Tuesday Morning, October 21, 2008

Thin Film
Room: 302 - Session TF-TuM

Applications of Atomic Layer Deposition
Moderator: G.N. Parsons, North Carolina State University

8:00am **TF-TuM1 Atomic Layer Deposition Templating Techniques and Materials for Photonic Crystals**, ***C.J. Summers,*** Georgia Institute of Technology, *E. Graugnard,* Rollins College, *D. Gaillot,* IEMN Laboratoire Central - CNRS, France, *J. Blair*, Georgia Institute of Technology **INVITED**

Atomic layer deposition is shown to be a powerful tool for the fabrication of novel 3D and 2D periodic dielectric structures. It is a unique complement to a variety of template technologies by providing a mechanism to invert, replicate and convert materials while precisely retaining the form of the original template. The ability to change material type not only enables additional functionalities to be added to the structure, but also significantly enhances the processing range when high melting point materials are substituted for low melting point materials. The ability to refine lattice geometries by the sacrificial layer and backfilling technique are shown to be powerful methods to enhance and tune structural and optical properties. This is demonstrated for both synthetic silica opal and polymer (holographically) derived templates, where dielectric lattice inversion, and the development of large pore structures offer significant enhancement to the photonic band gap by backfilling with different high-index materials. Additionally, the incorporation of luminescent, electro-optic and liquid-crystals can be used to significantly increase the functionality of the original structures. Theoretical and experimental investigations of these structures are presented and provide clear evidence of the precise control enabled by atomic layer deposition. Also we report further extensions of the ALD technique for surface preparation and functionalization for multilayer growth, and developments for the deposition of high index and optically transparent materials such as GaP and Zr3N4. The recent extension of these deposition techniques to the development of novel 2D slab waveguide structures is presented.

8:40am **TF-TuM3 Effect of Yb^{3+} co-Doping on the Luminescent Properties of Er^{3+}:Y_2O_3 Thin Films**, *J. Hoang,* ***J.P. Chang***, University of California, Los Angeles

Radical enhanced atomic layer deposition (ALD) has been previously shown to enable the control of the Er^{3+} spatial distribution in Y_2O_3 thin films, thereby achieving an enhanced direct absorption cross section at 1540 nm and much improved photoluminescence with well-resolved Stark features.[1] Given the larger index of refraction of Y_2O_3 compared to that of SiO_2, this suggests that Er:Y_2O_3 thin films has the potential to achieve compact optical amplification. In this work, we report the utilization of radical enhanced atomic layer deposition to synthesize controlled concentrations and spatial distances of Yb and Er in Yb^{3+} co-doped Er:Y_2O_3 thin films and the corresponding improvement in their optical characteristics. The electronic energy level and a large absorption cross section of Yb^{3+} make it an effective sensitizer for Er^{3+}. Thin films of approximately 10 nm are synthesized by sequential radical-enhanced ALD of Y_2O_3, Er_2O_3, and Yb_2O_3 at 350°C. The composition, microstructure, cation distribution, local chemical bonding and optical properties of the as-synthesized thin films were determined by x-ray spectroscopy, electron microscopy and photoluminescent measurements. To optimize the effect of the sensitizer and minimize the concentration quenching, the concentration of Yb^{3+} and Er^{3+} were controlled by changing the global deposition cycle sequence. Extended x-ray absorption fine structure analysis verified spatial control of Yb^{3+} and Er^{3+} in the Y_2O_3 host. Much improved effective absorption cross sections were estimated using the photoluminescence yield as a function of the pump power, as compared with measurements from thin films without Yb^{3+} sensitizers. From these measurements, an optimum concentration and spatial arrangement is chosen for the design of spiral ridge waveguide devices. These waveguides can achieve potential gains of two orders of magnitude over Er:SiO_2 and an order of magnitude over ion implanted Al_2O_3.

[1] Hoang, J., T. T. Van, et al. Journal of Applied Physics. 101(12).

9:00am **TF-TuM4 Atomic Layer Deposition of Gallium Nitride Using $GaCl_3$ and NH_3 Reactants**, ***O.H. Kim***, *D.J. Kim, T.J. Anderson*, University of Florida

GaN films were grown on silicon substrates by atomic layer deposition (ALD) using $GaCl_3$ and NH_3. It is postulated that incomplete purging of $GaCl_3$ for long $GaCl_3$ exposure times allows gas phase formation of $(Cl_2GaNH_2)_n$ species with n=1-3,[1] which results in higher chlorine content. X-ray photoelectron spectroscopy was used to determine N/Ga ratio in the film over exposure time, and showed a maximum N/Ga ratio in the saturation limit. Ab-initio calculations were implemented to understand the surface reactions in the saturation limit growth condition. Potential Energy Surface (PES) diagrams for the two adsorption reactions were used to explain the high N/Ga ratio in the ALD limit.

