Monday Morning, November 10, 2014

2D Materials Focus Topic
Room: 310 - Session 2D+EM+NS+PS+SS+TF-MoM

2D Materials Growth and Processing
Moderator: Thomas Greber, University of Zurich

8:20am 2D+EM+NS+PS+SS+TF-MoM1   Exploring the Flatlands: Synthesis, Characterization and Engineering of Two-Dimensional Materials, *Jun Lou*, Rice University **INVITED**
In this talk, we report the controlled vapor phase synthesis of MoS_2 atomic layers and elucidate a fundamental mechanism for the nucleation, growth, and grain boundary formation in its crystalline monolayers. The atomic structure and morphology of the grains and their boundaries in the polycrystalline molybdenum disulfide atomic layers are examined and first-principles calculations are applied to investigate their energy landscape. The electrical properties of the atomic layers are examined and the role of grain boundaries is evaluated. More importantly, if precise two-dimensional domains of graphene, h-BN and MoS_2 atomic layers can be seamlessly stitched together, in-plane heterostructures with interesting electronic applications could potentially be created. Here, we show that planar graphene/h-BN heterostructures can be formed by growing graphene in lithographically-patterned h-BN atomic layers. Our approach can create periodic arrangements of domains with size that ranging from tens of nanometers to millimeters. The resulting graphene/h-BN atomic layers can be peeled off from their growth substrate and transferred to various platforms including flexible substrate. Finally, we demonstrate how self-assembled monolayers with a variety of end termination chemistries can be utilized to tailor the physical properties of single-crystalline MoS_2 atomic-layers. Our data suggests that combined interface-related effects of charge transfer, built-in molecular polarities, varied densities of defects, and remote interfacial phonons strongly modify the electrical and optical properties of MoS_2, illustrating an engineering approach for local and universal property modulations in two-dimensional atomic-layers.

9:00am 2D+EM+NS+PS+SS+TF-MoM3   Influence of Substrate Orientation on the Growth of Graphene on Cu Single Crystals, *Tyler Mowll*, University at Albany-SUNY, *Z.R. Robinson*, U.S. Naval Research Laboratory, *P. Tyagi, E.W. Ong, C.A. Ventrice, Jr.*, University at Albany-SUNY
A systematic study of graphene growth on on-axis Cu(100) and Cu(111) single crystals oriented within 0.1° from the surface normal and a vicinal Cu(111) crystal oriented 5° off-axis has been performed. Initial attempts to grow graphene by heating each crystal to 900°C in UHV, followed by backfilling the chamber with C_2H_4 at pressures up to $5x10^{-3}$ Torr did not result in graphene formation on either the on-axis Cu(100) or on-axis Cu(111) surfaces. For the vicinal Cu(111) surface, epitaxial graphene was formed under the same growth conditions. By backfilling the chamber with C_2H_4 before heating to the growth temperature, epitaxial graphene was formed on both the on-axis Cu(100) and off-axis Cu(111) surfaces, but not the on-axis Cu(111) surface. By using an argon overpressure, epitaxial overlayers could be achieved on all three Cu substrates. These results indicate that the most catalytically active sites for the dissociation of ethylene are the step edges, followed by the Cu(100) terraces sites and the Cu(111) terrace sites. The need for an argon overpressure to form graphene the on-axis Cu(111) surface indicates that the Cu sublimation rate is higher than the graphene growth rate for this surface. This research was supported in part by the NSF (DMR-1006411).

9:20am 2D+EM+NS+PS+SS+TF-MoM4   Synthesis of Large Scale MoS_2-Graphene Heterostructures, *Kathleen McCreary*, A.T. Hanbicki, J. Robinson, B.T. Jonker, Naval Research Laboratory
A rapidly progressing field involves the stacking of multiple two-dimensional materials to form heterostructures. These heterosctructures have exhibited unique and interesting properties. For the most part, heterostructure devices are produced via mechanical exfoliation requiring the careful aligning and stacking of the individual 2D layered components. This tedious and time consuming process typically limits lateral dimensions to micron-scale devices. Chemical vapor deposition (CVD) has proven to be a useful tool in the production of graphene and has very recently been investigated as a means for the growth of other 2D materials such as MoS_2, $MoSe_2$, WS_2, WSe_2 and hexagonal boron nitride. Using a two-step CVD process we are able to synthesize MoS_2 on CVD grown graphene. AFM, Raman spectroscopy, and Photoluminescence spectroscopy of the MoS_2-graphene heterostructure show a uniform and continuous film on the cm scale.

9:40am 2D+EM+NS+PS+SS+TF-MoM5 Growth of 2D MoS_2 Films by Magnetron Sputtering, *Andrey Voevodin*, Air Force Research Laboratory, *C. Muratore*, University of Dayton, *J.J. Hu*, Air Force Research Laboratory/UDRI, *B. Wang, M.A. Haque*, Pennsylvania State University, *J.E. Bultman, M.L. Jesperson*, Air Force Research Laboratory/UDRI, *P.J. Shamberger*, Texas A&M University, *R. Stevenson*, Air Force Research Laboratory, *A. Waite*, Air Force Research Laboratory/UTC, *M.E. McConney, R. Smith*, Air Force Research Laboratory
Growth of two dimensional (2D) MoS2 and similar materials over large areas is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into novel devices. Typical preparation approaches with chemical or mechanical exfoliation lack scalability and uniformity over appreciable areas (>1 mm) and chemical vapor deposition processes require high substrate temperatures. We developed few-layer MoS_2 growth under non-equilibrium magnetron sputtering conditions selected to minimize the MoS_2 nucleation density and maximize 2D growth of individual crystals [1]. In this process, the thermodynamically driven tendency to form islands is accomplished by maximizing atomic mobility through the control of incident flux kinetic energies, densities, and arriving angle to the substrate while avoiding defect formation (i.e., vacancy creation by sputtering of S atoms). Amorphous SiO_2, crystalline (0001) oriented Al_2O_3, and (002) oriented graphite substrates were used to grow few monolayer thick MoS_2 films. Continuous 2D MoS_2 films were produced over 4 cm^2 areas. They were composed of nano-scale domains with strong chemical binding between domain boundaries, allowing lift-off from the substrate and electronic transport measurements with contact separation on the order of centimeters. Their characteristics were similar to few-layer MoS_2 films produced by exfoliation with a direct band gap in thin samples of approximately 1.9 eV from photoluminescense spectra. The electron mobility measured for as-grown MoS_2 films was very strongly dependent on film thickness and substrate choice.

[1] "Continuous ultra-thin MoS2 films grown by low-temperature physical vapor deposition", C. Muratore, J.J. Hu, B. Wang, M.A. Haque, J.E. Bultman, M. L. Jesperson, P.J. Shamberger, A.A. Voevodin, Applied Physics Letters (2014) in press.

10:00am 2D+EM+NS+PS+SS+TF-MoM6 Formation of Graphene on the C-face of SiC{0001}: Experiment and Theory, *Jun Li*, G. He, M. Widom, R.M. Feenstra, Carnegie Mellon University
There are two {0001} surfaces of SiC, the (0001) surface known as the "Si-face", and the (000-1) surface or "C-face". The formation of graphene (by heating the SiC to 1100 – 1600 ° C in various gaseous environments) has been studied for both surfaces, although it is much better understood on the Si-face. In that case, an intermediate C-rich layer, or "buffer layer" forms between the graphene and the SiC crystal. This buffer layer has 6√3x6√3-R30° symmetry; its structure is well established,[1] and it acts as a template for the formation of subsequent graphene layers. In contrast, graphene formation on the C-face is much less well understood. More than one interface structure between the graphene and the SiC has been observed,[2,3] and, with one notable exception,[4] the quality of the graphene formed on the C-face is generally lower than that for the Si-face.

In this work we provide new experimental and theoretical results that allow us to understand graphene formation on the C-face of SiC. Experimentally, by heating the SiC in a disilane environment, we map out the phase diagram of different surface and interface structures that form on the SiC as a function of disilane pressure and sample temperature. New surface structures that develop just prior to the graphene formation are observed. With additional heating, graphene forms on the surface, but some remnant of the surface structure prior to the graphene formation is believed to persist at the graphene/SiC interface. From first-principles theory, we find that the hydrogen in the disilane environment plays a critical role in the surface/interface structures that form. Experimentally, for disilane pressures below $5x10^{-5}$ Torr, we find a 2x2 surface structure forming prior to graphene formation. From theory we identify this structure as consisting of a silicon adatom together with a carbon restatom on the surface, with H-termination of those atoms being possible but not necessary. At higher disilane pressures we observe a 4x4 structure, and we identify that as consisting of a lower density of Si adatoms than the 2x2, now with at least some of the adatoms and restatoms being H-terminated. With graphene formation, this structure converts to the observed √43x√43-R± 7.6° interface structure. At higher disilane pressures we theoretically predict the formation of a surface consisting simply of H-terminated carbon restatoms. Experiments are underway to observe that surface, along with subsequent graphene formation on the surface.

(1) Y. Qi et al., PRL **105**, 085502 (2010).

(2) F. Hiebel et al., PRB **78**, 153412 (2008).

(3) N. Srivastava et al., PRB **85,** 041404 (2012).

(4) W. A. de Heer et al., PNAS **108**, 16900 (2011).

10:40am 2D+EM+NS+PS+SS+TF-MoM8 Graphene on Hexagonal Boron Nitride Heterostacks Grown by UHV-CVD on Metal Surfaces, *Juerg Osterwalder, S. Roth, A. Hemmi,* University of Zurich, Switzerland, *F. Matsui,* Nara Institute of Science and Technology, Japan*, T. Greber*, University of Zurich, Switzerland **INVITED**
Chemical vapor deposition (CVD) performed under ultra-high vacuum conditions on single-crystal metal surfaces enables the growth of large-area and high-quality graphene and hexagonal boron nitride (h-BN) single layers. We explore the CVD parameter space of precursor pressure and temperature in order to go beyond the self-saturating single-layer growth, or to grow heterostacks of the two materials. Formed layers are characterized structurally by LEED, STM and x-ray photoelectron diffraction. On Cu(111) a graphene layer could be grown on a pre-deposited single layer of h-BN when using 3-pentanone as a precursor at a pressure of 2.2 mbar and a substrate temperature of 1100 K [1]. On Rh(111) the same procedure leads to incorporation of carbon into the metal surface layers, while a graphene layer is formed only upon a second high-pressure dose [2]. In both cases the heterostructures show clearly the stacking sequence and structural and ARPES signatures of graphene on h-BN but are far from defect-free.

[1] S. Roth et al., Nano Lett. 13, 2668 (2013).

[2] S. Roth, PhD Thesis, Department of Physics, University of Zurich (2013).

11:20am 2D+EM+NS+PS+SS+TF-MoM10 Kinetics of Monolayer Graphene Growth by Carbon Segregation on Pd(111), *Abbas Ebnonnasir, H.S. Mok, Y. Murata,* University of California at Los Angeles*, S. Nie, K.F. McCarty,* Sandia National Laboratories*, C.V. Ciobanu,* Colorado School of Mines*, S. Kodambaka*, University of California at Los Angeles
In this research, using in situ low-energy electron microscopy and density functional theory calculations, we elucidate the growth kinetics of monolayer graphene on single-crystalline Pd(111). In our experiments, carbon saturated Pd(111) samples were cooled down from 900 ºC to segregate carbon on the surface in the form of graphene. Upon cooling the substrate, graphene nucleation begins on bare Pd surface and continues to occur during graphene growth. Measurements of graphene growth rates and Pd surface work functions along with DFT calculations establish that this continued nucleation is due to increasing C adatom concentration on the Pd surface with time. We attribute this anomalous phenomenon to a large barrier for attachment of C adatoms to graphene coupled with a strong binding of the non-graphitic C to the Pd surface.

