high maximum strain of over 2%.

8:40am **TF+PS-ThM3 Initiated Chemical Vapor Deposition of Functional Polymers onto Porous Materials and Liquid Surfaces.** *M. Gupta*, University of Southern California **INVITED**

This talk will present the mechanism, kinetics, and potential applications associated with the vapor phase deposition of functional polymers onto structured materials and liquid surfaces. Vapor phase deposition eliminates the need for organic solvents and thereby offers a safer and cleaner alternative to liquid phase polymer processing. We will demonstrate our ability to pattern functional polymers onto structured materials such as microfluidic devices, porous materials, and pillar arrays. We will also present our recent work demonstrating deposition onto liquids with negligible vapor pressures such as ionic liquids (ILs) and silicone oils. We will demonstrate that the polymer morphology at the liquid/vapor interface is controlled by surface tension interactions. The ability to controllably

tailor polymer morphology at the interface allows for the design of ultrathin free-standing polymer films, micron-scaled particles, and core-shell particles. We will also demonstrate that polymerization can occur within the liquid layer allowing for the fabrication of polymer/IL composite films.

9:20am **TF+PS-ThM5 Ultrasonic Spray Deposition of Mesoporous  $WO_3$  Films Displaying 100% Optical Modulation.** *C.-P. Li*, Colorado School of Mines, *C. Engrakul, R.C. Tenent*, National Renewable Energy Laboratory, *C.A. Wolden*, Colorado School of Mines

Smart windows employing electrochromic materials to reversibly modulate optical transmission and reflection can significantly improve building energy efficiency. However, further improvements in both performance and cost reduction are required for widespread implementation of electrochromic windows. Mesoporous films comprised of nanocrystalline domains can provide both high performance and good durability. Sol-gel chemistries combined with sacrificial templating agents is a well-established technique to introduce controlled porosity, but conventional techniques for film formation such as spin/dip coating are not amenable to large scale production. Ultrasonic spray deposition (USD) is an attractive technique for large scale, low cost thin film manufacturing of nanostructured thin films. USD provides high materials utilization and the use of benign solvents enables deposition under ambient conditions. Piezoelectric nebulizer technology addresses the quality and uniformity issues that were a concern with conventional pressure driven sprays. In this work mesoporous  $WO_3$  films were deposited by adapting sol-gel chemistry to ultrasonic spray deposition. The sol was formed by dissolving  $WCl_6$  and an organic templating agent (P123) in ethanol. The dynamics of both sol preparation and hydrolysis were investigated by UV-Vis spectroscopy. Electrochromic performance is strongly correlated to both the annealing conditions and the sol composition. Optimized films produced world record coloration efficiency ( $68 \text{ cm}^2/\text{C}$ ), resulting in never before achieved 100% optical modulation across the visible spectrum during cycling. The films also displayed good switching kinetics, producing a 75% change in absolute transmission in 4 and 19 s during coloration and bleaching, respectively. Achievement of optimum electrochromic performance could be achieved by controlling the sol concentration and/or the number of spray passes in this robust process. The films were smooth and uniform, and the excellent performance is attributed to the nanocrystalline nature of the films, which provides high specific surface area ( $>100 \text{ m}^2/\text{g}$ ) for efficient lithium ion intercalation.

9:40am **TF+PS-ThM6 Preparation and Characterization of CVD & ALD Tungsten & Molybdenum Thin Films for CNT-M Metallic Microstructures.** *D.D. Allred, R.R. Vanfleet, J.K. Anderson, C. Brown, R.S. Hansen*, Brigham Young University, *D. McKenna*, University of Notre Dame, *R.C. Davis*, Brigham Young University