[1] A. Kovács, Inorg. Chem. 2002, 41, 3067-3075.

9:20am **TF-TuM5 Ruthenium and Ruthenium Oxide Thin Films prepared by Atomic Vapor Deposition for MIM Applications**, ***P.K. Baumann***, *C. Manke,* AIXTRON AG, Germany, *G. Ruhl,* Infineon Technologies AG, Germany, *A. Schroeder-Heber, L. Pfitzner, M. Schellenberger*, Fraunhofer IISB, Germany

As outlined in the International Technology Roadmap for Semiconductors (ITRS), new electrode and high-k materials have to be introduced to replace polysilicon and silicon dioxide, to allow continued scaling of further device technologies. In this study ruthenium and its metallic oxide RuO2 have been examined as possible candidates for MIM (metal-insulator-metal) capacitors. Ruthenium has a low bulk electrical resistivity of 7 microOhmcm. Ruthenium and ruthenium oxide also have very good diffusion barrier properties. We have deposited ruthenium and ruthenium oxide films by AVD (atomic vapor deposition), a pulsed MOCVD (metal organic vapor deposition) method. This method allows to combine features of ALD (atomic layer deposition), such as atomic layer control with the high deposition rate of MOCVD. The electrode films with a typical thickness of 10 nm were deposited on hafnium oxide dielectrics and silicon dioxide as reference. Physical characterization was done by Transmission Electron Microscopy (TEM), Ellipsometry, Atomic Force Microscopy (AFM), and X-Ray Reflectometry (XRR). Near bulk densities of Ru and RuO2 of 12 and 7 g/cm3 have been obtained. For Ru on hafnium oxide a sheet resistance of 10 Ohm/square was achieved. Advanced MIM capacitors were fabricated and characterizes by I vs. U and C vs. U measurements. Even after 5 months storage in ambient conditions the structures showed almost no change in breakdown characteristics. Results from physical and electrical measurements will be presented and correlated. This work was performed within the SEA-NET project funded within the 6th Framework Program of the European Commission, SEA-NET Contract no.: 027982. See www.sea-net.info.

9:40am **TF-TuM6 In-Situ FTIR Study of Atomic Layer Deposition of Ruthenium**, *Y.J. Chabal,* ***S.K. Park***, *J. Kwon, M. Dai,* University of Texas at Dallas, *R. Kanjoliab,* SAFC Hitech, *R. Odedrac,* SAFC Hitech Ltd., UK, *N. Boagd*, University of Salford, UK

Ruthenium is a potential capacitor electrode material for DRAMs and FRAMs, and potential gate metal MOSFETs due to is relatively high work function (4.7eV).[1] There is also recent interest in Ru as a combined barrier and seed layer for copper. Since atomic layer deposition (ALD) is technique of choice for deposition of thin and conformal film growth even on structured surfaces such as trenches and via holes, there is an active search for Ru ALD precursors possessing appropriate physical and chemical properties, which are important for the development of a proper deposition process. There is also the need to understand the chemical interaction of these new precursors with various surfaces and the mechanism of ALD growth to advance the field. So far, surface nucleation, overall interface formation and growth mechanisms are not well understood since most of film characterization has been performed with ex-situ measurements. In this study, we present in-situ FTIR studies of ALD growth of Ru thin films on Si substrates using newly synthesized cyclopentadienyl methylruthenium dicarbonyl ($CpRuMe(CO)_2$) and D_2O. Film growth rates were determined from ex-situ RBS measurements. SiO_2/Si(100) and atomically flat hydrogen-terminated Si(111) surfaces were used as substrates for Ru film growth. For the H/Si(111) substrate maintained at 300°C during growth, the first half-cycle Ru precursor pulse almost completely consumes the surface hydrogen as evidenced by the loss of monohydride Si-H stretching mode at 2084 cm^{-1}, which suggests a very high reactivity of the precursor toward the H/Si(111) surfaces at 300°C. The initial Ru deposition on H/Si(111) is initially good at 300°C, then becomes harder (lower growth rate). The precursor reactivity strongly decreases at lower substrate temperatures, involving only 30% of the surface hydrogen at 250°C substrate temperature. More importantly, there is no measurable Ru deposition, presumably because of competitive surface reactions. The reactivity and Ru growth on oxides, specifically SiO_2/Si(100) substrate, are surprisingly lower than on H/Si(111) substrates at 300°C. Despite this low growth rate, the IR spectra give clear evidence for ligand exchange and adsorption of surface species, making it possible to identify and quantify surface chemical reactions during the ALD process.