Advanced Surface Engineering
Room: 302 - Session SE+EM+EN+PS+TF-MoM

New Developments in Atmospheric Pressure Plasma Deposition and Thin Films for Energy Applications

Moderator: Hana Barankova, Uppsala University, Sweden, Michael Stueber, Karlsruhe Institute of Technology

8:40am SE+EM+EN+PS+TF-MoM2 Real Time Characterization of Polymer Surface Modification by an Atmospheric Pressure Plasma Jet, *Andrew Knoll, P. Luan, E.A.J. Bartis, C. Hart,* University of Maryland, College Park*, Y. Raitses,* Princeton Plasma Physics Laboratory*, G.S. Oehrlein*, University of Maryland, College Park
Atmospheric pressure plasma jets (APPJ) have been shown to modify surfaces, leading to a variety of potential industrial and medical applications. APPJ treated surfaces are typically evaluated post treatment, but few studies exist showing surface changes in real time. In this study, we characterized both closely-coupled and remote APPJ treatments of a PMMA-based 193 nm photoresist polymer (PR193) using *in situ* ellipsometry to monitor film thickness and refractive index in real time. The kilohertz-driven, two-ring electrode APPJ was fed with low admixtures of O_2 and N_2 to Ar. Voltage and current waveforms were collected to electrically characterize the APPJ and measure power dissipation. In addition, high speed photography of the APPJ was conducted in order to characterize plasma interaction with various controlled environments and with PR193. Ellipsometry shows that PR193 etch rates depend on the feed gas chemistry and treatment time. Etch rates are reduced for Ar/O_2 compared with pure Ar and Ar/N_2. This reduction is correlated to a decrease in plasma density with O_2 addition. It is also shown that the etch rate changes over time initially during APPJ heating and reaches steady state as the temperature stabilizes. When the plasma is brought close enough to the sample, the discharge couples with the surface and arcing to the film occurs. This interaction greatly increases the etch rate and introduces major damage to the polymer, which can be observed by the naked eye. From electrical data and high speed photography we see that the pure Ar discharge exhibits filamentary behavior that is enhanced by O_2 addition and rendered more diffuse by N_2 addition. High speed photography shows that the coupling of the plasma and the environment increases when the environment matches the feed gas chemistry, which causes the plume to extend farther than in open air. While the Ar plume is confined to a single plasma channel, N_2 admixture to Ar branches out into many smaller discharges, similar to a Lichtenberg figure. We also correlate damage seen on the polymer surface with observed arcing. The authors gratefully acknowledge financial support by US Department of Energy (DE-SC0001939).

9:00am SE+EM+EN+PS+TF-MoM3 Gas-Liquid Mixed Phase Plasma at Atmospheric Pressure, *Akira Ando, G. Tang, R. Ohno, A. Komuro, K. Takahashi*, Tohoku University, Japan **INVITED**
A gas-liquid mixed phase plasma discharge is investigated using nanosecond high-voltage pulse generator. Non-thermal atmospheric pressure plasmas have recently attracted significant attention due to their good energy efficiency in production of reactive species. Plasma in water can generate many reactive species, such as ozone, hydroxyl radicals and oxygen radicals. These products have strong oxidizing power and is applicable for many applications without any thermal stress.

We have utilized a nanosecond high-voltage pulse to produce a discharge within bubbles introduced into water, where semiconductor opening switching (SOS) diodes are used in the pulse generator.

The reactor for the gas-liquid hybrid plasma consists of two regions, gas and liquid regions, separated by a thin plate with a small holes (1mm in diameter). Several working gases are fed into the reactor from the gas region and bubbles are formed via the separator holes in the water. High-voltage pulse with 10-15kV are applied to a wire electrode situated in the gas phase. A grounded electrode is set into the water. When the high voltage pulse with the duration of 40ns is applied, a streamer-like discharge occurs within the bubbles and the streamer extends along the surface of gas-liquid interface.

The formation process of discharge bubbles were observed with a high-speed CCD images of the discharge. The area of discharge extension depends on the gas species and conductivity. Production rate of reactive species, ozone and hydroxyl radicals in a discharge reactor was also depends on the parameters. As the life time of hydroxyl radicals is very short, the amount is estimated from concentration of hydrogen peroxide produced in treated water, which is produced by the recombination process of hydroxyl radicals.

In order to evaluate the oxidation power in the gas-liquid mixed plasma, we applied it to water purification, such as decolorization, sterilization and decomposition of persistent organic pollutants (POPs). The sterilization effect in the water is estimated from the survival ratio of bacillus subtilis and it reaches more than 99.5% after 15min treatment. The survival ratio is large in air discharge and the value of pH in water as well as ultraviolet (UV) ray generated by plasma discharge affects the sterilization. SEM images shows the surface of the bacteria were damaged by the treatment.

9:40am SE+EM+EN+PS+TF-MoM5 Atmospheric Pressure High Power Impulse Plasma Source (AP-HiPIPS) for Plasma Enhanced Chemical Vapor Deposition of Thin Films, *Vasiliki Poenitzsch, R. Wei, M.A. Miller, K. Coulter,* Southwest Research Institute
Southwest Research Institute is currently developing a High Power Impulse Plasma Source (HiPIPS) that supplies a high flux of energetic reactants to a surface while maintaining a low processing temperature. HiPIPS is a new plasma enhanced chemical vapor deposition technology that combines variable pressure plasma jets with advanced pulsed power technology. Several complementary techniques, including mass spectroscopy, optical emission spectroscopy (OES) and electrical and thermal probes were employed, for measuring and calculating the plasma characteristics in a wide range of the HiPIPS process parameters and conditions. The preliminary HiPIPS experiments have revealed that high peak power (~40 kW) in the pulses can be achieved resulting in a high peak current (~200 A) and increased plasma density (i.e. n = Ar: 10^{20} cm^{-3}s^{-1}) while maintaining a low average power (35W) and a low substrate processing temperature (50-150 °C). A prototype atmospheric-pressure HiPIPS (AP-HiPIPS) was successfully developed and proof-of-concept AP-HiPIPS diamond-like carbon (DLC) film deposition was demonstrated. Beyond DLC films, HiPIPS plasmas could be applicable to deposition of many classes of films and many types of surface treatments. In contrast to conventional state-of-the-art non-thermal atmospheric pressure plasma jets, typically driven by RF or AC, the power densities and currents during pulse on-time are 2-3

orders of magnitude higher in HiPIPS. Since plasma is created through inelastic electron collision with precursor gas molecules, the increased power and current directly equates to significantly improved ionization and dissociation of precursor gases in HiPIPS. Thus, distinguishing features of HiPIPS as compared to RF or AC APPJs are increased ionization, enhanced molecular gas dissociation, and higher flux of reactive species while maintaining the same low deposition temperatures. In this presentation, an overview of HiPIPS and AP-HiPIPS will be given with a specific focus on plasma characteristics and areas for further development.

10:00am SE+EM+EN+PS+TF-MoM6 Importance of Argon's Spectral Emission for Plasma Diagnostics at an Atmospherics Open Air Plasma Discharge, *Vladimir Milosavljevic*, *J. Lalor, P. Bourke, P.J. Cullen*, Dublin Institute of Technology, Ireland

In recent years, plasma on atmospheric pressure attracts a lot of attention due to their numerous applications in plasma biology, health care, and medicine, as well as surface and materials processing and nanotechnology. Among several atmospheric pressure plasma devices, a dielectric barrier discharge plasma jet (DBDPJ) is the most used, because of its simplicity and a fact that the generated plasma is in surrounding air and not in a confined space. The dynamics of DBDPJ in noble gases reveal that the plasma plumes propagate at a speed several orders of magnitude higher than the gas flow velocity. This is why it is generally accepted that the propagation of the plasma plumes is driven electrically rather than by the gas flow, which imposes in the first place the importance of the plasma diagnostics. Because of the frequent collisions between electrons and neutrals at high pressure, the electrical probe methods are generally less useful for plasmas produced at atmospheric pressure. Therefore, other diagnostic methods are needed and optical emission spectroscopy (OES) has been used as one of the alternative diagnostics because of its simplicity and non-intrusive nature.

Nitrogen dominates the ionic composition of atmospheric discharge and has an impact on the breakdown voltage. Nitrogen acts as a 'sensor gas' and OES diagnostics are applied in assumption that most nitrogen molecular emissions are excited during electron impact of ground state N2(X). When nitrogen is added/mixed with argon plasma discharges, the argon emission lines are significantly quenched and the resulting plasma spectral emission is changed. Measurements and analysis of neutral argon spectral emission lines give very important information about the plasma properties. In this work the absolute spectral emissions of the atomic and molecular lines associated with argon, oxygen, nitrogen and hydrogen are presented. Wavelength resolved optical emission profiles of argon's spectral lines shows that the change in electron energy distribution functions (EEDF) has taken place for a low gas flow rate only. After the gas flow rate goes above a certain limit, the EEDF remains constant. At the same time the density of argon metastable atoms are changed with the gas flow rate. Overall, analysis of the spectral intensities assist in the development of optimised plasma processing parameters for treatments such as surface activation or removal of contaminates.

The research leading to these results has received funding from the European Union´s Seventh Framework Programme managed by REA Research Executive Agency (FP7/2007-2013) under Grant Agreement number 605125

10:40am SE+EM+EN+PS+TF-MoM8 Hot 'n Flaky: Thermal Properties of Layered Atomic Structures, *Christopher Muratore*, University of Dayton, *V. Varshney*, Air Force Research Laboratory/UTC, *J.J. Hu*, Air Force Research Laboratory/UDRI, *A.A. Voevodin*, Air Force Research Laboratory **INVITED**

Synthesis capability for uniform growth of 2D materials over large areas at lower temperatures without sacrificing their unique properties is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into novel devices. We have demonstrated, for the first time, vapor phase growth techniques for precisely controlled synthesis of continuous, uniform molecular layers of all MoX_2 and WX_2 transition metal dichalcogenide (TMD) compounds on diverse substrates, including graphene, hexagonal boron nitride, highly oriented pyrolitic graphite (HOPG), SiO_2, and metal substrates over several square centimeters. Preliminary results show MoX_2 and WX_2 transition metal dichalcogenide materials grown in a novel ultra-high vacuum (UHV) physical vapor deposition (PVD) process demonstrate properties identical or even superior (e.g., electron mobilities >500 cm^2 V^{-1} s^{-1}) to exfoliated layers. Growth of bi-layer MoS_2 on few-layer graphene with a 30% lattice mismatch and TMD/TMD heterostructures are shown to demonstrate how natural accommodation of stresses at 2D van der Waals interfaces has the remarkable potential to transform the way materials selection is considered for synthetic heterostructures, as concerns regarding lattice constant matching can be abandoned with preference given to desired properties and performance. Investigations relating to application of these materials in thermoelectric device applications are presented. Thermal conductivity

values of TMD thin films were compared to bulk crystals, revealing expected trends with mass, but a >10 fold reduction in thin film thermal conductivity. Phonon scattering lengths at domain boundaries based on computationally derived group velocities were consistent with the observed film microstructure, accounting for the reduction. We also explore thermal anisotropy in MoS_2 films. Measurement results are correlated with MD simulations of thermal transport for perfect and defective MoS_2 crystals, demonstrating the importance of thermal boundary scattering.

Thin Film
Room: 305 - Session TF+PS+SE-MoM

Advanced PVD Methods
Moderator: Subhadra Gupta, University of Alabama

9:00am TF+PS+SE-MoM3 Ternary and Quaternary Thin Layers Deposited by Magnetron Sputtering, *Marie-Paule Besland*, *J. Tranchant, E. Janod, C. Benoit, L. Cario, P.Y. Jouan, M. Carette, A. Lafond*, Institut des Matériaux Jean Rouxel – Université de Nantes, France, *R. Meunier, S. Fabert*, Institut des Matériaux Jean Rouxel – Université de Nantes and Crosslux, France, *P.Y. Thoulon, M. Ricci*, Crosslux Company, France

Developing new functionalities mainly depend on the use of new functional material. Nevertheless, prior to envision any development of functional materials towards devices, two major challenges have to be tackled. The former one is to obtain thin layers of active and functional materials. The second challenge is to recover the functional properties on thin layers. For several decades, magnetron sputtering is a widely used deposition technique in microelectronics. Moreover, magnetron sputtering enables to deposit well-crystallized film of insulating or conducting materials, at low temperatures, over large areas, while controlling the film composition and microstructure, even for complex and multi-component materials. Thus, on the basis of well established know-how in deposition process and multi-layered functional structures [1], the deposition of GaV_4S_8 material in the form of thin layers has been investigated by both non-reactive RF magnetron sputtering and reactive process in Ar/H_2S mixture [2]. While the functionality (Resistive switching =RS) was first evidenced on single crystals, our studies demonstrated that metal-insulator-metal (MIM) structures based on GaV_4S_8 thin layers, deposited by magnetron sputtering, exhibit as well a similar RS [3]. More recently, we focus on the historical chalcogenide absorber for solar cells: CIGSe. We developed a dedicated and home-designed vacuum chamber for CIGSe thin films deposition using "one step sputtering". In that study, CIGSe thin films were deposited on SLG/Mo substrates by RF magnetron sputtering and then ex-situ annealed under controlled atmosphere. Deposition and annealing parameters can modify both chemical composition and structural properties. In particular, different preferential crystalline orientation may be induced and can modify functional properties in a large extend. Finally, the performances of CIGSe solar cell completely realized by magnetron sputtering technique will be compared to published efficiency values in the 8.9- 10.5 % range [5].

