

## Thin Film

Room: 613/614 - Session TF-MoM

### Atomic Layer Deposition and Applications

**Moderator:** G.N. Parsons, North Carolina State University

8:40am **TF-MoM3 Conformal Polymeric Thin Films via Initiated Chemical Vapor Deposition.** *S.H. Baxamusa, M. Gupta, K.K. Gleason,* Massachusetts Institute of Technology **INVITED**

Conformal surface modification of high aspect ratio micro- and nano-structures is desirable for a range of applications ranging from microelectronics to textiles. In this work, initiated chemical vapor deposition (iCVD) is demonstrated to conformally deposit thin polymer films (<500 nm) at high growth rates (up to 100 nm/min). The iCVD technique is a low energy process (0.01 W/cm<sup>2</sup>) that fully retains the pendent functionality in the deposited polymer films, a result that has been demonstrated with more than 40 different vinyl monomers. The iCVD method is particularly valuable for creating ultrathin layers of insoluble polymers. For the process, initiator and monomer vapors simultaneously flow into a vacuum where decomposition of the initiator results in free-radical polymerization of the monomer on the substrate. As iCVD relies on neutral chemistry, directional effects on deposition typically associated with the electric fields in plasma processes are avoided. Step coverage of trenches in silicon substrates by polymeric iCVD coatings will be shown to depend on the ratio of monomer to initiator. A kinetic model highlights the surface-driven nature of iCVD polymerization and that is analogous to free radical polymerization in the bulk phase, albeit on the surface. The iCVD process is often absorption limited and hence cool (~25 °C) substrates are essential for rapid film growth. From an applications perspective, low substrate temperatures are favorable for the coating of thermal sensitive materials, including paper, plastics, fabrics, and membranes. The iCVD process can be used to functionalize membranes with high aspect ratio (80:1) pores with a hydrophobic polymer coating. X-ray photoelectron microscopy data confirmed the presence of the iCVD coating on the topside and backside of the membranes and electron microprobe analysis confirmed the presence of the coating along the pore wall. Additionally, the iCVD process has been demonstrated conformally to coat carbon nanotube forests and microparticles. Superhydrophobic surfaces (contact angles >175 degrees) result from surface modification of nanostructured substrates by iCVD PTFE and polymerized perfluoroalkyl ethyl methacrylate.

9:20am **TF-MoM5 Nanolaminate Gas Diffusion Barriers on Polymers with Exceptionally Low H<sub>2</sub>O Permeabilities.** *A.A. Dameron, S.M. George,* University of Colorado at Boulder, *P.F. Carcia, R.S. McLean,* DuPont Research and Development

Flexible, ultrathin gas diffusion barriers are required for the protection of organic electronics, e.g. organic light emitting diodes (OLEDs) in flexible displays. Existing barriers provide insufficient protection from permeating H<sub>2</sub>O and O<sub>2</sub> gases. Our earlier work demonstrated that a low water vapor transmission rate (WVTR) of ~1 × 10<sup>-3</sup> g/m<sup>2</sup>/day could be achieved on polyethylene naphthalate (PEN) and Kapton using Al<sub>2</sub>O<sub>3</sub> ALD films with thicknesses of ~25 nm. These H<sub>2</sub>O transmission rates are not low enough to meet OLED requirements. The Al<sub>2</sub>O<sub>3</sub> ALD films also degrade over time with exposure to H<sub>2</sub>O vapor. To lower the H<sub>2</sub>O transmission rates further and to protect the Al<sub>2</sub>O<sub>3</sub> ALD films, we have used additional layers in combination with the ~25 nm Al<sub>2</sub>O<sub>3</sub> ALD layer. The additional layers were one layer of silicon nitride with a thickness of >60 nm deposited by plasma-enhanced chemical vapor deposition (PE-CVD) or one layer of SiO<sub>2</sub> with a thickness of ~60 nm deposited using rapid SiO<sub>2</sub> ALD. Both of these additional layers in combination with the ~25 nm Al<sub>2</sub>O<sub>3</sub> ALD layer reduced the measured WVTR to ~1 × 10<sup>-4</sup> g/m<sup>2</sup>/day. When deposited on top of the Al<sub>2</sub>O<sub>3</sub> ALD film, these silicon-containing layers also protect the Al<sub>2</sub>O<sub>3</sub> ALD film from H<sub>2</sub>O exposure. Nanolaminates of Al<sub>2</sub>O<sub>3</sub> ALD and SiO<sub>2</sub> ALD should further reduce the WVTRs. These nanolaminate films are fabricated by alternating the Al<sub>2</sub>O<sub>3</sub> ALD and SiO<sub>2</sub> ALD to create 2 bilayers, 3 bilayers or higher numbers of bilayers. Tests of multiple bilayer nanolaminate structures of Al<sub>2</sub>O<sub>3</sub> ALD and SiO<sub>2</sub> ALD on Kapton have yielded extremely low WVTRs of 5 × 10<sup>-5</sup> g/m<sup>2</sup>/day using the HTO testing technique. These exceptionally low WVTRs are approaching the range that is necessary for OLED devices in flexible displays.

