Thin Film
Room 105A - Session TF-FrM
CVD, ALD and Film Characterization

Moderators: David Adams, Sandia National Laboratories, Halil Akyildiz, North Carolina State University

8:20am **TF-FrM1 Assessing the Role of Temperature and Pressure on the Tungsten ALD Selectivity Window on Si/SiO_2 Substrates***, **Paul Lemaire**, G.N. Parsons,* North Carolina State University

Operating conditions such as temperature and pressure are critical variables for atomic layer deposition (ALD) processes. The ALD "temperature window" describes the temperature range in which the growth per cycle is relatively constant. Yet the temperature window typically is in reference to the growth surface and does not include deposition on less thermodynamically favored surfaces. Pressure is typically maintained at ~1 Torr in order to maintain a balance between gas interdiffusion and entrainment, but there has been little work investigating how pressure affects ALD nucleation. In this work we discuss how process temperature and pressure can be adjusted to improve an ALD "selectivity window" aka deposit more material on a growth surface over a non-growth surface. We specifically study a tungsten hexafluoride (WF_6) - silane (SiH_4) ALD process (W-ALD) to selectively deposit tungsten on silicon (Si) over silicon oxide (SiO_2). Ellipsometric and x-ray photoelectron spectroscopy (XPS) analysis shows that the W-ALD selectivity window increases at lower temperatures and at higher pressure. We suggest that this improved selectivity is due to the lowered probability of the WF_6 reacting with defect sites on the non-growth SiO_2 surface. In addition, we discuss how cyclic gas exposures during the ALD deposition can be used to rapidly change the operating pressure and temperature in order to improve the selectivity window. Results from ellipsometric, and XPS analysis show that dosing He, H_2, and CH_4 immediately prior to the WF_6 exposure improves the selectivity window. We attribute the improved selectivity window to rapid substrate heating which assists in desorption of WF_x species from the SiO_2 surface and helps limit undesired tungsten nucleation.

8:40am **TF-FrM2 X-ray Absorption Spectroscopy Study of Nanocomposite Thin Films Grown by Atomic Layer Deposition***, **Anil Mane**, S. Babar, A. Yanguas-Gil,* Argonne National Laboratory*; A. O'Mahony,* Incom, Inc.*; T. Wu, J.W. Elam,* Argonne National Laboratory

We have established an ALD approach to synthesize nanocomposite coatings comprised of conducting, metallic nanoparticles embedded in an amorphous dielectric matrix. These films are nominally composed of $M:Al_2O_3$ where (M= W and Mo) and are prepared using alternating exposures to trimethyl aluminum (TMA) and H_2O for the Al_2O_3 ALD and alternating MF_6/Si_2H_6 exposures for the metal ALD. By varying the ratio of ALD cycles for the metal and the Al_2O_3 components during material growth, we can tune precisely the various material properties such as microstructure, electrical, optical and chemical properties. We have exploited these nanocomposite coatings in several applications such as resistive coatings for large-area microchannel plates suitable for large area photodetectors, charge drain coatings for electron-optic MEMS devices (Digital Pattern Generation chips) for maskless reflection electron beam lithography, protective barrier coatings for Li-ion battery cathodes and solar selective absorber coating for high temperature concentrated solar power (CSP) components.

The ALD surface chemistry for these $M:Al_2O_3$ nanocomposite films is complex, particularly during the transitions between the Al_2O_3 and the metal ALD since the surface functional groups are completely different for these two types of processes. To better understand the relationship between the ALD surface chemistry and the resulting microstructure and composition of these nanocomposite materials, we used a suite of analytical methods including transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and synchrotron X-ray absorption spectroscopy (XAS) performed at the Argonne Advanced Photon Source to characterize $W:Al_2O_3$ films while varying the W cycle ratio, W%=(W cycles)/(total cycles)*100. A key result was that for W% < 50, W is present in both metallic and sub-oxide states whereas for W% ≥50, only metallic W is seen. This transition from dielectric to metallic character at W% ~50 is accompanied by an increase in the electrical conductivity and the disappearance of a clear bandgap in the absorption spectrum. TEM revealed that the conducting phase is composed of 1-2 nm metallic nanoparticles embedded in an amorphous matrix. We believe that these nanoparticles form spontaneously during the TMA exposure following a W ALD cycle, and that the TMA acts as a reducing agent.