1- C. Duquenne et al. J. Appl. Phys. 104 (2008) 063301; M.P. Besland et al. Thin Solid Films 495 (2006) 86.

2- E. Souchier et al. Thin Solid Films 533 (2013) 54 ; J. Tranchant et al. J. Phys. D: Appl. Phys. 47 (2014) 065309.

3- J. Tranchant et al. Thin Solid Films 533 (2013) 61.

4- J. A. Frantz et al. Thin Solid Films 519 (2011) 776; A.J. Zhou et al. Thin Solid Films 520 (2012) 6068.

5- C. Chen et al. Solar Energy Materials & Solar Cells 103 (2012) 25; Thin Solid Films 535, (2013) 122.

9:20am TF+PS+SE-MoM4 Molecular Dynamics Simulations of TiN/TiN(001) Growth, *Daniel Edström*, *D.G. Sangiovanni, V. Chirita, L. Hultman*, Linköping University, Sweden, *I.G. Petrov, J.E. Greene*, University of Illinois at Urbana Champaign

The Modified Embedded Atom Method (MEAM) interatomic potential within the classical Molecular Dynamics (MD) framework enables realistic, large-scale simulations of important model materials such as TiN. As a step toward s understanding atomistic processes controlling the growth of TiN on a fundamental level, we perform large-scale simulations of TiN/TiN(001) deposition using a TiN MEAM parameterization which reproduces experimentally-observed surface diffusion trends, correctly accounts for Ehrlich barriers at island step edges [1], [2], and has been shown to give results in excellent qualitative and good quantitative agreement with Ab Initio MD based on Density Functional Theory (DFT) [3], [4]. Half a monolayer of TiN is deposited on 100x100 atom TiN(001) substrates at a rate of 1 Ti atom per 50 ps, resulting in simulation times of 125 ns. The TiN substrate is maintained at a typical epitaxial growth

temperature, 1200 K during deposition using Ti:N flux ratios of 1:1 and 1:4 with incident atom energies of 2 and 20 eV to probe the effects of N_2 partial pressure and substrate bias on TiN(001) growth modes. We observe nucleation of Ti_xN_y molecules; N_2 desorption; the formation, growth and coalescence of mixed <100>, <110>, and <111> faceted islands; as well as intra- and interlayer mass transport mechanisms. For equal flux ratios at 2 eV incidence energy, islands begin to form atop existing islands at coverages $\gtrsim$ 0.25 ML, leading to 2D multilayer growth. At 20 eV, the film growth mode shifts toward layer-by-layer growth. We discuss the implications of these results on thin film growth and process tailoring. Our classical MD predictions are supported and complemented by DFT-MD simulations.

[1] D. G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Dynamics of Ti, N, and TiNx (x=1–3) admolecule transport on TiN(001) surfaces," *Phys. Rev. B*, vol. 86, no. 15, p. 155443, Oct. 2012.

[2] D. Edström, D. G. Sangiovanni, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Ti and N adatom descent pathways to the terrace from atop two-dimensional TiN/TiN(001) islands," *Thin Solid Films*, vol. 558, pp. 37–46, May 2014.

[3] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ab initio and classical molecular dynamics simulations of N2 desorption from TiN(001) surfaces," *Surf. Sci.*, vol. 624, pp. 25–31, Jun. 2014.

[4] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ti adatom diffusion on TiN(001): Ab initio and classical molecular dynamics simulations," *Surf. Sci (In Press)*. doi: 10.1016/j.susc.2014.04.007

9:40am TF+PS+SE-MoM5 Surface Chemistry of Pd and Ag Interaction with 3C-SiC Thin Films Deposited on Si(111) by Pulsed Laser Depositon, *Rachel Seibert, D. Velazquez, J. Terry,* Illinois Institute of Technology, *K.A. Terrani, C. Baldwin, F. Montgomery, K. Leonard, J. Hunn, P. Schuck, R. Stoller,* Oak Ridge National Laboratory, *S. Saddow,* University of South Florida

The surface interactions of nuclear fission products with the barrier SiC layer of Tri-Structural Isotropic (TRISO) coated fuel particles limit fuel cell performance. In particular, Pd and Ag reduce the structural integrity of SiC. An understanding of the reaction mechanisms and kinetics of these interactions under normal operation as well as accident conditions is critical for the development of advanced nuclear reactors, but currently is not well understood. This surface chemistry is examined both in spent TRISO fuel on SiC/Si(111) thin films and compared to theoretical calculations done by Schuck and Stoller at Oak Ridge National Laboratory [1]. Synchrotron extended X-ray absorption fine structure (EXAFS) spectroscopy measurements were conducted on the irradiated TRISO fuel pellet to characterize atomic interactions at the Pd K-edge (24350 eV). The thin films were grown epitaxially via pulsed laser deposition (PLD), as evidenced by reflection high energy electron diffraction (RHEED) patterns. Pd and Ag were deposited on separate SiC/Si(111) films in thickness increments from 0.5-5 monolayers. The chemical structure of the thin films is analyzed using X-ray photoelectron spectroscopy (XPS).

[1] Schuck, P.C. and R.E. Stoller, *Ab initio study of the adsorption, migration, clustering, and reaction of palladium on the surface of silicon carbide.* Phys. Rev. B **83**, (2011)

10:00am TF+PS+SE-MoM6 High Thermal Stability Nanocrystalline Gold, Part I, *Ronald Goeke, N. Argibay, J.E. Mogonye, K.M. Hattar, S.V. Prasad,* Sandia National Laboratories

Gold coatings that are ideally suited for low electrical contact resistance (ECR) applications are mechanically soft and exhibit unacceptable amounts of adhesion and friction. To mitigate these problems gold for ECR applications is typically alloyed with Ni, Co or Fe which increases the film hardness and wear resistance. A key limitation of hard gold coatings is the propensity for the non-noble alloying metal species to diffuse to the surface and form non-conductive oxide films that can severely impact the electrical contact behavior. These traditional hard gold films, which are fabricated via electro-deposition, have been limited to electrochemical compatible materials. Using co-deposition of Au-ZnO by electron beam evaporation we have eliminated the electrochemical material limitations and synthesized a new class of hard gold thin films. The ceramic phase is used to strengthen the composite via grain refinement. The resulting nanocrystalline gold thin film can replace typical hard gold films and exhibits enhanced thermal stability as the refractory ceramic phase is kinetically limited and has no oxidative potential for migration to the surface. The synthesis, characterization, and thermal stability against grain sintering will be discussed.

10:40am TF+PS+SE-MoM8 High Thermal Stability Nanocrystalline Gold Thin Films, Part II, *Nicolas Argibay, J.E. Mogonye, R.S. Goeke, K.M. Hattar, M.T. Dugger, S.V. Prasad,* Sandia National Laboratories

In the second part we present the result of investigations of the bulk transport properties, thermal and mechanical stability, and mechanical properties of electron beam codeposited Au-ZnO as a function of composition and temperature (up to a homologous temperature of 0.5). A high throughput method for determining the average grain size in electrically conductive metal-ceramic thin films will be presented, founded on a correlation between grain boundary density and electrical resistivity (Mayadas-Shatzkes and Sondheimer-Fuchs models), and compared to microstructural characterization using backscatter and transmission electron diffraction, SEM, and XPS.

11:00am TF+PS+SE-MoM9 Growth and Phase Stability of Zirconium Diboride Thin Films, *David Stewart, D.J. Frankel, R.J. Lad,* University of Maine

Zirconium diboride (ZrB_2) has metallic-like electrical and thermal conductivities up to its melting point of 3246°C and is also thermal shock resistant, making it an excellent material for use in harsh, high temperature environments. Presently, much of the literature on boride materials concerns bulk, sintered materials, and less is known about ZrB_2 thin films. Here we demonstrate the growth of ZrB_2 thin films by e-beam co-evaporation of elemental Zr and B sources on sapphire, silicon, and silica substrates. Films were deposited over a range of Zr:B compositions and were characterized before and after annealing up to 1000°C in air or under vacuum (10-8 Torr). Scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) indicated that as-deposited films are homogeneous, with a smooth morphology and covalent bonding character. X-ray diffraction (XRD) revealed that films deposited at temperatures from ambient to 600°C are typically amorphous, and annealing in vacuum up to 1000°C can cause the formation of a ZrB_2 crystalline phase that coexists with an amorphous matrix, depending on the Zr:B ratio. Films annealed in air as low as 800°C become heavily oxidized and boron-depleted, leaving behind a monoclinic ZrO_2 polycrystalline film. XPS depth profiles suggest the formation of a boron oxide phase in air that evaporates from the surface at high temperatures, consistent with surface oxidation behavior reported for bulk ZrB_2 materials. Electrical conductivities of as-deposited films, measured with a 4-point probe, range from $0.3 – 8.3 \times 10^6$ S/m depending on the Zr:B ratio, and the films retain their conductive nature after vacuum annealing. The ZrB_2 crystalline phases exhibit a preferred (100) crystallographic texture, and valence band XPS measurements confirm the existence of hybridized B2p-Zr4d bonding states. Understanding the high temperature stability of ZrB_2 films is important for developing it as a potentially stable conducting film for electronic device applications in harsh environments.

11:20am TF+PS+SE-MoM10 Thickness Dependence of High Frequency Magnetic Properties for Thin Films of Iron-Gallium-Boron, *Colin Rementer, Y. Kim, J.P. Chang,* University of California at Los Angeles

Iron gallium boron, i.e. $(Fe_{80}Ga_{20})_xB_{1-x}$ or FeGaB, is a material of considerable interest for high frequency, multiferroic applications. Lou *et al.* discovered that the addition of boron to the magnetostrictive material Galfenol ($Fe_{80}Ga_{20}$ or FeGa) led to a decrease in coercivity (~1 Oe), decrease in ferromagnetic resonance (FMR) linewidth (~20 Oe) at *X* band, and an increase in piezomagnetic coefficient (~7 ppm/Oe). The physical properties were optimized in $(Fe_{80}Ga_{20})_{88}B_{12}$ with ~100 nm thickness (Lou, J. et al. 2007). The material has been incorporated into several multiferroic systems with great success (Lou, J. et al. 2009). It is a material of great interest for integration into various multiferroic antenna systems. To have a better understanding of the material, a more thorough study on the fundamental properties of the material at different thicknesses is needed, as well as how that thickness can affect the tunability of resonant frequency and magnetoelectric coupling in multiferroic heterostructures when incorporated with ferroelectric single crystals.

FeGaB was grown via co-sputtering of $Fe_{80}Ga_{20}$ and boron targets via DC magnetron and RF magnetron sputtering, respectively. The FeGa target was held at 60 W and the boron power was adjusted to tune the boron concentration, from 9 - 18%. FeGaB films were grown with thicknesses ranging from 30 nm – 500 nm, and a growth rate of 7 nm/min was achieved. The coercivity and saturation magnetization of the FeGaB films decreased (~10 Oe), and increased (1200 emu/cc), respectively, with decreasing

thickness (30 nm). Ferromagnetic resonance (FMR) linewidth was measured at X band (9.6 GHz), and it was found that it narrowed to 140 Oe with decreasing thickness at 30 nm. Both $Fe_{75}Ga_{25}$ and $Fe_{60}Ga_{22}B_{18}$ were shown to be magnetoelastic, having magnetostriction constants of around 30 ppm and 60 ppm, respectively. The magnetic properties of FeGaB are being optimized to the properties measure by Lou et al. to ensure the rigor of the thickness dependence study (Lou, J. et al. 2007). The effect of inducing stronger in-plane anisotropy in the FeGaB films was investigated via an *in situ* magnetic field applied during deposition, and post-deposited magnetic annealing is being explored as a function of thickness.

11:40am TF+PS+SE-MoM11 Optimizing Magnetic Confinement for High Productivity PVD System Linear Scanning Magnetron, *V. Kudriavtsev*, **Robert Norris**, *T. Bluck, I. Latchford*, Intevac, Inc.
High productivity vacuum PVD system cost of ownership is very sensitive to sputtering target utilization. In this paper we discuss magnetic array design methodology that is required to achieve excellent plasma confinement that can lead to most uniform target erosion both magnetic and nonmagnetic targets. Design trade-offs are more challenging when using highly magnetic target materials, such as Nickel. These materials have lower PTF (pass through flux) and also affect magnetic field in all directions. Stronger magnets allow the fields to penetrate magnetic target material and judicious design process allows minimizing negative effects of field shunting.

