Thin Film
Room: 307 - Session TF+PS-TuM

ALD for Emerging Applications
Moderator: James Fitz-Gerald, University of Virginia

8:00am **TF+PS-TuM1 Atomic Layer Deposition: A New Strategy to Improve Metal Corrosion Resistance?**, ***Lorenzo Fedrizzi***, *E. Marin, A. Lanzutti*, University of Udine, Italy **INVITED**

Interests on nanometric conformal coatings are nowadays growing in a wide range of applications, from electronic components to corrosion protection, chemical barriers or even wear resistance. Atomic Layer Deposition (ALD) is one of the most promising nanometric deposition technologies which offers the possibility to obtain conformal coatings even on very complex tridimensional substrates of different chemical nature, with a strict thickness tolerance and strong adhesion. During an ALD cycle, only one molecular layer is deposited on the substrate surface, enabling the theoretical possibility to tailor the composition of the deposit up to molecular resolution, thus obtaining almost unique properties.

Therefore this technology appears to be an interesting and innovative alternative to the existing ones aimed to metal corrosion protection, such as electrodeposition, painting or other chemical or physical vapor deposition technologies.

This work describes the use of ALD for the corrosion protection of different metal alloys of common industrial interest such as stainless steels, aluminum or magnesium alloys. Moreover, the possibility of combining this deposition technology with some traditional ones is also discussed to the aim of obtaining improved protection properties by multilayer coatings able to enhance a protective barrier action.

8:40am **TF+PS-TuM3 Atomic Layer Deposition of Thin VO_2 Films for Thermal Management Applications**, ***Virginia Wheeler***, *M. Tadjer, N. Nepal, M. Currie, Z.R. Robinson, M.A. Mastro, K. Cheung, F. Kub, C.R. Eddy*, Naval Research Laboratory

Vanadium oxides are thermochromic materials which have significant changes in thermal emittance, optical transmittance and reflectance, and intrinsic electrical properties due to a metal-insulator phase transition (MIT). These materials offer great advantages in a variety of applications including electrochemical applications, energy storage, thermoelectric devices, Mott transistors, and smart windows. In this work, atomic layer deposition (ALD) was used to produce thin, highly uniform, amorphous VO_2 films which enabled the ability to investigate the impact structure (amorphous vs. crystalline) has on the rate of change of intrinsic properties due to the MIT.

Amorphous VO_x films (5-45nm) were deposited by ALD at 150°C using tetrakis(ethylmethyl)amido vanadium and ozone precursors. X-ray photoelectron spectroscopy (XPS) was used to verify the quality, stoichiometry, and depth uniformity of the films. All as-grown films exhibited carbon surface contamination due to atmospheric transfer from the ALD to XPS chambers. Moreover, the top ~1nm of the film exhibited V2*p* peaks at 517.7 and 516.3eV correlating to V_2O_5 and VO_2 components, respectively. At depths >1nm, XPS showed no residual carbon contamination and only a single VO_2 peak with a FWHM from 2-2.7 eV, which is similar to crystalline films and indicative of the high uniformity and quality of these films. XPS depth profiles near the VO_x/Si interface had a low binding energy shoulder at 513.5 eV, suggesting that initially the films are very oxygen deficient.

The influence of *ex situ* anneal temperature (200-550°C), time (0.17-2hr), and gas environment (forming gas, Ar, O_2, and ozone) on the ability to obtain single phase, crystalline VO_2 films was also examined. Initial results show that only O_2 anneals produce crystalline VO_2, but other factors such as gas flow, duration, and temperature require optimization to inhibit multiphase, polycrystalline films.

Electrical and optical performance of amorphous and crystalline ALD films was assessed from 77-500K and 300-380K, respectively. Unlike crystalline VO_2 films that exhibit an abrupt, up to five orders of magnitude change in resistance around the MIT at 60°C (333K), amorphous VO_2 films had an exponential change in resistance of ten orders of magnitude over the entire temperature range studied. Also, an average activation energy of -0.20eV and temperature coefficient of resistance of 2.39% at 310K was extracted. These results suggest that amorphous VO_2 films, with less structural order, have the potential to induce larger, more gradual electrical changes that could be useful for bolometers or passive thermal management on spacecraft.