9:00am **TF-FrM3 A Fundamental Study of Thermal Conductivity in ALD-deposited Amorphous Oxide Thin Films of Varying Density***, **Brandon Piercy**,* Georgia Institute of Technology*; K.E. Meyer, P.E. Hopkins,* University of Virginia*; M.D. Losego,* Georgia Institute of Technology

Non-crystalline materials are believed to follow the minimum thermal conductivity model first proposed by Einstein in 1911. This model predicts that the thermal conductivity (Λ) of an amorphous solid is proportional to the atomic density (n) via a Λ proportional to $n^{2/3}$ relationship. This theory implies that the thermal conductivity of amorphous oxide materials can be controlled via their density. While processing conditions in the microelectronics industry often focus on optimizing the dielectric and electrical resistivity properties of amorphous oxide materials, less attention is given to these layers' thermal properties. However, in high-power applications, the thermal conductivity of these materials begins to have importance. In this presentation, we will report on our new fundamental understanding of two industrially important amorphous metal oxide thin films: Al_2O_3 and TiO_2. ALD deposition of these materials—besides having industrial relevance—also enables direct control over atomic density of these amorphous materials via deposition temperature. In this study, amorphous thin films of Al_2O_3 and TiO_2 of varying density were deposited with ALD over a range of temperatures from 25 °C to 250 °C. The atomic density of these films is assessed with multiple techniques including ellipsometry, x-ray reflectivity, and gravimetric measurements. Time-domain thermoreflectance (TDTR) is used to measure thermal conductivity. TDTR is an ultrafast optical pump-probe measurement that is particularly well-suited for evaluating the thermal conductivity of thin films and other nanostructures. In this study, the density of Al_2O_3 films was increased by 15%, leading to an increase in thermal conductivity from 1.2 W/m-K to 1.7 W/m-K, a 42% change. TiO_2 films saw an increase from 1.4 W/m-K to 1.9 W/m-K (36%) with a 12% increase in density. Thermal conductivities as a function of film densities were fit with the Einstein minimum effective limit model modified with a differential effective-medium approximation, affirming the applicability of the amorphous limit to metal oxide systems. For the case of TiO_2, a discrete jump in thermal conductivity to 2.5 W/m-K was detected at the onset of film crystallization (125°C). This result suggests that TDTR can be more sensitive than XRD in detecting the onset of crystallization in amorphous thin films.

9:20am **TF-FrM4 The Development of ALD Barrier Layers for Harsh Environment Applications***, **Ankit Singh**,* Georgia Institute of Technology*; A. Perrotta,* Eindhoven University of Technology, Netherlands*; S. Graham,* Georgia Institute of Technology

Encapsulation of electronic devices using vacuum deposited moisture barrier films is a critical step for their protection and enhancement of lifetime. Devices like implantable devices, OLEDs, OPVs, thin film transistors and thin film solar cells are prone to rapid degradation through chemical reactions with surrounding gas or liquid media. Barrier layers help in avoiding direct exposure of these devices to their surrounding environment thus enhancing their lifetime. Several deposition techniques can be used for preparation of such layers. Atomic layer deposition (ALD) is known to be able to produce ultra-barrier films with water vapor transmission rates lesser than 10-4 g/m2/day. However, performance and reliability of ALD based barrier films is governed by their stability in corresponding environments where resistance to corrosion and material stability will remain a key parameter to their durability.