First we develop static magnetic simulations model; magnetic properties are assigned to magnets, magnetic materials and also properties to nonmagnetic elements. Resulting computations are presented in a form of magnetic field component and Bz component on the surface of the target or in the vicinity of that surface. The magnetic track is determined by searching for locations where perpendicular component of magnetic field Bz=0 and we review variations in Bx and By along this track. Magnetic field characteristics are studied at various distances from magnets, sizing the magnetic array configuration, magnet dimensions, and their polarity for a selected objective. Usually this objective is to provide certain field strength at certain distance away from magnets. One can increase the strength of N or S polarity in the array, creating balanced or unbalanced magnetron configuration, that affect maximum field strength, erosion profile and erosion in the middle of the target where the absolute value of magnetic field reaches a maximum. Magnetic field characteristics are extracted from the erosion track profile and theoretical erosion profile is calculated resulting from the current array design. These profiles allow estimation of the "static" target utilization and if necessary to create optimization cycle where magnetic characteristics of the design (parameters) are computationally changed to reach desired erosion profile. Once the final computer design is selected, engineers build the first prototype of magnetic array and evaluate its magnetic properties using a 2d magnetic scanner that provide B, Bx, By, Bz components of magnetic field in plane on a distance from magpack. The next step of the analysis utilizes experimentally extracted magnetic field (or previously computed theoretical magnetic field) to estimate resulting 2D erosion profile that is due to the magnet non-uniform and non-linear motion. Finally, using the ray tracing method we perform film uniformity analysis for a substrate of given size which is located on a defined distance away from the sputtering target. That analysis is transient and factors in substrate nonlinear motion. Resulting film uniformity is estimated as a superposition of multiple substrate positions as it moves under the target.

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

Atmospheric, Roll-to-Roll and other Manufacturing Advances in ALD
Moderator: Paul Poodt, Holst Centre / TNO

8:20am TF+PS-MoM1 Barrier Properties of Plastic Films Coated with Al_2O_3 by Roll-to-Roll ALD, *Charles Dezelah*, Picosun USA, LLC, *T. Hirvikorpi, R. Laine, W.-M. Li*, Picosun Oy, Finland, *M. Vähä-Nissi, E. Salo*, VTT Technical Research Centre of Finland, *V. Kilpi, S. Lindfors*, Picosun Oy, Finland, *J. Vartiainen, E. Kenttä, J. Nikkola, A. Harlin*, VTT Technical Research Centre of Finland, *J. Kostamo*, Picosun Oy, Finland **INVITED**
Atomic layer deposited (ALD) Al_2O_3 has proven to be effective in enhancing the moisture and gas barrier properties of various plastic films and coatings [1-3]. The key challenge in several applications is to find a flexible, reliable, and cost efficient means to protect sensitive goods from ambient atmosphere. In this presentation we describe the first deposition trials on plastic films with a new PICOSUN™ roll-to-roll (R2R) chamber.

This study demonstrated that a thin Al_2O_3 layer deposited with this continuous process enhances the barrier performance of these materials with results similar to those obtained in a non-R2R batch processing module.

Silicon wafers, cellophane, polylactic acid, and polyimide film substrates were coated with Al_2O_3 at 100 °C using both a batch PICOSUN™ reactor and a test setup for a R2R ALD fit to the same reactor. The precursors were trimethyl aluminum and H_2O, and 500 deposition cycles were used. The Al_2O_3 deposited samples were characterized for their barrier and surface characteristics. The deposition rate of Al_2O_3 on silicon wafer was similar for the batch and the R2R ALD processes. The results from the oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) measurements in 50 % relative humidity and 23 °C were compared between samples across substrate types and deposition modes. It was found that the R2R chamber provided barrier performance was comparable to traditional batch deposition in several cases, and considerably enhanced relative to uncoated substrates.

The initial mechanical properties of the polymeric substrate were found to be crucial for the barrier properties. For example, an Al_2O_3 coating fabricated on cellophane film was less sensitive to mechanical stresses, and the barrier values obtained were similar to those obtained with batch process for the same substrate. FTIR analyses detected Al_2O_3 covered surfaces after the R2R ALD. AFM images for the batch and R2R produced samples that were quite similar. The relative polarities of surface energy for Al_2O_3 deposited with R2R ALD on all three films were lower than for the batch samples. This indicates some differences in the thin film growth. Implications for manufacturability and scalability will also be discussed.

References:

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3 T. Hirvikorpi, M. Vähä-Nissi, A. Harlin, M. Karppinen, Thin Solid Films 518 (2010) 5463.

9:00am TF+PS-MoM3 An Industrial Approach to Roll-to-Roll Atomic Layer Deposition, *M.J. Söderlund, P.T. Soininen*, **Ville Malinin**, Beneq, Finland
Spatial ALD method has attracted considerable attention lately as means to increase the throughput and coating area of ALD processes to meet industrial requirements. This interest is driven largely by the superior film quality of ALD thin-films, but also by the other foreseen benefits associated with spatial ALD process (in addition to high process) such as high material utilization efficiency and low maintenance requirement. These benefits, enable by the spatial ALD concept, are coming together today specifically for flexible moisture barrier application, driven by need to improve the quality and reduce the costs of ultra barrier films for moisture sensitive devices (e.g. OLEDs). However, for ALD to break into mainstream in roll-to-roll manufacturing of e.g. various different moisture barrier films, the spatial ALD technological approach should be applicable to a wide range of substrates materials (e.g. polymer, metal, paper), as well as meters wide webs and web thicknesses ranging from tens up to hundreds of micrometers.

This paper describes a scalable roll-to-roll ALD system approach, and presents recent results using a commercial WCS 600 R2R ALD system. The approach is based on relative movement between a web, tensioned on a processing drum, and the spatial ALD coating head, which is in oscillating motion around the central process drum. Process for Al_2O_3 based on TMA and H_2O precursors at 100 C demonstrates growth rates between 0.7 - 1.0 Å/cycle with refractive index higher equal or higher than 1.61. Low non-uniformity of less than 10 % is measured across 480 mm effective coating area. Ultra barrier performance of $<5*10^{-4}$ g/(m^2 day) at 38 C/90 % conditions is demonstrated with only 20 nm thick Al_2O_3 films, made on roll-to-roll basis on 500 mm wide PEN film substrate. Prospects for scaling the technology further in web width and speed are discussed.

9:20am TF+PS-MoM4 Modular Rotating Cylinder Design for Spatial ALD on Porous Flexible Substrates, *Kashish Sharma*, *R.B. Hall, S.M. George*, University of Colorado at Boulder
Li-ion batteries (LIBs) have a capacity that typically decays versus number of charge-discharge cycles. Surface coatings on LIB electrodes fabricated using atomic layer deposition (ALD) can dramatically improve the capacity stability. The commercialization of these ALD coatings requires the ability to perform ALD on porous battery electrodes on flexible metal webs. In this work, a new spatial ALD (S-ALD) reactor is developed that is based on a modular rotating cylinder design. The outer cylinder remains fixed and contains a series of slits. The slits can accept a wide range of modules that attach from the outside and accommodate precursor dosing, purging or pumping. The inner cylinder rotates (0-200 RPM) and passes underneath

the various slits that are spatially separated. This new S-ALD reactor has been characterized using trimethyl aluminum (TMA) and ozone to grow Al_2O_3 ALD films at 40°C on metallized PET substrates. Spectroscopic ellipsometry measurements obtained Al_2O_3 ALD growth rates of 0.6 -1.1 Å/cycle depending on the O_2 pressure used to prepare the ozone. The Al_2O_3 ALD growth rate was also constant with changing rotation speeds from 60 to 150 RPM. Future experiments will deposit Al_2O_3 ALD films on porous electrodes on flexible metal webs. For these depositions, a "push-pull" design will be utilized where the pressure of the precursor dose will "push" the precursor and carrier gas into the evacuated porous electrode. The reaction products and carrier gas will then be "pulled" from the porous electrode by vacuum pumping. This new spatial ALD reactor has the potential to deposit uniform and conformal thin films on large area and flexible porous substrates at high deposition rates.

9:40am TF+PS-MoM5 Spatial Atmospheric Atomic Layer Deposition of Oxide and Oxysulfide Semiconductors, *Andrea Illiberi**, TNO, Netherlands **INVITED**
Oxide and oxysulfide semiconductors are key components in a wide variety of devices including displays and solar cells. Spatial ALD is emerging as a disruptive deposition technique for the electronic industry because it combines the advantages of temporal ALD, i.e. excellent control of film composition and uniformity on large-area substrates, with high growth rates (up to nm/s) at atmospheric pressure. In this paper we present *spatial atmospheric ALD* of Zn-based multi-component oxides for use as front window in CuInGaSe$_2$ (CIGS)*solar cells* (i.e. i-ZnO, Zn(O,S), Al:ZnO) and as active channel (i.e. InGaZnO) in *TFT-displays*. Films are grown by sequentially exposing the substrate to oxygen and/or sulfur precursors (H_2O, H_2S) and the metal precursor vapors (i.e. DEZ, TMIn, TEGa, or TMAl). By controlling the kinetics of surface reactions between vaporized precursors and reactive sites at the film surface, the composition of the films can be precisely tuned, achieving a constant concentration-depth profiles of the elements along the growth direction, as measured by EDX and XPS analysis.

CIGS solar cells: The front window of CIGS solar cells consists of a stack of CdS/i-ZnO/Al:ZnO layers. Zn(O,S) is emerging as a successful replacement for the CdS buffer layer, being free of toxic elements and having a wider band gap (> 2.4 eV). Both the [S] and [Al] content in ZnO are accurately controlled in the rage from 0 < [S]/[0] < 1 and 0 < [Al]/[Zn] < 1, enabling the deposition of the entire front window stack by spatial-ALD. The degradation of the electrical properties of Al:ZnO during damp heat test is prevented by a spatial-ALD Al_2O_3 moisture barrier. The use of spatial ALD Zn(O,S)/i-ZnO/Al:ZnO/Al_2O_3 stack as front windows in CIGS cells is being tested.

TFT-displays: InGaZnO (IGZO) has drawn great attention in the display industry over the last few years, because of its high electron mobility (> 10 cm^2/Vs), as compared to the commonly used amorphous silicon. The growth of IGZO has been investigated by Spectroscopic Ellipsometry, while the surface and bulk composition of the films has been measured by Low Energy Ion Scattering and XPS. An initial In-rich phase induces a nucleation phase of about 250 ALD-cycles, followed by film closure. IGZO films have an amorphous structure, as indicated by X-ray diffraction analysis. Spatial ALD IGZO films have been tested as active channel in TFT, achieving a maximum device mobility of 10 cm^2/Vs.

Upscaling: Large area (30 cm wide) spatial ALD of Zn(O,S), Al:ZnO and IGZO will be developed by the roll to roll and sheet-to-sheet technology, respectively, as a new nanomanufacturing platform for the solar and display industry.

10:40am TF+PS-MoM8 Large Area Atmospheric Spatial Atomic Layer Deposition of Zn(O,S) Buffer Layers for CIGS Solar Cells on Glass Substrates, *M.D. Bijker, R.S.R. Archer,* Smit Ovens B.V., Netherlands*, P. Poodt,* Holst Centre / TNO, Netherlands*, A. Illiberi,* Solliance / TNO, Netherlands*, **Karel Spee**,* Smit Ovens B.V., Netherlands
Spatial ALD (S-ALD) is emerging as a disruptive deposition technique for the electronics and photovoltaics industry because it combines the advantages of ALD, i.e. excellent control of film composition and uniformity, with high deposition rates (up to nm/s) at atmospheric pressure. This allows for a reduction of the Cost of Ownership (CoO) to a level where, for a range of high-volume and low-cost application areas, commercial exploitation is within reach.

S-ALD as developed by the authors makes use of an injector in close proximity (typically less than 100 µm) of a substrate which moves with high speed underneath the injector. This process has been proven to work very well for very flat substrates. Large area glass panels, however, provide quite a challenge as there are large thickness variations over the sheet due to

glass thickness variations, surface roughness, bow and warp of the glass. We will present the design and operation of an atmospheric pressure S-ALD sheet-to-sheet tool which can handle 30x40 cm^2 glass panels. The glass panels enter the system through a load lock, pass two heating zones to fast heat-up the substrates and enter a deposition zone. The glass plates are placed on a super flat susceptor and straightened using a vacuum clamp. Sensors detect the remaining thickness variations of each individual glass plate and adjust the injector head proximity for each glass plate. In high speed the glass plate is moved back and forth underneath the injector. Maximum deposition temperatures are 350°C. The injector is equipped with 7 slots, equipped with injectors for trimethylaluminium (TMA), diethylzinc (DEZ), H_2O and H_2S. Each precursor can be entered independently, but also TMA-DEZ premixing and H_2O-H_2S premixing is possible.