[1] Titta Aaltonen et al., Chem. Vap. Deposition 9, 45 (2003).

10:40am **TF-TuM9 Mechanistic Study of Atomic Layer Deposition of Copper**, ***M. Dai***, *J. Kwon,* Rutgers University, *S.Y. Park,* University of Texas at Dallas, *L.S. Wielunski,* Rutgers University, *Y.J. Chabal,* University of Texas at Dallas, *Z. Li, R.G. Gordon*, Harvard University

In microelectronics, Cu is replacing Al for IC interconnects because of its lower resistance and higher melting point. For such microelectronics applications, a controlled metallization method to deposit very thin, uniform and conformal copper films is required. Atomic Layer Deposition (ALD) is the best method but is dependent on the synthesis of appropriate precursors. As recently reported,[1] a novel precursor-Copper(I)di-sec-butylacetamidinate ($[Cu(^{s}Bu\text{-}amd)]_2$)-has shown good performance for ALD of Cu films with high conductivity. Given its novelty and the stringent microelectronics application, it is important to probe the chemistry of both interface formation and thin film growth. We have used in-situ FTIR spectroscopy to monitor the reaction of $[Cu(^{s}Bu\text{-}amd)]_2$ with two types of surfaces, the hydrogen-terminated Si(111) surface and silicon oxide surface, and to probe the next step of the ALD growth (H_2 reduction of the adsorbed Cu precursor). The Cu film growth rates were determined using ex-situ RBS measurements. We find that the reactivity of $[Cu(^{s}Bu\text{-}amd)]_2$ on these two surfaces is quite different. H/Si(111) surfaces are less reactive than oxidized surfaces. The IR vibrational spectra show that only ~20% of surface H react at 185°C. RBS measurements indicate that only 0.09 nm of Cu grows on H/Si(111) after 10 cycles. In contrast, there is a substantial loss of the SiO_x TO and LO phonon mode intensity at 1075cm^{-1} and 1247cm^{-1} after the 1st Cu precursor pulse at 185°C on SiO_2 surface, indicating that the surface SiO_2 matrix chemically interacts with the precursor. Meanwhile, a broad absorption band centered at 1010cm^{-1} is observed, corresponding to the formation of Si-O-Cu bonds. Upon H_2 exposure, the intensity of the SiO_x phonon modes is partial recovered, suggesting that Cu atoms diffuse and agglomerate as the Cu precursor is reduced to pure Cu at 185°C. As agglomeration takes place (i.e. Si-O-Cu bonds are broken), the initial hydroxylated oxide surface is restored (in a hydrogen environment) and is characterized by the original SiO_x phonon absorption. The ALD process is investigated by following the ligand exchange and ligand rearrangement on the surface. RBS measurements show 1.18nm of Cu is deposited on SiO_2 after 10 cycles.

[1] Z. Li, S. T. Barry, R. G. Gordon, Inorganic Chemistry, (2005)44, 1728.

11:00am **TF-TuM10 Modification of Nonwoven Polymer Fiber Structures by Atomic Layer Deposition**, ***J.C. Spagnola***, *G.N. Parsons*, North Carolina State University