In this work, we explore the use of TiO2, HfO2, ZrO2, and Al2O3 ALD based barrier films in harsh conditions like high temperature and a range of chemical exposure. The barrier layers were coated over ZnO sensors in order to test their ability to protect the ZnO in harsh environments and can be detected optically using photoluminescence. The exposure included DI water, salt water, phosphate buffer saline solution and low pH (HCl) solution. Degradation in ZnO films was monitored by photoluminescence testing in order to track the decrease in PL signal with time. To compliment the PL study, electron microscopy and a detailed EIS study was conducted in order to understand the mechanism of ALD barrier degradation in different environments. Several of ALD based metal oxides have shown enhanced corrosion resistance outperforming aluminum oxide which showed the least resistance. Finally, application of these barrier layers in protection of organic electronics and inorganic solar cells has been demonstrated.

9:40am **TF-FrM5 Conformal CVD Growth of HfB_xC_y and HfB_xAl_y Hard Coatings with Low Coefficient of Friction and High Oxidation Resistance***, **Elham Mohimi**, T. Ozkan, S. Babar, Z. Zhang, S. Liu, G.S. Girolami, A.A. Polycarpou, J.R. Abelson,* University of Illinois at Urbana Champaign

Conformal hard coatings with low coefficient of friction, high oxidation resistance and chemical stability are desired for applications such as components with convoluted structures, cutting tools that sustain high temperature, thermal protection systems for extreme environments, and machines with relative motion of parts. We previously reported the conformal growth and excellent mechanical properties of HfB_2 and HfB_xN_y hard coatings by chemical vapor deposition (CVD) below 300°C using the high vapor pressure precursor hafnium borohydride, $Hf(BH_4)_4$. Here we report a further improvement in the properties of HfB_2 films by alloying with C to reduce the coefficient of sliding friction, and with Al to impart high temperature oxidation resistance.

All Depositions are performed in a high vacuum chamber using 0.1-0.5 mTorr of the hafnium borohydride precursor. Carbon-alloyed HfB_xC_y films are grown using a co-flow of 0.1-0.4 mTorr dimethylbutene (DMB) as the C source at substrate temperatures of 250-600°C. The resulting films contain 5-33 at. % C. DMB also acts as growth inhibitor that reduces the growth rate by a factor of 2-6 compared to growth using the precursor alone; this affords almost perfect conformality, e.g., a step coverage > 90% in a trench of aspect ratio 30:1. The nanoindentation hardness varies from 21 to 9 GPa for films with 5-21 at. % C grown at 300°C, and from 23-25 GPa for films with 28-35 at. % C grown at 600°C. The coefficient of sliding friction is remarkably low, 0.05-0.08 for films with the highest and lowest carbon content, respectively. In addition, the elastic response is more compliant, which is expected to improve the tribological wear performance.

Al-alloyed HfB_xAl_y films are grown using a co-flow of 0.05-0.20 mTorr trimethyl amine alane (TMAA) as aluminum source at a temperature of 250-300°C. In the absence of alloying, HfB_2 films exposed to an oxygen ambient at 800°C will oxidize deeply because HfO_2 does not provide a protective layer and B_2O_3 evaporates rapidly. In sharp contrast, films containing 1-20 at. % Al form a protective aluminum oxide surface layer. Compositional depth profiles confirm the absence of oxidation below this surface layer. In addition these films are morphologically stable: whereas HfB_2 crystallizes, densifies and forms a network of cracks at temperatures above ~ 600°C, the HfB_xAl_y films do not crystallize or crack upon annealing to 800°C in inert or oxidizing atmospheres. Future work, including the co-alloying with C and Al, will explore property optimization in which both low friction and oxidation resistance are desired.