9:00am **TF+PS-TuM4 Atomic Layer Deposition of $Pb(Zr_XTi_{1-X})O_3$ Thin Films to Engineer Nanoscale Multiferroic Composites**, ***Diana Chien***, *T. Kim, J.P. Chang*, UCLA

As one of the best dielectric, piezoelectric, and ferroelectric materials, PZT is a promising material to engineer nanoscale multiferroic composites. The magnetoelectric (ME) effect occurs indirectly through strain at the interface. Using atomic layer deposition (ALD), a surface-reaction controlled process based on alternating self-limiting surface reactions, a thin film of PZT can be synthesized with precise control of the elemental composition (Zr/Ti = 52/48) and film thickness. ALD provides much superior uniformity and conformality over complex surface structures with high aspect ratios.

In this work, ALD PZT thin films were synthesized by depositing alternating layers of PbO, ZrO_2, and TiO_2 layers using $Pb(TMHD)_2$, $Zr(TMHD)_4$, and $Ti(O^iPr)_2(TMHD)_2$ as metal precursors and H_2O as the oxidant. The number of local cycles and global cycles were regulated to achieve the desired stoichiometry and thickness, respectively. ALD of PZT was studied to obtain (100) oriented $Pb(Zr_{0.52}Ti_{0.48})O_3$ on Pt (111) oriented platinized silicon substrates. In order to attain a highly oriented PZT thin film, a (100) textured $PbTiO_3$ seed layer was required because PZT orientation is generally governed by nucleation. The stoichiometry and crystallinity of PZT films were confirmed by XPS and XRD measurements. The conformality was confirmed over hollow Si_3N_4 cylinders with aspect ratio of 2.2.

By controlling the composition, thickness, and conformality of ALD PZT thin films, the properties of PZT can be exploited to increase the ME coefficient. Specifically, PZT was coupled with MgO/CoFeB to fabricate magnetic tunnel junction for memory applications. With co-mediated effects from higher dielectric constant and strain transfer via the interface, the voltage-controlled magnetic anisotropy effect is expected to increase, thereby realizing magnetic anisotropy energy per area per electric field greater than 37 fJ/(V·m) (Zhu, J. et al., *Phys Rev Lett.*, 108, 2012). ALD PZT thin films were shown to uniformly coat the walls of nanoscale porous CFO template to form a 3-D composite and a larger ME coefficient is expected due to an increase in surface area to volume ratio.

9:20am **TF+PS-TuM5 Atomic Layer Deposition Enabled Synthesis of Nanoscale Multiferroics**, ***Calvin Pham***, *Y. Kim, J.P. Chang*, University of California at Los Angeles

Complex metal oxides exhibit remarkable tunability in their ferromagnetic, ferroelectric, and multiferroic properties that enable future applications such as non-volatile memory, miniaturized antenna, sensors and actuators. Nano-composites based on a magnetostrictive ferro/ferrimagnet paired with a piezoelectric have shown unique multiferroic behavior from effective strain-coupling at the interface. Motivated by the promise of high magnetoelectric coupling from nanostructured multiferroics, an atomic layer deposition (ALD) process was developed to synthesize $CoFe_2O_4$ (CFO) and $BiFeO_3$ (BFO), thereby enabling the formation of 2-D multilayered films with nanometer scale precision, as well as 3-D composites based on a mesoporous template. The highly conformal coating of ALD, due to self-limiting surface reactions, promises an intimate interface of the various ferroic phases to realize tunable magnetoelectric coupling by nano-texturing.

In this work, a radical enhanced ALD process was used to synthesize the complex oxide nano-structures, using metallorganic precursors $Bi(tmhd)_3$ (tmhd = 2,2,6,6-tetramethylheptane-3,5 dione), $Co(tmhd)_2$, and $Fe(tmhd)_3$ and oxygen atoms produced from a microwave power atomic beam source. The processing-structure-property relations were systematically studied. First, the nucleation delay for the initiation of the growth of one constituent oxide on another was quantified and a variety of process conditions were systematically examined to assess the effects of process temperature, precursor pulsing time, and precursor pulsing ratio on film composition, growth rate, and structure. The ALD BFO and CFO films were confirmed to be conformal and of the exact stoichiometry with a linear growth rate, and their individual ferroic responses are comparable to those reported in literature, as synthesized by other techniques. The 2D BFO/CFO multilayers were synthesized with each layer measuring between 2-50 nm each, while the 3D composites consisted of mesoporous templates with ~15 nm diameter pores that were filled with ALD films. The attainable magnetic, ferroelectric, and magnetoelectric properties, including magnetoelectric coupling, are shown to be sensitive to the composition, morphology and microstructure of the composites as they interrelate and affect the strain state at the interface.