The tool will be used for the deposition of Zn(O,S) buffer layers in CuInGaSe$_2$ (CIGS) solar cells as an alternative for Chemical Bath Deposition (CBD) of CdS. This replaces an environmentally polluting process with a Cd-free solution. Several authors have reported CIGS solar cells utilizing Zn(O,S) buffer layers with properties very comparable or even somewhat better (+0,5%) to existing CIGS cells using CdS. Cost of ownership (CoO) calculations show that the production cost using S-ALD are also comparable (~\$0,02/Wp).

First Zn(O,S) layers have been prepared using a S-ALD lab-reactor, using DEZ and a mixture of H_2O and H_2S. The composition, optical- and electrical properties of the films can be continuously controlled by different H_2O/H_2S mixing ratios from ZnO. Further experiments are ongoing, including the deposition of Zn(O,S) buffer layer in full CIGS solar cells and its effect of solar cell performance.

11:00am TF+PS-MoM9 Growth Rates and Mechanisms for Al_2O_3 ALD using TMA/ O_3 at Atmospheric Pressure, *MoatazBellah Mousa, C.J. Oldham, G.N. Parsons*, North Carolina State University
Under typical low pressure ALD conditions, ozone (O_3) is reported to speed up ALD processes compared to water-based reactions because shorter purge times are needed to fully desorb ozone O_3. Many high-throughput ALD processes are designed to operate at atmospheric pressure where viscous fluid transport can have significant effects. We developed an ALD process using trimethyl aluminum (TMA) and O_3 in a variable-pressure flow tube reactor and measured growth rates, film composition and film uniformity in the growth zone for pressures between ~2 Torr and 760 Torr and temperature ranging from 70°C to ~250°C. We also adjusted overall gas flow rate to study the role of gas residence time. Film thickness was determined by ellipsometry and growth was monitored using an in-situ Quartz Crystal Microbalance (QCM). We observe self-limiting growth between ~150 °C and 250 °C at both ~2 Torr and 760 Torr, and larger growth rate at lower temperature. At high pressure the growth rate is ~20% larger than at low pressure, which is ascribed to slower transport of desorbing product species through the boundary layer at high pressure. We also find that longer O_3 exposure times are needed compared to low pressure growth. This is consistent with a model for the ozone dissociation kinetics showing that higher pressure enhances the rate of ozone loss. The ozone depletion also predicts an observed gradient in film growth rate under sub-saturation conditions along the length of the reactor. During TMA/O_3, O insertion leads to surface methoxy and formate groups at low temperature, whereas surface hydroxyls form at higher temperature. In our reactor, QCM analysis shows evidence for this temperature-dependent surface reaction mechanism at 2 Torr, and it persists at 760 Torr under saturated conditions. Under saturated growth conditions, TOF-SIMS analysis shows films deposited at 2 Torr and 760 Torr have similar composition, with some extra carbon contamination at higher pressure. Overall, similar ALD growth can be achieved for TMA/O_3 at 760 Torr and ~2 Torr, where care must be taken to take into account the faster rate of O_3 dissociation at higher pressures, especially at higher temperature.

11:20am TF+PS-MoM10 Integration of Feature and Reactor Scales during the Simulation of ALD Scale Up, *Angel Yanguas-Gil, J.A. Libera, J.W. Elam*, Argonne National Laboratory
As the number of ALD processes, materials and applications increase, it is becoming increasingly important to develop the ability to screen and identify the most prominent candidates for scale up. Precursor pressure, reaction probability, ideality of the surface chemistry, but also other considerations like throughput, surface area, and materials utilization, are critical factors that will determine the feasibility of a particular process. In particular, there are three questions that need to be answered in the transition from lab-scale to manufacturing: 1) what is the impact of a particular precursor chemistry, 2) what are the best processing conditions for a given precursor and substrate, 3) what is the optimal reactor design?

In this talk we will focus on the issue of predicting the scalability and fundamental economics (throughput, precursor utilization) of lab-scale ALD processes. Our approach, developed as part of our work on process

development and scale up, combines the experimental characterization of ALD processes in bench-scale reactors, the use of simple analytic models, and the development of new 3D multiscale simulation tools that are optimized to the conditions typically found under ALD conditions, including providing simulated quartz crystal microbalance and mass spectrometry data at any point of the reactor.

Our code, based on open-source libraries, is able to incorporate high-surface area substrates on reactor scale simulations for both cross-flow and roll-to-roll processes, and it takes advantage of the ALD surface chemistry to achieve an extremely efficient two-way coupling between reactor and feature length scales. This method is based on a new approach to simulate feature scale coating that essentially provides the infinite trajectory-limit of the Monte Carlo simulations typically used in the literature.

Besides the description of the model and its implementation, we will exemplify our methodology by presenting results of different metal oxides by ALD, including the validation of the code in a large area reactor. We will also show the results of a parametric study on the impact of non-ideal surface chemistry as well as the presence of high surface area materials / nanostructured features on the substrate. According the results obtained, the presence of high surface area materials makes continuum ALD processes like R2R more efficient. This is a consequence of a more general result of our parametric study, which shows that high reaction probabilities play an important role in ALD scale up.

Advanced Surface Engineering
Room: 302 - Session SE+PS+TF-MoA

Pulsed Plasmas in Surface Engineering
Moderator: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Michael Stueber, Karlsruhe Institute of Technology

2:00pm SE+PS+TF-MoA1 Complex Magnetic Systems for High Power Pulsed Magnetron Sputtering, *Priya Raman*, I.A. Shchelkanov, J. McLain,* University of Illinois at Urbana Champaign, *S. Armstrong,* Kurt J. Lesker Company, *B. Zhang, M. Schilling,* DEXTER Magnetic Technologies, *D.N. Ruzic,* University of Illinois at Urbana Champaign
High Power Pulsed Magnetron Sputtering (HPPMS) is a type of magnetron sputtering technique where high peak power pulses reaching tens of kilowatts are applied to the sputter magnetron target keeping the average power equal to that of direct current magnetron discharges by using low duty cycles. Due to very high power densities, HPPMS discharge leads to high degree of ionization of the sputtered material. These ionized sputtered materials assist in film growth leading to more adhesive, dense, and smoother films. Therefore, HPPMS is considered an ideal candidate for the next generation magnetron sputtering systems, however these techniques suffer from low deposition rate due to "return effect" of the ionized sputter material [1]. One way to solve this problem is to have a magnetic field configuration that is optimized for HPPMS discharges. Magnetic pack design is critical as it helps in achieving full-face target erosion and higher deposition rate in HPPMS. Magnet pack design is generally selected by experimental observation. It has been confirmed from our previous work on HPPMS that a spiral-shaped magnetic field design on 14 inch (36 cm) diameter copper target was able to produce superior plasma uniformity on the substrate in addition to improved target utilization without the need for magnet rotation [2]. Commercial 4 inch (10cm) magnetron sputter guns function with a variety of power supplies like DC, Pulsed-DC, Modulated Pulsed Power Magnetron sputtering (MPP) and HPPMS. These 4 inch magnetron sputter guns typically have a conventional circular magnetic field configuration and suffer from low deposition rate in HPPMS discharges. To optimize the magnet field configuration in HPPMS for the 4 inch magnetron sputter gun, the spiral design from the 14 inch target was scaled down and modified to fit into 4 inch magnetron sputter gun. A new "ε" design magnet pack with enhanced discharge parameters was developed by modifying the spiral magnet pack in COMSOL Multiphysics, which leads to higher deposition rate and better target utilization in HPPMS compared to the conventional magnet pack. The influence of "ε" design magnet pack configuration on deposition rate, plasma parameters, and discharge stability with HPPMS (Huettinger's HiPIMS), MPP(zPulser), DC and pulsed DC power supplies were investigated. The deposition rate for "ε" pack is 2.1±0.2 times the conventional pack for an average discharge power of 500W with zPulser power supply.

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2:20pm SE+PS+TF-MoA2 Triple Langmuir Probe and Ion Fraction Measurements in an Industrial PVD Deposition System, *YuiLun Wu, S.S. Ma, I.A. Shchelkanov, D.N. Ruzic,* University of Illinois at Urbana-Champaign
High Power Pulsed Magnetron Sputtering (HPPMS) discharges are an ideal candidate for the next generation PVD magnetron sputtering systems. Compared with traditional DC sputtering, HPPMS discharges offer high degree of ionization of the sputtered material with very high peak power on the target. An industrial size chamber will be used to investigate the HPPMS discharge operation in full scale production environments utilizing different power supplies. Plasma was observed to be originated from the race track region then expanded downward afterwards. Plasma density was very high ($\sim 10^{19}$-10^{20} m^{-3}) when generated then decreases as it expanded [1] In order to understand the temporal evolution of the plasma between the target and the wafer plane, a time resolved triple Langmuir probe was employed to measure the plasma parameters such as electron temperate and density and scanning in a three dimensional map. Plasma parameters between traditional DC discharge and HPPMS discharge will be compared. Quartz crystal microbalance and 2 inch gridded energy analyzer will be designed to determine fluxes of metal ions, metal atoms and argon ions. The

setup will be able to tilt around 10 degrees about the wafer plane in 1 degree intervals and measure the angular distribution of the ion and neutral fluxes generated by the HPPMS discharge.
Reference:
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2:40pm SE+PS+TF-MoA3 Understanding the Physics of Magnetron Discharges: Ionization Zones and Their Role in Transport of Charged Particles, *Matjaž Panjan, R. Franz, A. Anders*, Lawrence Berkeley National Laboratory **INVITED**
Magnetron sputtering is one of most commonly used techniques for the deposition of thin films. The physics of magnetron discharges has been intensively studied, however, recent investigations revealed that our understanding is rather incomplete. To the naked eye the ionization process appears to be homogeneously distributed along the racetrack – i.e. the region of strongest target erosion caused by sputtering. Imaging of the magnetron discharges with intensified CCD cameras using short exposure times revealed differently, namely, the plasma is concentrated in several zones along the racetrack [1-3]. These so-called ionization zones or spokes are organized in periodic or quasi-periodic patterns that move in the $\mathbf{E} \times \mathbf{B}$ direction with approximately 1/10 of the electron drift speed (where $\mathbf{E}$ and $\mathbf{B}$ are the electric field and magnetic field vectors). Recent experiments further revealed that ionization zones are a fundamental feature of magnetron discharges run in pulsed and continuous mode [4]. In this talk, recent advances in understanding the ionization zone phenomenon will be reviewed. The interpretation of the formation, drift, self-sustainability, and self-organization of ionization zones will be presented with emphasis on potential, electric field and ionization rate distributions. It will be shown that ionization zones play a critical role in the transport of both electrons and ions [4-6].

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3:40pm SE+PS+TF-MoA6 Properties of Ionization Zones in Magnetron Sputtering Observed in the Transition Region between dc and HiPIMS, *André Anders, Y. Yang, J. Liu, Y. Qiu,* Lawrence Berkeley National Laboratory
Research in the last years revealed that the plasma in high power impulse magnetron sputtering (HiPIMS) is rich in structure, featuring self-organized patterns [1], plasma flares [2], and azimuthally asymmetric particle jets [3]. Most prominent are drifting regions of enhanced excitation and ionization, which are called ionization zones but sometimes also labeled spokes in analogy to similar phenomena seen in other $\mathbf{E} \times \mathbf{B}$ devices such as Hall thrusters. Fast imaging of ionization zones in HiPIMS revealed the presence of several distinct ionization zones, for example 3-5 zones in the case of sputtering with a 3-inch magnetron at peak currents of the order 100 A. The zone drift velocity is several 1000 m/s, up to 10^4 m/s, yet much slower than the $\mathbf{E} \times \mathbf{B}$ drift of electrons, which is of the order of 10^5 m/s. In contrast, when sputtering continuously (dc) at very low current (less than 1 A), and at low pressure (less than 1 Pa), we find only one ionization zone moving at low velocity in the reverse, i.e. the $-\mathbf{E} \times \mathbf{B}$ direction. Increasing the current and pressure tends to split the zone into two and occasionally three zones. The appearance of each zone depends on current and other factors such as the pressure of the process gas. In this contribution, we explore the transition regime between dc operation at low current and HiPIMS operation with high peak currents. Using fast streak and frame imaging cameras we detect even more structures and structure changes than anticipated. We conclude that the discharge and its particle transport is governed by zone-related instabilities and turbulence.

[1] A. Anders, et al., J. Appl. Phys. 111 (2012) 053304.

[2] P.A. Ni, et al., Appl. Phys. Lett. 101 (2012) 224102.