10:00am **TF-FrM6 Chemical Vapor Deposition of Silanes for Surface Modification***, **Brian Johnson**, M.R. Linford,* Brigham Young University

Silanes are arguably the most important reagents for chemically modifying surfaces. They have the unique ability to attach to silanol (SiOH) groups while imparting desired functionality. Indeed, they are extensively used to modify silica for chromatography and silicon wafers to create attachment layers for biosensors and bioarrays. Of course, HMDS is an important silane that is widely used in the semiconductor industry. Interestingly, most of the reports in the literature on silane deposition describe their liquid phase deposition. The obvious drawbacks of this approach are its lack of reproducibility and the consumption of large amounts of solvent both in the deposition and rinsing of the surfaces. Clearly there are health/safety issues associated with this use of solvent. Its advantages are simplicity – only beakers/simple glassware are required. The gas phase deposition of silanes has exactly the opposite advantages. It offers greater reproducibility and control, but the equipment required is much more complex and expensive. Nevertheless, the semiconductor and related industries much prefer the latter chemical vapor deposition (CVD) direction. Here we describe the CVD of various silanes under the controlled conditions offered by a commercial deposition system. We describe the effect of reactive functionality in the silane on deposition. We show how varying the temperature substantially changes film growth (silane deposition). We describe system cleanliness issues and the means by which carry over between runs can be nearly eliminated. We discuss the deposition of both monofunctional and trifunctional silanes. Films are characterized by X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and contact angle goniometry. Water contact angles and film thicknesses of hydrophobic silanes are strongly correlated. Best conditions for the gas phase deposition of some important silanes are presented.

10:20am **TF-FrM7 Iron CVD from Iron Pentacarbonyl: Growth Inhibition by CO Dissociation and Use of Ammonia to Restore Constant Growth***, P. Zhang, E. Mohimi, T. Talukdar, G.S. Girolami, **John Abelson**,* University of Illinois at Urbana Champaign

The precursor $Fe(CO)_5$ can be used to deposit Fe and Fe alloy thin films by CVD. However, at temperatures of 200-300°C this system exhibits undesirable behaviors – a reduction in growth rate with increasing temperature, a change in morphology from faceted to irregular, and a self-limiting film thickness – that make film growth very difficult to control and reproduce. We hypothesize that decomposition of CO ligands poisons the growth surface with graphitic carbon, on which further precursor reaction is suppressed.

Here, we report a novel solution based on surface chemistry: injection of NH_3 along with $Fe(CO)_5$ eliminates the poisoning effect, i.e., Fe CVD becomes stable and reproducible in the temperature range of 200-300°C with little change in morphology or growth rate. We propose that NH_3 removes CO from the growth surface before it can decompose based on mechanisms that were previously investigated for CO on static Fe surfaces[1].

We report that co-flow of NH_3 entirely restores the growth rate and morphology of pure Fe and of Fe_xCo_{1-x} films. The use of NH_3 may be applicable to other set carbonyl-based CVD precursors.

1. Johnston, Colin, Norman Jorgensen, and Colin H. Rochester. "Infrared study of ammonia–carbon monoxide reactions on silica-supported iron catalysts."*Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 84.10 (1988): 3605-3613.

10:40am **TF-FrM8 New Insights on the Structure and Chemistry of the Tin Oxide-emitter Interface in CdTe Solar Cells as revealed by Thermomechanical Cleavage and Electron Spectroscopy***, **Craig Perkins**, C. Beall, J.M. Burst, A. Kanevce, M.O. Reese, T.M. Barnes,* National Renewable Energy Laboratory

CdTe solar cells having superstrate architectures have a poorly understood, complex front surface formed via interdiffusion of the CdS-based emitter and the CdTe absorber. Interfaces in this region of the cell are difficult to probe by standard surface analytical methods because they are bound by glass on one side and microns of CdTe on the other. Post-growth processing with $CdCl_2$ and for back contacting is likely to further change these buried interfaces, making the traditional scheme of interface analysis – interleaved depositions and analyses – impractical. Yet these front interfaces are important. Recent modeling shows that recombination at the cell front will be increasingly critical to cell efficiency as doping levels are improved from ~$10^{14}/cm^3$ to $10^{16}/cm^3$. In this study we make use of a LN2-based thermomechanical cleavage technique and a surface analysis cluster tool to probe in detail the tin oxide-emitter interface in completed CdTe solar cells. We show that this thermomechanical cleavage occurs within a few angstroms of the SnO_2-emitter interface. An unexpectedly high concentration of chlorine, ~20%, was determined from a calculation that assumed a uniform chlorine distribution. Angle-resolved X-ray photoelectron spectroscopy was used to further probe the structure of the chlorine containing layer, revealing that both sides of the cleave location are covered by a single unit cell of $CdCl_2$. Exposing these newly formed surfaces to water showed that CdTe solar cells made using $CdCl_2$ and CdS:O emitters contain water-soluble components at their front surfaces, raising questions pertinent to cell reliability. We show that the SnO_2-emitter interface is also characterized by an extremely strong gradient in oxidation of the chalcogens present as well as a high fraction of oxidized tellurium. Selenium addition to the front of the device, done to improve carrier lifetimes, also affects the extent of chalcogen oxidation. Our work provides new and unanticipated details about the structure and chemistry of front surface interfaces and should prove vital to improving materials, processes, and reliability of next generation CdTe-based solar cells.