9:40am **TF+PS-TuM6 Laser Assisted Electron Beam Induced Deposition: Towards a Nanoscale Atomic Layer Deposition Process**, ***Michael Stanford***, *B.B. Lewis*, *J.H. Noh*, University of Tennessee, *H. Plank*, Graz University of Technology, Austria, *J. Fowlkes*, Oak Ridge National Laboratory, *N.A. Roberts*, Utah State University, *P.D. Rack*, University of Tennessee

Electron beam induced deposition (EBID) is a direct-write process which can be used to selectively deposit material with nanoscale resolution. EBID utilizes a scanning focused electron beam to dissociate adsorbed precursor molecules which subsequently condense onto the substrate. One of the major limitations of the EBID process is low material purity resulting from incomplete by-product removal of the typically organometallic precursor. Therefore, the development of EBID purification strategies for enhanced materials functionality is a grand challenge for wider application of this synthesis technique. While recently EBID deposits have been used as selective atomic layer deposition catalyst, here we demonstrate an in-situ ALD-like process driven by electron and laser-induced thermal half reactions. We have developed an O_2-assisted laser anneal process to enhance the purity of patterns deposited using $MeCpPt^{IV}Me^3$ precursor gas. Additionally, we have demonstrated a laser assisted electron-beam-induced-deposition (LAEBID) process as an effective method to provide *in-situ* purification during deposition. The synchronized process is initiated by an approximately monolayer EBID cycle followed by a laser pulse which thermally desorbs by-products of the condensed phase. The process is repeated until the desired shape and size is achieved. The addition of a reactive O_2 gas and a synchronized electron and laser pulse begins to look a lot like a nanoscale atomic layer deposition process (ALD), however the half reactions are electron and thermally stimulated, respectively. We will demonstrate how factors such as laser pulse width, laser duty cycle, EBID beam current, and EBID dwell time have significant effects on the laser anneal and LAEBID processes. Importantly, the carbon reduction and apparent densification lead to higher resolution relative to standard EBID.

11:00am **TF+PS-TuM10 Effect of Film Stress on the Shape of Nanostructures Grown Using Atomic Layer Deposition**, ***Jonas Gertsch***, *N.T. Eigenfeld*, *J.M. Gray*, *V.M. Bright*, *S.M. George*, University of Colorado, Boulder

Controlling the shape of nanostructures is crucial to the performance of nanodevices. Nanostructure shape can be tuned by varying stress in the various films that comprise the nanostructure. In this work, we explore the shape of Al_2O_3/W/Al_2O_3 trilayers fabricated using Al_2O_3 ALD and W ALD. Trilayer films were initially grown on polyimide molds that were formed into free standing "umbrella" nanostructures after processing and release. Depending on the stresses in the trilayer films and the thicknesses of the individual layers, the nanostructures can either remain flat or may curl up or down. The resulting shape can be controlled by varying the thicknesses of the individual Al_2O_3 ALD and W ALD layers in the trilayer. These "umbrella" nanostructures may be useful for microbolometer and other microelectromechanical systems (MEMS) applications. Additional studies will present stress measurements using atomic force microscope (AFM) investigations of ALD films in fixed-fixed and fixed-free cantilever structures.

11:20am **TF+PS-TuM11 Atomic Layer Deposition and Nucleation on Metallic Nanostructures for Plasmonic Devices**, ***Jie Qi***, *X. Jiang*, *B.G. Willis*, University of Connecticut

Atomic layer deposition (ALD) has become an important technique for the deposition of nanometer thin dielectric and metallic thin films with applications in semiconductors, nanotechnology, catalysis, and energy. In particular, nanoscale metallic structures are gaining importance for fabrication of plasmonic antenna with applications in biochemical sensors, photocatalysis, and solar energy harvesting devices. A key feature of nanoscale plasmonic materials is a strong dependence of the plasmon resonance on size and shape of the nanostructure. ALD offers a unique means to control the size, composition, and particle-particle junctions of nanostructures with high precision. The latter is particularly important for creating hot spots where electric fields are strongly enhanced. A key challenge for ALD is the strict control of film composition and uniformity. Although a number of works have been published on the uniformity and layer by layer growth of amorphous dielectric thin films, the crystalline structures of metals present significantly increased complexity. Moreover, when seed layers, prefabricated nanostructures, or particles are involved, the sensitivity of film growth to surface structure has received relatively little attention so far.