Nonwoven polymer fiber structures are receiving much recent attention due to their potential industrial, medical, and military applications. We report the modification of nonwoven fiber structures by the deposition of thin metal oxide films via ALD. Fiber substrates coated to date include melt blown polypropylene micro and nanofibers, electrospun PVC nanofibers and nylon hydroentangled microfibers. Our specific focus is to characterize the effect of film thickness and/or coating material the resulting mechanical properties of coated fiber structures Initial experiments involved the deposition of Al2O3 by trimethylaluminum and water at temperatures from 50 to 100C. The gas pulse and purge times used resulted in film growth rates of 1.2A/cycle on planar silicon independent of temperature. Substrates for ALD coating consisted of fiber mats approximately 1cm x 3cm x 0.05cm. After ALD, some samples were calcined in air at ~850°C for 30 min to remove the polymer substrate to allow SEM analysis of the deposited oxide layer. SEM images show good macroscopic uniformity of the ALD coating over the substrate surface area. Other samples that were not heat treated were analyzed under tensile testing to observe the stress-strain behavior as a function of ALD process conditions and film thickness. Specifically, melt-blown polypropylene nonwoven fiber mats were tested using a microstrain analyzer to determine elastic modulus, yield stress and material toughness. Coating the polypropylene with Al2O3 ALD at 50°C or 100°C lead to an increase in the elastic modulus that scaled linearly with the number of ALD cycles, resulting in an increase of ~50% after 200 ALD cycles (~25nm). In addition, when the ALD was performed at 50C, the samples showed an increase in yield stresses with some improvement in material toughness. However, when processed at 100C, the coated polypropylene structures showed a decrease in yield stress and toughness as compared to untreated substrates, consistent with some degradation of the starting material properties at elevated temperature. Strengthening of the fiber structure by the deposition of a thin metal-oxide film may allow coated nonwovens to be used in applications where the traditional low-strength of nonwoven structures prevents the required level of performance.

11:20am **TF-TuM11 Mechanical and Tribological Property Comparison of Melt-Compounded Nanocomposites of Atomic-Layer-Deposition-Coated Polyamide Particles and Commercial Nanofillers**, *K.M. Nevalainen, R.J. Suihkonen,* Tampere University of Technology, Finland, ***N.A. Isomäki***, Beneq Oy, Finland, *C. Hintze,* Technical University of Chemnitz, Germany, *P.S. Eteläaho, J.E. Vuorinen, P.K. Järvelä*, Tampere University of Technology, Finland

A recently developed process to form homogenously dispersed nano-sized titanium dioxide (TiO_2) particles within a polymer matrix was introduced and compared to traditionally melt-compounded nanofillers. Micron-sized polyamide particles were pre-coated with thin TiO_2 films by atomic-layer-deposition (ALD). ALD coating was performed at 40 °C by alternately exposing polyamide powder to titanium tetrachloride and water, separated by nitrogen purge steps. TiO_2 coatings on polyamide particles possessed nominal thicknesses of 10 nm or 40 nm. The ALD-coated polyamide particles and the composites manufactured from the two different commercial TiO_2 nanofillers were melt-compounded using a 5 cm^3 micro-compounder. The dispersion of the crushed TiO_2 shells in the polyamide matrix were studied after extrusion using a transmission electron microscopy and the results suggested very different morphology from the traditional TiO_2 nanocomposites. The ALD-created TiO_2 appeared as ribbons in the polyamide matrix whereas the commercial TiO_2 fillers formed spherical clusters. The effect of these TiO_2 morphology changes on the mechanical response of the specimens subjected to tensile and impact loading was investigated. The results demonstrated that the nanocomposites based on ALD-coated polyamide particles possess 50-150% higher Young's modulus than pure and commercially filled polyamide matrix whereas yield strength is only slightly increased for 10 nm ALD-coated composite and in fact somewhat decreased for 40 nm ALD-coated composite. Furthermore, the ductility upon tensile loading is significantly affected. A transition from ductile to brittle deformation occurs for both ALD-coated nanocomposites. Notched impact strength experiments supported this phenomenon showing that the impact strength of ALD-coated composites decreased 50% compared to pure and traditionally filled polyamide matrix whereas the traditional TiO_2 nanocomposites showed no significant changes. The fracture surfaces of the nanocomposites examined with scanning electron microscope suggested that the nanoparticle dispersion was good but some impurities in the matrix were found and their origin is discussed. The tribological properties of the selected specimens were also determined using pin-on-disc type apparatuses and the effect of the titanium dioxide fillers on the friction and wear properties of polyamide matrix is examined.