11:00am **TF-FrM9 Defect Tolerance in Methylammonium Lead Triiodide Perovskite***, **Xerxes Steirer**, P. Schulz, G. Teeter, V. Stevanovic, M. Yang, K. Zhu, J.J. Berry,* National Renewable Energy Laboratory

X-ray photoelectron spectroscopy (XPS) is used to track dynamic chemical and electronic changes in hybrid perovskite ($CH_3NH_3PbI_3$) thin-films used in photovoltaic applications. We report in detail X-ray induced transformations with implications on theoretical predictions of hybrid perovskite defect tolerance. Large changes in perovskite composition are analyzed with simultaneously acquired valence band spectra. A clear and reproducible trend is found that provides evidence for vacancy-type defect formation upon X-ray irradiation as $CH_3NH_3PbI_3$ is continuously converting to PbI_2. Remarkably, the position of the valence band edge with respect to the Fermi level (E_F) is invariant to significant losses of both CH_3NH_3 and I. It is not until the I/Pb ratio drops below 2.5 that E_F shifts toward the valence band edge indicating that the $CH_3NH_3PbI_3$ film becomes less *n*-type. This shift is correlated with the formation of PbI_2 as demonstrated in Pb 4f and I 3d core level spectra. Results gained from these XPS studies demonstrate that the electronic structure of the hybrid perovskite compound investigated is tolerant to defects (CH_3NH_3 and iodine vacancies) on the order of one defect pair per octahedron.

11:20am **TF-FrM10 Non Uniform Deposition Rate Profile during the Growth of SiO_2 Films Deposited by Atmospheric Pressure PECVD**, ***Anna Meshkova,*** FOM Institute DIFFER, Netherlands*; F.M. Elam, S.A. Starostin,* FUJIFILM Manufacturing Europe, Netherlands*; M.C.M. van de Sanden,* FOM Institute DIFFER, Netherlands*; H.W. de Vries,* FOM institute DIFFER, Netherlands

It was recently demonstrated that high quality dense inorganic oxide films can be synthesized on polymers utilizing the roll-to-roll Atmospheric Pressure PECVD process assisted by the diffuse dielectric barrier discharge (DBD) between cylindrical drum electrodes. In such a reactor configuration the local deposition rate as well as the local plasma chemistry is highly non-uniform along the gas flow due to the depletion of the precursor and spatial-temporal non uniformity of the discharge.

It is therefore expected that the properties of the film will vary depending on deposition location within the reactor. Hence the analysis of the spatially averaged layer deposited on the substrate roll-to-roll transported through the active reactor length is not sufficient for understanding the film growth process. The aim of the present contribution, therefore, is to study the local kinetics, gas phase transport and film growth mechanisms by means of spatially resolved analysis of the film properties in the gas flow direction of the AP-PECVD reactor, by analysis of the deposition rate profile, morphology, chemical composition and microstructure.

The set of SiO_2 films was grown in an AP-PECVD reactor with parallel bi-axial cylindrical electrode geometry on PEN foil. TEOS was used as a precursor for silica-like thin films and the process gasses were argon, nitrogen and oxygen. The variation the of deposition rate along the gas flow was accessed by measuring the film thickness profile by means of a focused beam SE with a beam size of 120 µm. The composition and microstructure was analysed by spatially resolved XPS and ATR-FTIR.