[3] M. Panjan, et al., Plasma Sources Sci. Technol. 23 (2014) 025007.

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* Coburn & Winters Student Award Finalist

4:00pm SE+PS+TF-MoA7 Observation of Multiple Charge States and High Ion Energies in High-Power Impulse Magnetron Sputtering (HiPIMS) and Burst HiPIMS using a LaB$_6$ Target, *Robert Franz*, Montanuniversität Leoben, Austria, *C. Clavero*, Lawrence Berkeley National Laboratory, *R. Bolat*, Nazarbayev University, Kazakhstan, *R. Mendelsberg, A. Anders*, Lawrence Berkeley National Laboratory

In high-power impulse magnetron sputtering (HiPIMS), a variation of pulsed magnetron sputtering, short high-voltage pulses are utilized to create discharges with high current densities and a high degree of ionization of the target atoms. In recent years, more complex pulse patterns than the single pulses used in the original or conventional HiPIMS have been developed, e.g. burst-HiPIMS where a series of very short (few μs) pulses are bunched to form bursts.

In the present work, the charge-state-resolved ion energies of HiPIMS discharges were measured, using a LaB$_6$ target, as a function of charging voltage, pulse length, pulse frequency and on/off time ratio within applied HiPIMS bursts [1]. The highest charge states can reach +2 and +3 for boron and lanthanum ions, respectively. At high discharge powers, the B/La ion ratio can exceed the respective atom ratio in the target producing B-rich plasma with up to 98% boron ions. In the case of two-segmented bursts with high on/off time ratios, La^{3+} is the dominating lanthanum ion species and the ion energy distribution of B$^+$ shows a pronounced high-energy tail extending up to 750 eV. The measured plasma compositions, ion charge states and ion energies are discussed within the established framework of HiPIMS discharges and the recent postulation that potential humps are associated with drifting ionization zones. The recorded high B/La ion ratios are a result of complex effects related to particle fluxes in the HiPIMS plasma of compound targets, as explained with the help of an expanded schematic representation of self-sputtering and gas atom recycling. The high energies of the B$^+$ ions are based on a combination of the self-sputtering of boron, backscattering of incident boron ions on lanthanum atoms in the target and acceleration by localized potential humps [2]. Further evidence for potential humps is provided by the observed charge-state dependence of ion energies and features between the thermal peak and high-energy tail of the ion energy distribution functions.

[1] R. Franz, C. Clavero, R. Bolat, R. Mendelsberg, A. Anders, Plasma Sources Sci. Technol. 23 (2014) 035001.

[2] A. Anders, M. Panjan, R. Franz, J. Andersson, P. Ni, Appl. Phys. Lett. 103 (2013) 144103.

4:20pm SE+PS+TF-MoA8 Pulsed Magnetron Sputtering of Novel Multifunctional Films, *Jaroslav Vlcek, J. Rezek, J. Kohout*, University of West Bohemia, Czech Republic

High-power impulse magnetron sputtering with a pulsed reactive gas flow control was used for the reactive deposition of Ta-O-N films with tunable composition and properties [1]. The depositions were performed using a strongly unbalanced magnetron with a planar directly water-cooled Ta target in Ar-O$_2$-N$_2$ gas mixtures at an average target power density of up to 2.4 kWcm^{-2} in a pulse. The repetition frequency of pulses was 500 Hz at a fixed 50 μs voltage pulse length and the total pressure close to 2 Pa. An effective reactive gas flow control made it possible to adjust the film composition from Ta$_2$O$_5$ to a mixture of Ta$_3$N$_5$ and TaN. We prepared Ta-O-N films possessing appropriate band-edge levels for water splitting and a narrow optical band gap of 2.5 eV that permits a visible light absorption up to 500 nm.

Pulsed dc magnetron co-sputtering of a single target (B$_4$C-Si, B$_4$C-Zr or B$_4$C-Hf-Si) in Ar-N$_2$ gas mixtures was used for deposition of different multifunctional films. The repetition frequency of pulses was 10 kHz at a fixed 85 μs voltage pulse length and the total pressure of 0.5 Pa. We present the results obtained for amorphous Si-B-C-N films with an exceptionally high thermal stability (above 1500°C) and very high optical transparency [2], for nanostructured Zr-B-C-N films with a high hardness (37 GPa) and high electrical conductivity [3], and for nanostructured Hf-B-Si-C films with a high hardness (34-37 GPa), high electrical conductivity and significantly improved oxidation resistance in air up to 800°C [4].

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[3] J.Vlcek, P.Steidl, J.Kohout, R.Cerstvy, P.Zeman, S.Proksova, V.Perina, Surf. Coat. Technol. 215 (2013) 186.

[4] J.Kohout, J.Vlcek, J.Houska, P.Mares, R.Cerstvy, P.Zeman, M. Zhang, J.Jiang, E.I. Meletis, S. Zuzjakova, Surf. Coat. Technol. (submitted).

4:40pm SE+PS+TF-MoA9 Surface Engineering of Magnesium and Magnesium Alloys for Improved Corrosion Resistance, *Michael Melia*, *J.R. Scully, J.M. Fitz-Gerald*, University of Virginia

Due to the need for significant weight reduction of structural components, the development of Mg alloys has been ongoing over the last 100 years. One long-standing obstacle regarding the use of Mg alloys for widespread field application is their intrinsically poor corrosion resistance and lack of surface films or oxides that enable "self-healing" or active scratch protection. Micro-galvanic induced "self-corrosion" due to alloy heterogeneity is a key concern. The effects of Excimer laser surface modification and electric arc surface processing on the corrosion resistance of commercially pure Mg (99.8 wt% Mg) and Mg alloy (AZ31B) is investigated. Non-equilibrium processing is being investigated to control surface chemistry, microstructure, and phase formation in order to mitigate the micro-galvanic corrosion with the initial goal of microstructural and composition homogenization. In an attempt to achieve surface homogenization and control Mg evaporation, a range of operating parameters (energy density, dwell time, and processing atmosphere) were explored.

Surface morphology, composition, and local phase imaging were performed with scanning electron microscopy in secondary and backscattered electron imaging modes. X-ray diffraction was used to examine phase and surface regions in grazing incidence mode. Corrosion characterization was performed in a standard three electrode corrosion cell with an aerated 0.6 M NaCl solution. Electrochemical Impedance Spectroscopy (EIS) (10,000 to 0.001Hz) and potentiodynamic polarization scans (0.1 mV/s) were used to determine corrosion resistance, anodic/cathodic behavior, pitting potential and open circuit potential (OCP).

Preliminary results confirm that a measured level of surface homogenization was achieved irrespective of process gasses used (Ar, N$_2$, He). Moreover, in the case of N$_2$ processed 99.8% purity Mg samples, the formation of Mg$_3$N$_2$ was found to have a significant impact on the corrosion resistance. The AZ31B samples processed in Ar exhibited a similar corrosion response to the N$_2$ processed surfaces, suggesting homogenization was a larger factor than nitriding. The cathodic behavior consistently exhibited a significant reduction in the rate of the H$_2$ evolution reaction, more apparent in 99.8% purity Mg. Furthermore, the OCP was reduced by 100-350 mV. Impedance results support these findings with a significant improvement in polarization resistance after treatment. However, processed samples exhibited a minimal change in anodic behavior besides minor fluctuations in pitting potential. Possible mechanisms for the inhibition of the cathodic reaction rate will be presented and discussed.

5:00pm SE+PS+TF-MoA10 Designing a Precious Metal-Free Catalyst for Purification of Automotive Exhausts: NO Reduction and CO Oxidation on CuO(110) Surface, *H. Kasai, J. Moreno, A.A. Padama*, Osaka University, Japan, *C. Matsuda, K. Naito, M. Uenishi, H. Tanaka*, Daihatsu Motor Co., Ltd, Japan, *Y. Nishihata*, Japan Atomic Energy Agency, Japan, *Mamoru Sakaue*, Osaka University, Japan

Nitrogen oxide (NO$_x$) and carbon monoxide (CO) are known by-products of fossil fuel combustion, which greatly contribute to atmospheric pollution. Thus, understanding the conversion process of NO$_x$ and CO into less hazardous gases is of utmost importance. It is well known that precious metals (such as Rh, Pd and Pt) work well to reduce these pollutant gases, but their high cost is a road block to a more prevalent use. Therefore, a more readily available and inexpensive material with comparable, if not better, catalytic performance is needed. Our group has investigated the role of surfaces as a foundation to realizing designer materials, in this case for exhaust purification [1]. In particular, we have previously studied the dissociation of nitric oxide (NO) on Cu$_2$O(111) surface [2-4]. In this work, we look at the possibility of using a CuO catalyst for NO reduction and CO oxidation. Using density functional theory, we first investigated the dissociation process of NO on CuO(110) surface [5]. We found that NO is molecularly adsorbed perpendicular to the surface on the active hollow site between the surface Cu-atoms with an N-end configuration. An energy barrier of 1.1 eV was obtained for NO dissociation. The dissociated state was found to be most stable when the coadsorbed N and O atoms are on adjacent hollow sites. In comparison with the Rh(111) surface, the CuO(110) provides lower activation barrier for NO dissociation and lower adsorption energies for coadsorbed N and O atoms. To further investigate the oxidation of CO after the NO dissociation process, CO was adsorbed on the CuO(110) surface with coadsorbed N and O atoms. In this case, CO was molecularly adsorbed on top of a surface Cu atom while attracting the adsorbed O atom. An energy barrier of 0.9 eV was obtained for the CO oxidation process. This barrier was lower than the case of CO oxidation on Rh(111) surface with adsorbed oxygen atoms. The resulting CO$_2$ molecule was stably adsorbed with its center on top of a surface Cu atom. The results obtained in this study are in agreement with our experimental findings. In conclusion, we believe that CuO is a very promising catalyst for the purification of automotive exhausts.

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

ALD Surface Reactions and Precursors
Moderator: Andrew Cavanagh, University of Colorado, Boulder

2:00pm TF+PS-MoA1 Broadband Sum-frequency Generation: Studying the Initial Growth of ALD Al$_2$O$_3$ by Nonlinear Surface Vibrational Spectroscopy, *Vincent Vandalon, R.H.E.C. Bosch, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The understanding of the atomic layer deposition (ALD) processes has advanced significantly through the insight obtained with in situ linear vibrational surface spectroscopy, in particular by Fourier transform infrared (FTIR) spectroscopy. In this work we apply a nonlinear vibrational spectroscopy technique, the so-called broadband sum-frequency generation (BB-SFG) method, to study the ALD surface chemistry in situ. BB-SFG is a laser based technique, new to the field of ALD, in which a short visible spectrally-narrow laser pulse (~1 ps) is combined with an ultrashort broadband IR pulse (~90 fs) impinging simultaneously on the sample. The generated sum-frequency spectrum, detected in the visible, contains a part of the vibrational fingerprint of the IR region (bandwidth ~100 cm-1) which can detected "background-free" with a high sensitivity even at short integration times (1-100 s). Moreover, the surface selective nature of BB-SFG is uniquely suited for the study of the ALD surface chemistry in which the surface groups can be monitored accurately. In this presentation, first the BB-SFG method developed in our group in the last few years will be explained. Subsequently, the application of the method during ALD Al2O3 (from Al(CH3)3 and H2O) will be addressed. In particular the initial film growth of Al2O3 on H-terminated Si(111) will be followed by probing the Si-H stretch mode (2084 cm-1) with BB-SFG. The decrease in Si-H signal due to Al(CH3)3 and H2O exposure will be correlated with the increase of the second-harmonic signal [1], revealing insight into the kinetics of initial film growth as well as the surface chemistry during steady-state growth. The results will be combined with observations by FTIR studies from our own work and from literature [2]. The surface reactions during the initial growth of Al2O3 by ALD will be addressed.