9:40am **TF-MoM6 Atomic Layer Deposition for Passivation and Corrosion Protection of Metal Substrates.** *S.I. Sneek,* Baneq, Finland

The unique features of Atomic Layer Deposition; capability to produce highly conformal pin-hole free films on complex structures and excellent adhesion to most surfaces, have been utilized mainly by the semiconductor industry. However, these properties are often highly appreciated by many other industries as well. As an example, silver industry has recently started using ALD to protect silver jewelry from tarnishing. Tarnishing is mostly caused by airborne sulfur compounds forming black silver sulfide on the surface of a silver object. In this application, the most important criteria are invisibility and anti-tarnish properties of the coating. A uniform 10nm thick aluminum oxide layer increases the tarnishing time by two orders of magnitude while being invisible to human eye. The same method can also be applied to other silver products as well as other metals, including copper and copper containing alloys. In addition to passivation of silver and copper based products, more demanding anti-corrosion coatings can be done on stainless steel and other common construction metal parts used in extreme conditions. Relatively low growth rate of ALD compared to other thin film techniques can be compensated with large batch size, since ALD is one of the easiest thin film processes to scale-up. ALD films can also often be much thinner compared to films prepared with other thin film techniques, for example if certain barrier properties are required. This is due to higher film uniformity and fewer pin holes in ALD films. Even though most work with ALD has been done on silicon and glass substrates, metal substrates offer many applications for ALD, since complex shaped parts are often made of metal. By careful selection of coating structure, it is possible to combine anti-corrosion coatings with other functions, including decorative and wear resistant functions.

10:20am **TF-MoM8 Combinatorial Atomic Layer Deposition of Nanolaminates.** *W.L. Gladfelter, T. Moersch, L. Zhong, B. Luo,* University of Minnesota **INVITED**

Nanolaminates of HfO<sub>2</sub> and SiO<sub>2</sub> were prepared using atomic layer deposition methods. Successive exposure of substrates maintained at 120 or 160°C to nitrogen flows containing Hf(NO<sub>3</sub>)<sub>4</sub> and (tBuO)<sub>3</sub>SiOH led to typical bilayer spacings of 2.1 nm with the majority of this being SiO<sub>2</sub>. Combining the Hf(NO<sub>3</sub>)<sub>4</sub>/(tBuO)<sub>3</sub>SiOH ALD with ALD cycles involving Hf(NO<sub>3</sub>)<sub>4</sub> and H<sub>2</sub>O allowed the systematic variation of the HfO<sub>2</sub> thickness within the nanolaminate structure. This provided an approach towards controlling the dielectric constant of the films. The dielectric constant was modeled by treating the nanolaminate as a stack of capacitors wired in series. The nanolaminate structure inhibited the crystallization of the HfO<sub>2</sub> in post-deposition annealing treatments. As the HfO<sub>2</sub> thickness decreased, the preference for the tetragonal HfO<sub>2</sub> phase increased. Nanolaminates of SiO<sub>2</sub> with compositionally graded mixture of HfO<sub>2</sub> and ZrO<sub>2</sub> were deposited using a combinatorial ALD process. Exposure of repeated cycles of co-dosed alkoxide precursors Hf(OtBu)<sub>4</sub> and Zr(OtBu)<sub>4</sub> with counter-reactant pulses of Si(OtBu)<sub>3</sub>(OH) formed films of uniform thickness (±5%) and uniform silicon oxide concentration. The hafnium and zirconium concentrations exhibited smooth graduation across the film from 18% - 82% (per Hf and Zr metals basis). Self-limiting deposition rates of 1.5 nm/cycle were measured, and a linear relationship of film thickness to number of deposition cycles was observed, both consistent with a true ALD process. Elemental analysis by Rutherford backscattering spectrometry, thickness measurements by ellipsometry, capacitance measurements, electron microscopy, X-ray reflectivity and X-ray diffraction results were used to map the composition and determine the film microstructure. Deposition of mixed films of SrO and HfO<sub>2</sub> were deposited by the related combinatorial chemical vapor deposition process using Sr(tmhd)<sub>2</sub>[HN(CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>], where tmhd = 2,2,6,6-tetramethylheptane-3,5-dionato, as the strontium precursor and Hf(OtBu)<sub>4</sub> as the HfO<sub>2</sub> source. XRD showed that films with low Sr concentrations, e.g. < 15% Sr, exhibited a crystalline phase consistent with Sr-stabilized cubic hafnia. Films with higher Sr contents were amorphous. The dielectric constants of the films increased as the proportion of the cubic phase increased. A maximum value of 25 was obtained for the film with a Sr/(Sr + Hf) ratio of 0.07. We will report on our attempts to extend this CVD process to ALD.