11:40am **TF-TuM12 Atomic Layer Deposition of Zinc Hybrid Films from Diethyl Zinc and Ethylene Glycol**, *Q. Peng, R.M. VanGundy, G.K. Hyde,* ***G.N. Parsons***, North Carolina State University

Atomic/molecular layer deposition of organic-inorganic hybrid materials could significantly expand the range of materials available in thin film applications. However, the detailed mechanisms associated with the integration of organic materials into the ALD process scheme need to be more fully understood. In this study, zinc hybrid films were formed by atomic layer deposition using alternative dosing of diethyl zinc (DEZ) and ethylene glycol (EG). The process was characterized using in-situ quartz crystal microbalance (QCM), as well as a range of external characterization tools and results were compared directly to the ZnO ALD process (DEZ/H2O) performed under similar reaction conditions. Consistent with literature results, during the ZnO ALD process at 120degree C, the mass uptake during the DEZ exposure is ~130 ng/cm2 per cycle, with a small mass loss during H2O exposure. The QCM results confirmed the self-limiting surface adsorption during both reaction steps of ZnO ALD. When H2O is replaced with ethylene glycol in the process sequence at 120 degree C, the mass uptake during the DEZ pulse is reduced significantly to ~19 ng/cm2 , and the positive mass uptake of ~ 4 ng/cm2 is observed during the EG pulse in the steady-state deposition of Zn hybrid. The reduced mass uptake during DEZ exposure is likely due to the lower density of reaction sites resulting from: (i) the twice reaction of EG with surface bonded –O-Zn-C2H5 ligands; (ii) steric hindrance of bulky EG molecules and its related surface bonded ligands; (iii) the possible dehydration reaction between the surface bonded EG ligands. Self-limiting adsorption of DEZ and EG, which is consistent with a typical ALD process, was confirmed by QCM. The process steps of Zn hybrid can continue for several hundred cycles with consistent and repeatable mass uptake. The growth rate per cycle of the hybrid material decreases as the deposition temperature increases. Infrared analysis of as-formed Zn hybrid films shows modes consistent with EG and Zn-O bonds. Upon exposure to laboratory air, the resulting hybrid films readily undergo hydrolysis, resulting in films consisting of ZnO and hydroxide with significant carbon content, as evidenced by FTIR and XPS analysis. AFM shows the films are uniform, and TEM analysis indicates that hydrolysis process results in conformal and porous layers. Further results of in-situ characterization and post-deposition analysis of the zinc hybrid materials will be presented.

Authors Index

Bold page numbers indicate the presenter

— A —

Anderson, T.J.: TF-TuM4, 1

— B —

Baumann, P.K.: TF-TuM5, **1**
Blair, J.: TF-TuM1, 1
Boagd, N.: TF-TuM6, 1

— C —

Chabal, Y.J.: TF-TuM6, 1; TF-TuM9, 2
Chang, J.P.: TF-TuM3, **1**

— D —

Dai, M.: TF-TuM6, 1; TF-TuM9, **2**

— E —

Eteläaho, P.S.: TF-TuM11, 2

— G —

Gaillot, D.: TF-TuM1, 1
Gordon, R.G.: TF-TuM9, 2
Graugnard, E.: TF-TuM1, 1

— H —

Hintze, C.: TF-TuM11, 2
Hoang, J.: TF-TuM3, 1
Hyde, G.K.: TF-TuM12, 2

— I —

Isomäki, N.A.: TF-TuM11, **2**

— J —

Järvelä, P.K.: TF-TuM11, 2

— K —

Kanjoliab, R.: TF-TuM6, 1
Kim, D.J.: TF-TuM4, 1
Kim, O.H.: TF-TuM4, **1**
Kwon, J.: TF-TuM6, 1; TF-TuM9, 2

— L —

Li, Z.: TF-TuM9, 2

— M —

Manke, C.: TF-TuM5, 1

— N —

Nevalainen, K.M.: TF-TuM11, 2

— O —

Odedrac, R.: TF-TuM6, 1

— P —

Park, S.K.: TF-TuM6, **1**
Park, S.Y.: TF-TuM9, 2
Parsons, G.N.: TF-TuM10, 2; TF-TuM12, **2**
Peng, Q.: TF-TuM12, 2
Pfitzner, L.: TF-TuM5, 1

— R —

Ruhl, G.: TF-TuM5, 1

— S —

Schellenberger, M.: TF-TuM5, 1
Schroeder-Heber, A.: TF-TuM5, 1
Spagnola, J.C.: TF-TuM10, **2**
Suihkonen, R.J.: TF-TuM11, 2
Summers, C.J.: TF-TuM1, **1**

— V —

VanGundy, R.M.: TF-TuM12, 2
Vuorinen, J.E.: TF-TuM11, 2

— W —

Wielunski, L.S.: TF-TuM9, 2