References:

[1] Höfler, APPL PHYS A-MATER 63, 533-547, 1996

[2] Frank, Chabal, Wilk, APL 82, 4758, 2003

2:20pm TF+PS-MoA2 *In Situ* FTIR Analysis of Reaction Mechanisms between Trimethylaluminum and Carbonyl-Containing Polymers During ALD, *Philip Williams, E.C. Dandley, A. Brozena, C. Needham, C.J. Oldham, G.N. Parsons*, North Carolina State University

New methods to modify polymers are of interest for numerous applications. The chemical mechanisms during trimethylaluminum (TMA) and water exposure during Al$_2$O$_3$ ALD onto polymers depends strongly on the polymer substrate and ALD conditions. Under some conditions, a solid oxide film can form with a relatively abrupt polymer/oxide interface. Typically however, TMA can diffuse sub-surface and react with the polymer in the substrate near-surface or bulk. Recently, we studied mechanisms during TMA vapor infiltration into various polymers using *in situ* infrared spectroscopy. In many polymers, the TMA coordinates with a polymer functional group, either on the backbone or on a side-chain, to form a Lewis acid/base adduct. For example, in poly(vinylpyrrolidinone) (PVP), the carbonyl of the amide moiety (~1780 cm^{-1}) is observed to coordinate strongly with trimethylaluminum and shift to ~1725 cm^{-1}, and the adduct remains stable until water exposure. After water treatment, the adduct mode decreases and the original amide carbonyl signal appears to return. This could indicate release of TMA, but aluminum oxide formation in the polymer shows clearly that the TMA reacts within the polymer. Ab initio calculations (B3LYP) were performed to support mechanistic analyses of TMA within the polymer. A similar TMA/carbonyl adduct formation/release mechanism is observed during TMA/water exposure to poly(methyl methacrylate). On the other hand, when poly(acrylic acid) is exposed to TMA, the carbonyl mode disappears then does not reappear after water exposure. This suggests that in PAA, the TMA reacts with the carbonyl to form a stronger covalent bond that does not change upon water exposure. This difference in reactivity for TMA in the polyacid is likely associated with the presence of acidic hydrogens aiding in the formation of the methane byproduct and more stable covalent aluminum-oxygen bonds. These results help expand understanding of ALD onto polymers and can enable better control of coating and infiltration processes.

2:40pm TF+PS-MoA3 Time-resolved FT-IR Spectroscopy during ALD using La(^{i}PrCp)$_3$ and H$_2$O, *Brent Sperling, J.E. Maslar, W.A. Kimes*, NIST

In situ Fourier transform infrared (FT-IR) spectroscopy has provided many valuable insights into various chemistries used for atomic layer deposition (ALD). Frequently, it is used to observe the molecular fragments remaining on a surface after exposure to each precursor or the phonon modes of films as they are deposited layer-by-layer. The limitations of FT-IR spectroscopy, however, have restricted it to quasi-static conditions that differ dramatically from most growth studies. Spectra cannot easily be obtained with the temporal resolution needed to keep pace with typical ALD cycle times. We have developed a method that signal averages time-resolved spectra over multiple ALD cycles to improve the rate of data acquisition to around 150 ms. Additionally, by using external reflection from a metal surface, absorption by surfaces species is enhanced; alternating polarization states allows the surface to be differentiated from gas-phase species and deposition on the windows. We apply this method to La(^{i}PrCp)$_3$/H$_2$O chemistry (^{i}PrCp = isopropyl-cyclopentadienyl), which has proved to be difficult to understand from growth studies. We present our attempts to recreate literature conditions in our laminar flow reactor with *in situ* FT-IR spectroscopy to observe surface and gas-phase species.

3:00pm TF+PS-MoA4 Surface Reactions and Interface Evolution during the ALD of HfO$_2$ on GaAs Surfaces Studied by *In Situ* ATR-FTIR, *Liwang Ye, T. Gougousi*, University of Maryland, Baltimore County

In situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was utilized to study the surface reactions and interface evolution during the Atomic Layer Deposition (ALD) of HfO$_2$ on GaAs(100) surfaces. The chemistry studied involves the use of tetrakis (dimethylamino) hafnium (TDMAH) and H$_2$O. The experiments were performed on chemical oxide and HF etched GaAs(100) starting surfaces. For the deposition of HfO$_2$ on chemical oxide GaAs surface at 275°C, which corresponds to the optimal ALD process temperature, considerable arsenic oxide consumption was observed at the 1st TDMAH exposure. The arsenic oxide removal continued during subsequent ALD cycles albeit at a reduced rate. For similar experiments performed at 200°C, the arsenic oxide consumption was significantly lower than that at 275°C in agreement with the observations of Suri et al.[1] A clear ligand exchange process is identified through the alternate appearance of the CH and OH terminated surfaces. However, additional byproducts that contain -C=N- bonds are produced during the water pulse and accumulate in the film. Isotope exchange experiments indicate that these species are compatible with the formation of methylmethyleneimine (MMI) that may be produced through a beta hydride elimination pathway.[2,3]

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[2] C. M. Truong, P. J. Chen, J. S. Corneille, W. S. Oh, and D. W. Goodman, J. Phys. Chem. **99**, 8831 (1995).

[3] M. Bouman and F. Zaera, J. Electrochem. Soc. **158**, D524 (2011).

3:40pm TF+PS-MoA6 Precursor Design: Controlling Melting Point, Volatility, Reactivity and Other Important Characteristics of CVD and ALD Precursors, *Seán Barry*, Carleton University, Canada **INVITED**

Chemical vapour deposition methods (CVD) including atomic layer deposition (ALD) are relatively forgiving processes in many respects: the pressure does not have to be very low or strictly controlled, and to some extent the temperature of deposition likewise can have a certain amount of error. These forgiving conditions are largely due to the fact that growth of a film by CVD and ALD is controlled by the surface chemistry of the precursor used, as well as the behaviour of the precursor under thermal stress and in the gas phase. It is often said that precursor "design" is important in these fields: this refers to the control over several key characteristics of the precursor with respect to thermal and chemical behaviour.

My research hinges on the design of precursors with respect to four key characteristics, and each will be discussed using examples. Control of melting point is important to allow better kinetics of evaporation, and this can be tuned by ligand design and asymmetry in the precursor compound. Volatility is a key factor for a precursor, and this can be controlled many ways, including the coordinative saturation of the central (typically metal) atom of the precursor. Thermal stability and chemical reactivity are intimately related, and here choice of ligand, and knowledge of gas phase and surface chemistry is critical for fine control over the difference between a CVD precursor (which undergoes continual deposition) and an ALD precursor (which requires at least a measure of surface stability to allow for self-limiting behaviour).

4:20pm TF+PS-MoA8 Characterizing Vapor Delivery of μ^2-η^2-(^{t}Bu-Acetylene)Dicobalthexacarbonyl (CCTBA) for Deposition Processes, *James Maslar, W.A. Kimes, B.A. Sperling,* National Institute of Standards and Technology (NIST)*, R. Kanjolia*, SAFC Hitech

Cobalt metal is a promising material for the formation of enhanced copper barrier and/or seed layers for copper interconnects in integrated circuits. For these applications, atomic layer deposition of cobalt using a gas-phase precursor can provide advantages in the device fabrication process. μ^2-η^2-(^{t}Bu-acetylene)dicobalthexacarbonyl (CCTBA) is a cobalt precursor that can be delivered as a vapor in a carrier gas. However, CCTBA exhibits a relatively low vapor pressure at ambient conditions and typically must be delivered at elevated temperatures to increase the amount of material delivered to the growth surface. As is typically the case for deposition precursors, prolonged heating can lead to decomposition of CCTBA. Therefore, this work was undertaken to help identify optical delivery conditions for CCTBA by investigating 1) the decomposition of CCTBA in an ampoule at various ampoule temperatures and 2) the delivery of CCTBA from an ampoule as a function of carrier gas flow rate, system pressure, and ampoule temperature. CCTBA decomposition in an ampoule was investigated by using Fourier transform infrared (FT-IR) spectroscopy to identify the species present in the headspace of a CCTBA-containing ampoule as a function of time and ampoule temperature. CCTBA delivery was investigated using two optical techniques installed onto a delivery line from the ampoule. Optical access to the delivery line was achieved using two custom-built in-line optical flow cells that were designed to minimize perturbations to the gas flow. One flow cell was utilized for time-resolved FT-IR spectroscopy. This technique was used to identify the species entrained in the carrier gas. However, time response was limited to ~150 ms which is insufficient to resolve many thermal processes impacting CCTBA entrainment. In order to improve time resolution, a CCTBA-specific region of the mid-IR spectrum was identified and a direct optical absorption technique designed for CCTBA. This techinque employed a broadband infrared source with a mid-IR bandpass filter for isolating CCTBA-specific absorption features. This technique was installed on the second optical flow cell and used to measure the time-dependent CCTBA partial pressure as a function of gas flow rate, system pressure, and ampoule temperature for each CCTBA pulse with a time resolution of ~5 ms. In this manner, the dependence of CCTBA partial pressure on delivery conditions was identified. From these data and the time-dependent partial pressure data obtained with this optical measurement, the dependence of the actual amount of CCTBA delivered on delivery conditions was calculated.

4:40pm TF+PS-MoA9 Effect of Precursor on Coating Uniformity in Mesoporous Metal Oxide Films during Steady and Hold-Step ALD Processes, *Berç Kalanyan, M.D. Losego, G.N. Parsons*, North Carolina State University

Mesoporous film substrates with surface areas greater than 100 m^2/g see use in a variety of applications, most notably in photovoltaic and photoelectrochemical energy conversion. Pastes composed of 10-20 nm diameter metal oxide particles (ITO, FTO, ATO, TiO$_2$) are cast as a thick film and sintered to form conductive substrates. Atomic layer deposition (ALD) is uniquely suited to apply conformal coatings into these types of mesostructured films. To date, ALD coatings have been used in this fashion for dye sensitized solar cells, photoelectrochemical cells, and thermal photovoltaic devices. Beyond common "steady" or "continuous-flow" ALD processes, several research groups have explored the use of "gas hold steps", where the reactor is isolated from the pump for some period of time during the precursor exposure, for example, to enhance precursor infusion into high surface area or porous substrates.

In this study we examine ALD processing under steady and hold-step sequences for applying TiO$_2$ coatings into mesoporous Sn-doped indium oxide (ITO). Typical mesoposous films are up to 10 μm thick, which represents the minimum distance (without tortuosity) that precursor vapors need to travel in order to reach the bottom of the mesostructure. We choose two Ti-containing precursors, titanium tetrachloride (TiCl$_4$) and titanium tetraisopropoxide (TTIP), to understand the influence of bulky functional groups on precursor diffusion. The TTIP diffusivity will be smaller than TiCl$_4$, but it is also sterically hindered by its larger molecular size. We characterize film uniformity in mesoporous substrates by dynamic time-of-flight secondary ion mass spectrometry (TOF-SIMS), in-situ quartz crystal microbalance (QCM), and Krypton gas adsorption experiments.

We show that the TiCl$_4$/H$_2$O process can readily infiltrate into nanoporous ITO films as thick as 15 μm using a typical ALD process sequence, without gas "hold" steps. On the other hand, SIMS analysis shows that TiO$_2$ films deposited using TTIP and H$_2$O under the same exposure condition reach a depth of only 6 μm before exhibiting a large decay in TiO$^-$ secondary ion intensity. While the TiCl$_4$ shows much better coverage, the process suffers from potential contamination, for example, from Cl which is observed in SIMS analysis. Therefore the use of bulky precursors such as TTIP is

critical for ALD infiltration into mesoporous substrates, especially under conditions where coating impurity content is an important concern.

5:00pm TF+PS-MoA10 Study of the Growth of Zinc Tin Oxide As Model System for Ternary Metal Oxide Atomic Layer Deposition, *Adriaan Mackus, R.W. Johnson, W.-H. Kim, S.F. Bent*, Stanford University

In recent years there is increasing interest in atomic layer deposition (ALD) processes that go beyond traditional AB cycles to enable the deposition of alloyed, doped, or ternary materials. The composition of a ternary material can be tuned by mixing the cycles of two different AB processes in a certain ratio ((AB)$_n$(CD)$_m$). However, in practice, the composition and the growth rate tend to deviate from what is expected based on the cycle ratio n/m, whereas the formation of a certain crystallographic phase strongly depends on the mixing of ALD cycles and post-deposition anneal conditions. A detailed understanding of how to deposit ternary metal oxides with control of composition and crystallographic phase is currently lacking.

In this work, the material zinc tin oxide (ZTO) has been selected as a model system for studying ternary metal oxide ALD, motivated by its applications as transparent conducting oxide (TCO)[1] or buffer layer[2] in solar cells. For these applications it is important that ZTO consists of earth-abundant non-toxic elements, and therefore has the potential to replace indium-based TCOs or Cd-based buffer layers. ZTO films were deposited by combining the ALD processes of ZnO from diethylzinc (DEZn) and water, and SnO$_2$ from tetrakis(dimethylamido)tin (TDMASn) and water.[1,3] Synchrotron-radiation X-ray diffraction (SR-XRD) has been performed at the Stanford Synchrotron Radiation Lightsource (SSRL) to investigate the crystallographic phase of the films as a function of composition, cycle ratio, and anneal conditions. It was found that the zinc orthostannate (Zn$_2$SnO$_4$) phase forms upon high-temperature annealing, thereby confirming the deposition of ZTO. In addition, Fourier transform infrared spectroscopy (FTIR) was employed to elucidate the surface chemistry of the ZTO ALD process.