11:00am **TF-MoM10 Combinatorial Strategy to Address the Complexities of Surface Chemistry and Multicomponent Materials in Atomic Layer Deposition.** *L. Henn-Lecordier, E. Robertson, P. Banerjee, G.W. Rubloff,* University of Maryland

While atomic layer deposition (ALD) shows unique promise for highly controlled deposition of super-conformal thin films, its perfection and practice are limited by (1) reactant dose (inter)dependencies that reflect

deviations from perfect self-limiting reaction and (2) the numerous permutations of stoichiometry that must be investigated to exploit ternary and higher materials systems. We have developed a combinatorial ALD approach to efficiently address these challenges. A wafer-scale (4- OD) substrate-heated ALD mini-reactor delivers reactant gases across the wafer, maintained in a small reactor volume to achieve short cycle times. Downstream mass spectrometry reveals the ALD surface chemistry in real time, enabling direct observation of reaction product generation as a function of dose, as well as direct thickness vs. time determinations during nucleation and growth stages of the ALD process.<sup>1,2</sup> With increasing dose, nominally complete surface saturation conditions are observed. As reactant dose is decreased, incomplete surface coverage is expected and identified, which corresponds to across-wafer depletion conditions in the cross-flow geometry of the mini-reactor. By achieving such depletion, various combinations of reactant dose ratios for binary constituents provide a combinatorial gradient library for ALD process recipe optimization. Results for Al<sub>2</sub>O<sub>3</sub> deposited by ALD from TMA and H<sub>2</sub>O demonstrate the ability to create linear thickness gradients across the wafer. This combinatorial synthesis is coupled with post-process electrical characterization of MIS capacitors using I-V and C-V measurements automated to assess several hundred devices across the wafer, complemented by wafer maps of thickness and composition. Together these directions reflect an effective strategy for evaluating and optimizing ALD process recipes as well as extending the approach to ternary systems, e.g. Hf aluminates. Work supported in part by MKS Instruments.

<sup>1</sup>"Real-time observation and optimization of tungsten ALD process cycle", W. Lei, L. Henn-Lecordier, M. Anderle, Gary W. Rubloff, M. Barozzi, and M. Bersani, J. Vac. Sci. Technol. B 24 (2), 780-789 (Mar/Apr 2006).

<sup>2</sup>"Real-time sensing and metrology for atomic layer deposition processes and manufacturing", L. Henn-Lecordier, W. Lei, M. Anderle, and G.W. Rubloff, J. Vac. Sci. Technol. B 25 (1), 130-139 (Jan/Feb 2007).