In this work, we study the effects of surface preparation and seed layer properties on ALD Cu thin films relevant to plasmonic devices. Pd and Pt are used as seed layers for both planar thin films and two dimensional nanostructures. ALD growth was studied for different sized nanostructures and surface preparations including: e-beam deposition, high temperature annealing, solvent cleans, and UV/Ozone (UVO) pretreatment, as well as different ALD growth conditions. Samples were analyzed by XPS, SEM, AFM, EDS, and other techniques to compare film uniformity and surface structures. A strong dependence of Cu ALD growth quality was found for different nanostructures and surface preparations. Nucleation of Cu was greatly enhanced when UVO pre-treatment was performed on e-beam evaporated seed layers, but AFM results showed surface roughness increased with UVO cleaning time, which indicates rough, non-uniform growth. Seed layer thickness also played a role and it was observed that smoother and more uniform Cu thin films are obtained with thinner seed layers. Overall, planar thin films are poor models for nanostructure growth. Nanostructures are significantly more sensitive to surface preparations and growth conditions because of the similar length scales of nuclei and nanostructure size.

11:40am **TF+PS-TuM12 Infrared and Thermoelectric Power Generation in Thin Atomic Layer Deposited Films**, ***Harkirat Mann***, *B.N. Lang*, *Y. Schwab*, James Madison University, *J. Petteri-Niemelä*, *M. Karppinen*, Aalto University, Finland, *G.S. Scarel*, James Madison University

A mechanism for alternative energy, thermoelectric (TE) power generation, converts a temperature difference across two junctions into an electric potential. Although not as energy-efficient as solar panels or wind turbines, this mechanism is used in a wide variety of fields, e.g. to recapture waste heat. Recently it was discovered that a solid state TE power generators respond differently to heat or infrared (IR) radiation [1, 2]. To test the robustness of this finding, this research compares TE and IR power generation in the case of a nanometric TE device in which the active element is a thin TE film. The thin TE film is a 70 nm thick n-type Nb-doped titanium oxide film deposited by atomic layer deposition (ALD) onto a borosilicate glass substrate [3]. The interactions observed with heat show a linear relationship between temperature and voltage, whereas in IR radiation this linear relationship is broken down. The efficiency and the voltage stability obtained with the thin TE film is larger than that obtained by closing the electric circuit without the thin TE film. The possibility of using thin ALD films for IR power generation suggests that in the future the response to IR radiation can be tuned by exploiting the properties of the thin atomic layer deposited TE films.

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12:00pm **TF+PS-TuM13 Atomic Layer Deposition of Tin Doped Titanium Oxide on Type-V Titanium Implant Surface for Enhanced Photoactivated Antibacterial Property**, *S.K. Selvaraj*, *A. Butt*, ***Christos Takoudis***, University of Illinois at Chicago

Atomic layer deposition (ALD) is used for the first time to modify type-V titanium (Ti-6Al-4V) surface, a commonly used dental and orthopedic implant material.[1] ALD of titanium oxide and tin doped titanium oxide thin films were deposited on Ti-6Al-4V disks to enhance photoactivated antibacterial property of its surface. Tetrakis(diethylamino)titanium (TDEAT) kept at 65 °C and tin(II)acetylacetonate ($Sn(acac)_2$) kept at 70 °C were used as titanium and tin sources, respectively. Custom built hot-wall flow-type ALD reactor was used to deposit antibacterial thin films at 200 °C substrate temperature and 0.5 Torr.[2,3] Different composition of tin doping was achieved by changing the number of tin oxide ALD cycles. X-ray photoelectron spectroscopy was used to study the composition and purity of the thin films. Films were found to have titanium, tin, oxygen and trace amount of carbon. Excellent composition tunability of the ALD process was achieved. The resultant films were studied for photoactivated antibacterial property using a gram negative Escherichia coli bacterial strain ATCC 8739. The ALD coated Ti-6Al-4V disks were immersed in bacterial solution and illuminated with UV light for 3 min. Irradiated bacterial samples were plated on agar plate and incubated for 12 hours at 37 °C. Two fold increase in antibacterial property was achieved on ALD TiO_2 coated disks compared to uncoated (control) disks. Tin doping further increased the activity by about two fold. Any increase in tin composition beyond 15 atom % was found to have no effect on antibacterial activity.

References

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