Thin Film
Room: 11 - Session TF-MoM

ALD Enabled Applications
Moderator: W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

9:00am **TF-MoM3 Atomic Layer Deposition Films as Diffusion Barriers for Silver Artifacts**, ***A.E. Marquardt***, University of Maryland, *E. Breitung,* E-Squared Art Conservation Science, *G. Gates, T. Drayman-Weisser,* The Walters Art Museum, *G.W. Rubloff, R.J. Phaneuf*, University of Maryland

In this work we investigate atomic layer deposition (ALD) to create transparent oxide diffusion barrier coatings to reduce the rate of tarnishing for silver objects in museum collections. Elevated heating and H_2S pressure tests determined the effect of various thicknesses of Al_2O_3 ALD thin films, ranging from 5 to 100nm thick, and the effect of annealing temperature on the thickness of the tarnish layer (Ag_2S) created at the interface of the ALD coating and the silver substrate. Reflectance spectroscopy and an integrated sphere spectrophotometer were used to measure the thickness of the tarnish layer and indicate the effectiveness of the Al_2O_3 ALD thin films in reducing the tarnishing rate of silver while minimally affecting the visual appearance of the silver. X-ray photoelectric spectroscopy (XPS), and time of flight secondary ion mass spectroscopy (TOF-SIMS) analysis determined the concentration profile of sulfur through the ALD oxide film. A model for predicting the tarnishing kinetics of sulfur diffusion through ALD oxide films is established, influenced by the composition of the alloy, phase of sulfide at the interface, and non-uniformity of diffusion due to pinhole and concentration dependence. Evidence was found for the slow diffusion of sulfur through the bulk of the films and faster diffusion through pinholes in the ALD oxide films.

9:20am **TF-MoM4 Quasi-ALD for Deposition of a Water Resistive Barrier Layer and Prevent Electronic Devices from Water Shock**, ***V. Gupta***, *M.R. Linford*, Brigham Young University

Water resistant surfaces and devices have an ever increasing importance in various areas of technology, including electronics (e.g., cell phones), fabrics, shoes, chemical handling equipment, and hearing aids to name only a few. However, while important and effective against splashes, ultrathin hydrophobic films are not always sufficient for water proofing devices. Herein we describe the development of a water resistant barrier layer, deposited by a method similar to atomic layer deposition, which can also be made hydrophobic by deposition of fluorosilanes, for imparting improved protection against water to underlying surfaces and devices. The resulting barrier has been found effective in resisting the infiltration of water and preventing underlying surfaces such as electronic circuits from water shock. The precursors we use appear to have low toxicity in their molecular and (especially) deposited form, are inexpensive, have good vapor pressures so they can be deposited at low temperature, and can be deposited in a straightforward manner because of their high reactivity. Different plasma pre-treatments of substrates have been studied, although good uniformity in the deposition takes place on substrates, such as Si/SiO_2 and nylon, that have not been primed in any way. Film growth on Si/SiO_2 and nylon spin coated onto Si/SiO_2 has been monitored by spectroscopic ellipsometery, which shows consistent increases in film thickness with deposition cycles, contact angle goniometery, which shows similar wetting properties for all layers of the films and is consistent with deposition of a constant surface chemistry, XPS, which shows the expected elements in the film, AFM, which provides surface roughness, and ToF-SIMS, which is also a probe of the surface chemistry.This barrier layer has been tested on model circuit boards and results are consistent with both the number of layers deposited and their mode of deposition. That is, water damage shows a proportional decrease with an increase in the number of the above mentioned layers. This process appears to be applicable on multiple substrates ranging from inorganic to organic surfaces. Presently we are working on increasing the number of layers and more effective crosslinking of the films. Additional film characterization will also be done by RBS and NRA.

9:40am **TF-MoM5 Atomic Layer Deposition for Astronomy and Space Applications**, ***F. Greer***, Jet Propulsion Laboratory/California Institute of Technology **INVITED**

Future UV, X-ray, infrared, and sub-millimeter telescopes and spectrometers have the potential to revolutionize our understanding of the formation and habitability of the modern universe. Star formation, dark energy, and the composition of the intergalactic medium are only some of the key scientific topics that can be addressed by UV astronomy and astrophysics. Infrared astronomy enables the hunt for new planets and stars, even through clouds of interstellar dust, while sub-millimeter astronomy can probe the fine structure of the cosmic microwave background, giving glimpses into the early universe immediately following the Big Bang. While existing technology has allowed us to probe deep into the universe, materials or fabrication challenges still limit the sensitivity and capability of the detectors and instruments used in these applications. In this talk, we will first discuss, in general, how the precision and control afforded by atomic layer deposition can be used to substantially increase the capability of astronomers to make new discoveries. Then, we will focus on specific cases to show the impact of ALD films on the coating, passivation, and fabrication of UV, infrared, and submillimeter detectors, respectively. For example, atomic layer deposition coatings utilized in UV instruments, once fully optimized, can yield as much as a 100X increase in signal to noise ratio over conventional technology. Here, we will demonstrate how small changes in nucleation and growth conditions of ALD fluorides, oxides, and transition metal nitrides have a significant effect on the performance of these detectors and other instrument components, even for films with comparable indices of refraction and resistivity. We will also discuss the novel ALD chemistries that we have pursued, *e.g.* for MgF_2 deposition, in order to achieve reliable processes. Finally, this presentation will detail the unique surface engineering approaches such as the combination of atomic layer deposition and MBE, demonstrating the advantages that are obtained by achieving atomic level precision at key steps in detector fabrication processes.