Microelectromechanical systems (MEMS) fabrication traditionally uses the same limited methods and materials as those used in the silicon-based microelectronics industry. In order to make MEMS out of a much richer suite of materials, such as metals, Brigham Young University researchers are investigating chemical vapor infiltration and atomic layer infiltration of patterned carbon nanotube (CNT) forests, using the surface of the carbon nanotubes as nucleation sites for the metal deposition. Our goal has been to fill in the spaces between CNTs by atomistic deposition, thus creating a CNT-composite material possessing the original pattern of the CNT forest. We have investigated two 2 metals: tungsten and molybdenum and 3 precursors: tungsten carbonyl, molybdenum carbonyl and tungsten hexafluoride with hydrogen. molybdenum carbonyl proved to be more successful than tungsten carbonyl for infiltration. As deposited the materials are not pure metals, but contain substantial amounts of carbon and oxygen. As deposited the materials are not pure metals, but contain substantial amounts of carbon and oxygen. Efforts to remove impurities as well as the electrical and mechanical properties of the resulting composite material will be reported. Most recently tungsten fluoride via both CVI and ALI has been used to deposit purer tungsten structures.

10:40am **TF+PS-ThM9 Silica Structures by Plasma-enhanced Chemical Vapor Infiltration of a Carbon Nanotube Template.** *J.M. Lund, B.D. Jensen, R.C. Davis, R.R. Vanfleet*, Brigham Young University

This work investigates the advantages of infiltrating carbon nanotube structures with silica by plasma-enhanced chemical vapor deposition (PECVD). Carbon nanotube (CNT) forests have unique porous structures created through CNT interaction during the growth process. It is possible to coat individual nanotubes with silicon oxide using a PECVD process. Oxidation of the carbon nanotubes then removes the initial CNT template, resulting in a uniquely structured silica material. One application of this work is the fabrication of ultra-low thermal conductivity films.

Measurements indicate a thermal conductivity less than 0.05 W/m-K. However, with this particular process the coating is invariably thicker near the top surface and the silica typically penetrates no more than 17  $\mu\text{m}$  into the CNT forest. The current challenge in this work is to keep the structures as porous as possible while coating enough at the base to keep the structure continuous and attached to the substrate. Some investigation is made into the parameters influencing, and possible uses of, the infiltration depth. This includes the usefulness in capping or sealing porous structures so they can be planarized in preparation for other films and structures.

11:00am **TF+PS-ThM10 High Deposition Rate and Uniformity of Silicon Thin Films Deposited Via Efficient, Low-Damage Surface Wave Plasma Source**, J. Peck, P.S. Zonooz, D. Curreli, University of Illinois at Urbana Champaign, M. Reilly, R. Stubbers, B. Jurczyk, Starfire Industries, LLC, D.N. Ruzic, University of Illinois at Urbana Champaign

An innovative surface wave plasma source provided by Starfire Industries, LLC has been tested by the Center for Plasma-Material Interactions at the University of Illinois Urbana-Champaign. Operating in the microwave range, the source efficiently generates high-density ( $10^{11-12} \text{ cm}^{-3}$ ) and low electron temperature ( $\sim 1$  eV) plasmas. Thin silicon films were deposited with the interest of characterizing a cost-effective PECVD process for high quality silicon photovoltaics. Parameters of interest included substrate temperature, total operating pressure, silane dilution, RF power, discharge gap width, and process gas flowrate. Through a  $\text{SiH}_4:\text{H}_2$  discharge, films were deposited and subsequently analyzed via profilometry, SEM, Raman microscopy, and X-ray diffraction. For a 15 cm source, consistent radial uniformity was maintained across a 12 cm diameter from  $2.0 \pm 0.4 \text{ nm/s}$  up to  $3.5 \pm 0.9 \text{ nm/s}$  at a 2.5 cm discharge gap. Well-formed films were produced with substrate temperatures above 285C. With decreasing operating pressure and increasing flowrate, area of coverage is shown to increase without compromising speed of film growth. An assessment on deposition rate optimization, film uniformity, and large-area scalability is presented.