11:20am **TF-MoM11 Physical and Electrical Characteristics of Zr<sub>x</sub>Hf<sub>1-x</sub>O<sub>y</sub> Films Deposited by Atomic Layer Deposition Method**, S. Bang, S. Lee, S. Jeon, S. Kwon, W. Jeong, I. Kim, H. Jeon, Hanyang University, Korea

Zirconium and hafnium-based dielectric materials have been widely studied as a gate oxide for the next generation of CMOS technology due to high dielectric constant, a relatively wide band gap and thermodynamic stability on Si. However, ZrO<sub>2</sub> and HfO<sub>2</sub> films can be crystallized at the temperature below 500°C. For gate dielectrics, an amorphous structure is always preferred to a polycrystalline structure, because a crystalline film can induce high grain boundary leakage current and lead to non-uniformities in k value and in film thickness. Thus, efforts have been made to improve the properties of HfO<sub>2</sub> and ZrO<sub>2</sub> by adding different elements such as Si, Al, N, Ti, and Ta. Addition of Si, Al, or N allows for the increased crystallization temperature of HfO<sub>2</sub> and ZrO<sub>2</sub>. However, there is a drawback of a lowered dielectric constant. Although the addition of Ti can increase dielectric constant of HfO<sub>2</sub> and/or ZrO<sub>2</sub> films, it can degrade the leakage current characteristics by decreasing a band offset. The addition of metal elements to improve the quality of high-k oxide film, without reducing dielectric constant and increasing leakage current, is important. ZrO<sub>2</sub> has similar chemical structure to HfO<sub>2</sub> and is completely miscible with HfO<sub>2</sub>. Zr addition can yield stability to the higher dielectric constant tetragonal phase. In this study, we deposited Zr<sub>x</sub>Hf<sub>1-x</sub>O<sub>y</sub> films varying with the content of Zr on Si substrates by adding Zr into HfO<sub>2</sub> film using atomic layer deposition (ALD) process and investigated its physical and electrical characteristics. Auger electron spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) were used to analyze the chemical composition and bonds. AES and RBS data indicated that the composition ratio of Zr<sub>x</sub>Hf<sub>1-x</sub>O<sub>y</sub> films is varied as the Zr content change in those films. And X-ray diffraction (XRD) was used to analyze the structure properties of Zr<sub>x</sub>Hf<sub>1-x</sub>O<sub>y</sub> films. The capacitance values of Zr<sub>x</sub>Hf<sub>1-x</sub>O<sub>y</sub> films showed about 415 ~ 620pF/cm<sup>2</sup> on capacitance-voltage (C-V) measurement. For the analysis of other electrical properties, C-V and current-voltage (I-V) analyses were measured to evaluate the dielectric constant, EOT, and leakage current of Zr<sub>x</sub>Hf<sub>1-x</sub>O<sub>y</sub> films, etc.

11:40am **TF-MoM12 An ALD Growth Study of ZrO<sub>2</sub> on Si(100)**, P.J. Evans, G. Traini, J. Murison, M.J.Y. Tayebjee, N. Loh, D.-H. Yu, A.P.J. Stampfl, Australian Nuclear Science and Technology Organisation, T.-W. Pi, National Synchrotron Radiation Research Center, Taiwan

Zirconium and some of its alloys, oxides and nitrides are known for their anti-corrosive and excellent wear resistant character. For this reason the nuclear industry uses Zr-based materials due to their low neutron absorption character, mechanical strength, toughness and ability to withstand harsh environmental conditions such as high temperatures and intense radiation. ZrO<sub>2</sub> has also been singled-out as a candidate material for inert matrix fuels to be used in Generation IV nuclear reactors. The formation of ZrO<sub>2</sub> under different growth conditions leads to variations in electronic properties and crystal structure. Control of growth will enable tuning the electronic and structural properties of this material for specific applications. The current

preliminary study investigates the effect of deposition conditions on the electronic and crystal structure of ALD grown ZrO<sub>2</sub> films on silicon, using synchrotron-based high resolution photoemission, TEM, SIMS and glancing angle x-ray diffraction. The precursors used in the deposition were ZrCl<sub>4</sub> and H<sub>2</sub>O using two growth temperatures of 200°C and 300°C. In addition, ZrO<sub>2</sub> films were subjected to rapid thermal annealing at 600°C to investigate their valence electronic structure on crystallization.

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