10:40am **TF-MoM8 ALD-Enabled $Pt/HfO_2/Ti$ and $Pt/TiO_2/Ti$ Tunneling Diodes with Enhanced Tunneling Characteristic**, ***O. Ajayi***, *G. Mumcu, J. Wang*, University of South Florida

Due to its unique resistive switching capability, Metal-Insulator-Metal (MIM) diodes have attracted substantial interests ever since 1960's. The early generation of MIM device (point-contact diode) is composed of a sharp metal tip placed right on top of a planar metal electrode coated with an ultra-thin layer of insulator. It has been envisioned that MIM diodes hold great promise for detecting and mixing high frequency signals up to Terahertz (THz) range. Particularly, several prior works have suggested for operation at THz frequencies, the MIM diodes are anticipated to outperform heterojunction diodes, which have limited cutoff frequency (<3THz). Hence, the MIM devices are well-suited for a wide range of applications in security, imaging and energy scavenging. In lieu of this, microfabricated MIM diodes with low zero-bias impedance have been actively pursued in this work for a strategically-designed antenna-coupled detector with high responsivity.

With introduction of ultra-thin tunneling layer sandwiched between two planar metal electrodes, the microfabricated MIM diodes are amenable for direct integration with ICs. In particular, we have devoted most of our efforts on developing techniques to improve the overall diode characteristics through tuning its tunneling properties. The effective junction capacitance and resistance limit the operation frequency range of tunneling diode. The key factors that affect the frequency range of tunneling diodes are the junction area, defect density, permittivity and thickness of the tunneling layer. For the MIM diode, a small deviation in tunneling barrier thickness can cause a significant change in the junction resistance and its I-V responses. Hence, atomic layer deposition (ALD) process was employed which offer superb uniformity, low defect density, and precise thickness control of the tunneling layer. In this work, MIM diodes with a variety of junction areas ranging from 3µm´3µm to 100µm´100µ have been fabricated with different ALD thin films (e.g., TiO_2 and HfO_2) of varied thicknesses. By systematic investigation of the measured I-V characteristics for MIM devices with a variety of junction materials, junction thickness and junction area, it is evident that the performance of the MIM tunneling diodes can be greatly enhanced through optimizing junction properties (material, thickness, area, etc.). As compared to similar devices reported previously, we have successfully demonstrated high-yield MIM diodes with 1.5nm-thick tunneling junction with unprecedented low junction resistance in the range of 500Ω or even less, thus resulting in greatly enhanced responsivity.

11:00am **TF-MoM9 Uniform Adsorption of Ligand Free Ag Nanoparticles onto TiO_2 Thin Films Deposited by Atomic Layer Deposition**, ***J.C. Halbur***, *J.S. Jur*, North Carolina State University

Nanoparticle modification of inorganic thin films, such as TiO_2 or Al_2O_3, represents a method to enhance or alter the catalytic, antimicrobial, or responsive behaviors of a material. The use of nanoparticle inks for application is challenging, as the nanoparticles tend to be stabilized using surfactants or other molecules during the synthesis process, and these ligands can interfere with or prevent nanoparticle adsorption onto the oxide.

This work shows the efficacy to attach ligand-free Ag nanoparticles onto TiO_2 surfaces formed by atomic layer deposition (ALD). Sonochemical synthesis is used to create Ag NPs of 14-20 nm diameter in an aqueous solution at room temperature without the need for additives such as stabilizing agents. After ALD of TiO_2 thin films onto polymer substrates, a facile dip coating process at ambient conditions results in the uniform decoration of the ligand free Ag nanoparticles on the TiO_2 surface. The efficiency of nanoparticle adsorption is examined by TEM and EDS. Finally, the photocatalytic degradation of methylene blue is used to assess the photocatalytic efficiency of the fiber based composite.

11:20am **TF-MoM10 Alloy Films Grown Using Al_2O_3 ALD and Alucone MLD: Critical Tensile Strains, Water Vapor Transmission Rates and Compliant Interlayers**, *S.H. Jen, B.H. Lee,* ***S.M. George***, University of Colorado, Boulder, *P.F. Carcia, R.S. McLean*, DuPont Central Research and Development

Hybrid organic-inorganic alloy films can be grown using Al_2O_3 ALD and alucone MLD. These alloy films may display the excellent gas diffusion barriers properties of Al_2O_3 ALD films and also may be more flexible than Al_2O_3 ALD films. Critical tensile strains (CTSs) and water vapor transmission rates (WVTRs) were measured for the ALD:MLD alloy films using trimethylaluminum, ethylene glycol and H_2O as the reactants. The alloy composition was controlled by varying the ratio of ALD: MLD cycles during film growth. The CTS reached its highest values of ~1.0 % for the 3:1 alloy. The WVTR decreased 4 orders of magnitude versus alloy composition. The 7:2, 5:1 and 6:1 alloys had the lowest WVTRs of $\sim 1\times10^{-4}$ g/m^2/day at the sensitivity limit. These alloys are more flexible than Al_2O_3 ALD and may serve as gas diffusion barriers for flexible thin film devices. The alucone MLD film was also used as a compliant interlayer to minimize stress caused by thermal expansion mismatch between Al_2O_3 ALD films and Teflon FEP substrates. Without the alucone MLD interlayer, the Al_2O_3 ALD films are susceptible to cracking resulting from the high coefficient of thermal expansion mismatch between Al_2O_3 ALD and Teflon FEP. With an alucone compliant interlayer, the Al_2O_3 ALD film has a crack density that is reduced progressively versus alucone interlayer thickness.

Authors Index

Bold page numbers indicate the presenter