11:20am **TF+PS-ThM11 Ab-initio and Classical Molecular Dynamics Study of Diffusion of Ti and N Adatoms on the TiN(001) Surface**, D.G. Sangiovanni, D. Edström, L. Hultman, Linköping University, Sweden, I.G. Petrov, J.E. Greene, University of Illinois at Urbana Champaign, V. Chirita, Linköping University, Sweden

We carry out *ab-initio* and classical molecular dynamics (MD) simulations to investigate fundamental atomistic processes and surface properties responsible for TiN surface evolution during thin film growth. We find that Ti adatoms are highly mobile on TiN(001) terraces where they diffuse between fourfold hollow sites primarily via  $\langle 100 \rangle$  channels.  $\langle 110 \rangle$  diffusion via atop N terrace atoms, double and triple  $\langle 100 \rangle$  jumps are also observed, and their occurrence is a function of TiN(001) temperature. When placed on TiN/TiN(001) islands, Ti adatoms funnel toward cluster edges and corners, where they rapidly descend by either direct hopping or push/out-exchange. Ti and N adatoms diffusion on square islands is anisotropic and results in preferential channels for mass transport. N adatoms, considerably less mobile than Ti adatoms, can form strong chemical bonds with underlying terrace or island N atoms. As an effect of this bonding, N adatoms can diffuse on TiN(001) terraces by exchange with N terrace atoms. At high temperatures, the rapid lattice vibrations assist the desorption of  $\text{N}_2$  (N-adatom/N-terrace) dimers, and anion vacant sites are produced in the TiN(001) terrace. When placed on square TiN/TiN(001) clusters, N adatoms can pull Ti corner atoms onto the island to form TiN dimers which descend via direct hop over the island edge. Both N and Ti adatoms slowly diffuse along island edges. In contrast, due to the high degree of ionicity in Ti-N bonds, Ti and N adatoms easily diffuse around island corners of the same chemical type via 1D push-out/exchange due to electrostatic repulsion. Corners of opposite chemical type are rapidly rounded by direct diffusion. Finally, we combine the Arrhenius plots obtained from classical, and quantum-mechanical simulations to determine, with high accuracy, Ti and N adatom diffusion energy barriers and diffusion coefficients on TiN(001). The excellent agreement between empirical and *ab-initio* methods results further demonstrates the ability of classical interaction potentials for accurate, fully-deterministic, simulations of thin films deposition.

11:40am **TF+PS-ThM12 Quantum Chemistry Analysis of the Role of Radicals in Plasma Assisted Atomic Layer Deposition of Silicon Nitride Films**, J. Yoshikawa, N. Fukiage, S.Y. Kang, Tokyo Electron Ltd., P. Ventzek, Tokyo Electron America, H. Ueda, Tokyo Electron Ltd.

Silicon nitride films are well known as important dielectric components for semiconductor device fabrication because of their good physical and electrical properties for 3D structure device construction. High quality silicon nitride film deposition has been demonstrated in high density plasma sources by using RLSA<sup>TM</sup> in which a nitrogen and hydrogen containing plasma nitrates a silicon surface deposited by a thermal adsorption process.

[1] A typical precursor for the silicon component is Dichlorosilane (DCS), used in thermal CVD of silicon nitride. [2] In plasma assisted atomic layer deposition of silicon nitride films, silicon nitride deposition is effected by alternating deposition and nitridation steps. The film quality, defined by the 0.5% DHF solvent wet chemical etching ratio, is a function of many process parameters. It has been shown experimentally that hydrogen radicals produced in this plasma are important for film quality. The exact film growth mechanism in plasma assisted deposition processes is, as yet, not fully clarified and most studies are related to thermal CVD. *Ab-initio* studies focusing on the role of radicals are rare. In this presentation a quantum chemistry analysis (Gaussian 09) of the film formation mechanism in Atomic layer Deposition sequence is presented. Hexachlorodisilane (HCD) is used as a model surface in the study. We revealed the role of H as a critical precursor for the growth of high quality films. Un-dissociated ammonia or hydrogen interacts with Si-Cl to liberate chlorine from silicon. Hydrogen liberates H from the new  $\text{NH}_2$  structure. Silicon containing structures with dangling bonds interact with the structure then complete the formation of Si-N-Si bonding. Hydrogen and  $\text{NH}_x$  limit restoration of the Si-Si chain.

[1] T. Karakawa, M. Oka, N. Fukiage, H. Ueda, T. Nozawa, PS+TF-ThM1 AVS Symposium Nashville (2011) [2] A. A. Bagatur'yants, K. P. Novoselov, A. A. Safonov, L. L. Savchenko, J. V. Cole and A. A. Korokin, Materials Science in Semiconductor Processing 23, 3 (2000)

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