Surprisingly it was found that deposition rate profile along the gas flow has two distinct maxima. The presence of two maxima indicates a difference in the transport kinetics of the precursor fragments arriving to the surface. This coincides well with the observed variation in film microstructure in the downstream direction, assessed by ATR-FTIR analysis, with higher network porosity for lower gas residence time and denser films deposited in high residence time regions. This spatial non-uniformity within the reactor results in a depth gradient of the film properties synthesized on web-rolled substrate. One can conclude that, for the studied AP-PECVD process, the film density will increase from the silica/polymer interface towards silica/air interface when the polymer substrate is transported along gas flow. By controlling the gas flow speed the density of the layer can be modified. The last observation is especially relevant regarding the design of the gas diffusion barrier layers.

11:40am **TF-FrM11 X-Ray Diffraction from Pseudomorphic GaAs/$In_{0.3}Ga_{0.7}$As Superlattice High Electron Mobility Transistor Heterostructures on GaAs (001) Substrates**, ***Fahad Althowibi,*** *J.E. Ayers,* University of Connecticut

Pseudomorphic high-electron mobility transistors (HEMTs) are of great of interest for high-frequency applications. One approach to pseudomorphic transistors involves a superlattice structure, thereby decreasing the individual active layer thicknesses and extending the range of composition for pseudomorphic realization. Generally, X-ray characterization of pseudomorphic HEMTs is difficult to implement due to the complexity of the resulting diffraction profiles. In this work we show for the first time that superlattice implementation of HEMTs aids in the characterization of the pseudomorphic/metamorphic transition by x-ray diffraction means.

Here we report a study of the dynamical x-ray diffraction from GaAs/$In_{0.3}Ga_{0.7}$As superlattice high electron mobility transistor heterostructures on GaAs (001) substrates both with (metamorphic) and without (pseudomorphic) dislocations. We show that the threading dislocation density may be estimated from non-destructive x-ray rocking curve measurements, using the rocking curve peak intensity ratios and widths for superlattice diffraction peaks. Here, the peak widths are obtained from the broadening of the individual rocking curve peaks, while the reduction in peak intensity values may be also used to serve as a sensitive tool for the characterization of threading dislocations. These approaches therefore allow characterization of HEMT structures as pseudomorphic or metamorphic.

12:00pm **TF-FrM12 Flexible CIGS Nanorod Array Photodetectors**, ***Emad Badradeen,*** *M. Brozak, K.M. Al-Mayalee, F. Keles, T. Karabacak,* University of Arkansas at Little Rock

In this study, we fabricated core-shell nanostructured flexible photodetectors on flexible substrates of Kapton. For this purpose, p-type copper indium gallium selenide (CIGS) nanorod arrays (core) were coated with aluminum doped zinc oxide (AZO) films (shell) at relatively high Ar gas pressures. CIGS nanorods were prepared by glancing angle deposition (GLAD) technique using a RF magnetron sputtering unit at room temperature. AZO films were deposited by RF sputtering at Ar pressures of 1.0×10^{-2} mbar (high pressure sputtering, HIPS) for the shell and at 3.0×10^{-3} mbar (low pressure sputtering, LPS) for top contact. The morphological characterization was carried out by field-emission scanning electron microscope. The photocurrent measurement was conducted under 1.5 AM sun under zero electrical bias. GLAD nanostructured flexible photodetectors were shown to demonstrate enhanced photoresponse with a photocurrent density value of 2.88 µA/cm^2. On the other hand, conventional planar thin film devices did not show any notable photoresponse. Improved photoresponse of CIGS nanorod devices are believed to be due to their enhanced light trapping property and the reduced inter-electrode distance as a result of core-shell structure, which allows the effective capture of the photo-generated carriers. This approach can open up a new strategy to boost the performance of flexible photodetectors.

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