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Thin Film
Room: 305 - Session TF-MoA

Self-Assembled Monolayers, Layer-by-Layer Assemblies, and Hydrophobic/Amphiphobic Thin Films
Moderator: Subhadra Gupta, University of Alabama

2:40pm TF-MoA3 Embedded Dipole in Alkanethiolate Self-Assembled Monolayers: Electronic Structure and Work Function Effects, *Swen Schuster*, Heidelberg University, Germany, *N. Sullivan, O. Cabarcos,* Pennsylvania State University, *I. Hehn,* Graz University of Technology, Austria, *J.-F. Morin,* Université Laval, Canada, *E. Zojer,* Graz University of Technology, Austria, *M. Zharnikov,* Heidelberg University, Germany, *D.L. Allara*, Pennsylvania State University

Self-assembled monolayers (SAMs) bonded to metal-electrodes are frequently used to modify charge-carrier injection and also serve as prototypical systems for studying charge transport processes through molecular assemblies. Usually, control over charge-carrier injection is achieved by use of the terminal dipolar groups (terminal dipole) comprising the SAM-ambience interface. But this architecture affects the growth mode of an organic semiconductor (in the standard device configuration) entangling it with the dipole control. In contrast, for the molecules with an embedded dipolar element, the dipole control and the chemistry at the SAM-ambience interface are decoupled. In this context, we studied a series of SAMs on Au{111} prepared from the mid-chain ester functionalized thiols, HS(CH$_2$)$_m$CO$_2$(CH$_2$)$_{n-1}$CH$_3$ (CmECn) with different combinations of m and n, different dipolar group orientations, and partial deuteration for some of these films. Electronic properties were analyzed by high resolution x-ray photoelectron spectroscopy (HRXPS), near edge x-ray absorption fine structure spectroscopy, work function measurements, and theoretical simulations with supporting characterization by infrared spectroscopy and AFM. The presence of the ester moiety leads to the formation of a strong electric dipole layer with a component of ~1.05 Debye normal to the surface for most of the CmECn SAMs and results in a strong electrostatic effect on the HRXPS spectra in which the C 1s photoelectron kinetic energies are consistently shifted by 0.7-1.0 eV between the alkyl segments below and above the e mbedded ester group. In addition, this group affects the work function of the entire assembly, with the direction of the change following the direction of the embedded dipole. There is however no perfect correlation between the behavior of the HRXPS spectra and the work

function, which has to be understood with the help of theoretical simulations.

3:00pm TF-MoA4 Formation of Highly Ordered Self-Assembled Monolayers of Alkynes on Au (111) Substrates, *T. Zaba, A. Noworolska,* Jagiellonian University, Poland, *C.M. Bowers, B. Breiten, G.M. Whitesides,* Harvard University, ***Piotr Cyganik***, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) based on C-Au bonding and prepared by reaction of terminal *n*-alkynes (HC≡C(CH$_2$)$_n$CH$_3$, n = 5, 7, 9, and 11) with Au(111) at elevated temperatures (60 °C), were characterized using scanning tunneling microscopy (STM), infra-red reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS) and contact angle of water.[1] In contrast to previous spectroscopic studies[2-4] of this type of SAM, these combined microscopic and spectroscopic experiments confirm the formation of highly-ordered SAMs having packing densities and molecular chain orientations very similar to those of alkanethiols on Au(111). Physical properties—hydrophobicity, high surface order, and packing density—also suggest that SAMs of alkynes are similar to SAMs of alkanethiols. The preparation of high-quality SAMs from alkynes requires careful preparation and manipulation of the reactants in a rigorously oxygen-free environment: trace quantities of oxygen lead to oxidized contaminants and disordered surface films. The influence of oxygen on the quality of the SAM is apparently not related to reaction of the Au−C bonds in a SAM with oxygen as suggested earlier,[3] but instead, suggests gold-catalyzed oxidation of the terminal acetylene in solution before incorporation into the SAM. Importantly, once clean alkyne based SAM is formed it becomes resistant to further oxidation in ambient conditions. This stability, together with high structural order, provides the basis for potential applications of this new type of SAM.

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3:40pm TF-MoA6 Dynamic and Angle-Resolved XPS Analysis of Ultra Thin Polyelectrolyte Films Containing Metal Nanoparticles, *Merve Taner-Camci*, S. Suzer*, Bilkent University, Turkey

Ultra thin polyelectrolyte layers have been constructed by sequential adsorption of PAH (polyallylamine hydrochloride) as cationic polyelectrolyte and PSS (polystyrene sulfonate) as anionic polyelectrolyte on silicon substrates using layer-by-layer assembly. Negatively capped AgCu nano-sized particles are incorporated as the outermost layer on the ultra thin film. The sequential order of adsorbed layers and nanoparticles are monitored by relative depth profile of the sample with respect to the intensity changes of corresponding photoelectron peaks, via Angle Resolved XPS analysis at different take off angles. Dynamic XPS analysis is performed under the application of external voltage bias with a known amplitude and frequency to control and probe the charging shifts, as well as polarity dependent intensity changes. The shifts in the binding energy position and the intensity fluctuations of photoelectron peaks reveal information about the relative position of the adsorbed polyelectrolyte layers, as well as proximity of atomic constituents of the nanoparticles.

4:00pm TF-MoA7 Growth Ambient Dependent and Photoinduced Reversible Wetting Property of Indium Oxide Nanowires, *Kavita Yadav, B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi, India

In recent years, production of materials with tunable wetting properties is of immense interest. The extreme water repellent property of superhydrophibic surfaces and complete water spreading on superhydrophilic surface allow them to have considerable technical potential for various applications. The wetting properties of the materials can be explained by their surface chemistry and topographical structures.

In this report, we demonstrate that the growth ambient induced drastic change in wetting properties of indium oxide (IO) nanowires. The IO nanowires were synthesized by using chemical vapor deposition method where Ar gas (200 sccm) was used as carrier gas. The deposition parameters were calibrated in such a way to obtain nanowire morphology. Three different ambient conditions were used for growth of IO nanowires; (a) Ar gas mixed with water vapors, (b) only Ar gas and (c) Ar gas mixed with

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* TFD James Harper Award Finalist

hydrogen gas (50 sccm) and keeping other deposition parameters constant. The Scanning electron microscope (SEM) images confirm that all the three samples have nanowires like morphology. The diameter and length of nanowires ranges from 50 - 120 nm and 6 - 15 μm. The contact angle measurements were done on all the three samples. It is found that the nanowires prepared in presence of Ar gas mixed with water vapors (oxidising ambient) are superhydrophilic in nature with contact angle of 8° ± 5°. The IO nanowires synthesized in presence of only Ar gas are hydrophobic in nature with contact angle of 144° ± 4° whereas the IO nanowires synthesized in presence of Ar gas mixed with H$_2$ gas (reducing ambient) are superhydrophobic in nature with contact angle of 168° ± 2° and water droplet rolling downward with a roll-off angle of 3° over the superhydrophobic surface. The mechanism behind the drastic change in contact angle on IO nanowires prepared in different growth ambient is examined by using photoluminescence (PL) and electron paramagnetic resonance (EPR) measurements. The mechanism of change in wetting properties of IO nanowires has been proposed and can be attributed as on the reduced surface where oxygen vacancy are more, only molecular water is stable and absorb weekly. This is most likely because of the lack of surface oxygen that could accept hydrogen from dissociated water or decrease water dissociation probability and hence the surface is superhydrophobic. Whereas the sample prepared in oxidizing ambient have more surface oxygen and hence both molecular and dissociative adsorption of water is possible results in superhydrophilic surface. The photoinduced reversible wetting properties of IO nanowires (sample b) are also studied.

4:20pm TF-MoA8 Ultralow Friction and Adhesion on Fluorinated Covalently Surface-Bound Polymer Brushes, *S. Pujari, N. Bhairamadgi, Han Zuilhof*, Wageningen University, Netherlands

For an ever increasing range of applications, such as in MEMS and NEMS, highly stable surfaces with minimal adhesion and friction are desired. In the current paper we present a method to achieve such polymer surfaces via a combination of high-density attachment of surface-bound initiators on the Si(111) surface followed by a surface-initiated ATRP reaction with a series of fluorine-rich methacrylate monomer. Subsequently, the adhesion and friction forces were determined using colloidal probe scanning force microscopy. The resulting surfaces display the lowest adhesion force and friction coefficient in air currently reported for any flat surface, which is for example about 1 order of magnitude less than teflon, yet with an appreciably higher chemical and mechanical stability. The presentation will focus on preparation and characterization (both structural and tribological) of these surface-bound polymer brushes, and outline the potential of such minimally interacting surfaces.

4:40pm TF-MoA9 Proton Conductive Crystalline Coatings by Initiated Chemical Vapor Deposition, *Anna Maria Coclite, C. Ranacher*, Graz University of Technology, Austria

Proton conductive copolymers of perfluorodecylacrylate (PFDA) and methacrylic acid (MAA) are synthesized by initiated Chemical Vapor Deposition (iCVD). The MAA provides the –COOH groups useful to conduct protons, while the PFDA is responsible for creating the hydrophobic backbone to stabilize the structure during tests in water. The ultimate goal is to use these copolymers as proton exchange membranes in fuel cells. Preliminary experiments have shown that proton conductivities in the range of 70 mS/cm can be reached with these copolymers.[1] The aim of the new research is to study the effect of preferred crystallographic orientation on the proton conductivity and water / temperature stability of the copolymers. Preferred crystallographic orientation (texture) in thin films frequently has a strong effect on the properties of the materials and it is important for stable surface properties. Poly-PFDA has a high tendency to give organized molecular films. Crystalline poly-PFDA have been fully obtained also by iCVD.[2] The degree of crystallinity and the preferred orientation of the perfluoro side chains, either parallel or perpendicular to the surface, can be controlled by tuning the CVD process parameters (i.e. initiator to monomer flow rate ratio, filament temperature, and substrate temperature). Super-hydrophobicity (advancing water contact angle, WCA, of 160°, low hysteresis of 5°), and oleophobicity (advancing CA with mineral oil of 120°) were achieved.[3] Low water contact angle hysteresis was obtained with high crystallinity, particularly when the orientation of the crystallites resulted in the perfluoro side groups being oriented parallel to the surface. The latter texture resulted in smoother film (RMS roughness < 30 nm) than the texture with the chains oriented perpendicularly to the surface. This can be very advantageous for our application that require smooth but still crystalline films. When the PFDA is copolymerized with MAA, the degree of crystallinity decreases and therefore also the stability in water, but the proton conductivity increases due to the higher number of acid groups embedded in the structure. A good trade-off has been obtained when using 20% of MAA in the gas feed.

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5:00pm **TF-MoA10 Tailoring Polymeric Structures on Surfaces for Lubrication**, *Nicholas Spencer*, ETH Zürich, Switzerland **INVITED**
Nature generally lubricates its tribosystems in water, using sugar chains for lubricity, immobilized on a protein backbone that links them to the surface. These glycoproteins function by being able to immobilize water near the sliding surfaces. Man's attempts to mimic this behavior have involved end-grafted, hydrophilic polymers, and much has been published on the use of poly(ethylene glycol) (PEG) to this end. Man-made machines are more challenging to lubricate than those in nature, since they generally involve hard-hard contact, which nature usually avoids. PEG has been useful as a model system for aqueous lubrication, but has certain inherent problems, including a lack of stability. This presentation will therefore focus on "life after PEG", covering alternative water-compatible, polymer-brush systems, those created by grafting-from methods, and finally the extension of these approaches into a non-aqueous environment: oil.

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 V$2p$ 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 $Ti(O i-Pr)_2(TMHD)_2$ 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 ${}^{o}C$ and tin(II)acetylacetonate ($Sn(acac)_2$) kept at 70 ${}^{o}C$ 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 ${}^{o}C$ 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 ${}^{o}C$. 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.

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Thin Film
Room: 305 - Session TF+SE-TuM

Energetic Thin Films/Optical Characterization
Moderator: David Adams, Sandia National Laboratories, Christophe Vallee, LTM - CEA/LETI, France

8:00am TF+SE-TuM1 Investigations on LiMn$_x$Ni$_y$O Thin Films Deposited by RF Sputtering using Powder Target for Thin Film Battery Applications, *Kosuri Yellareswara Rao*, Indian Institute of Science, India
Cathode materials in the form of thin films for all solid state Li ion batteries (thin film batteries) application have attracted wide attention among the scientific community because of the inherent benefit of studying pure phase of the active materials without any binders and conductive additives such as carbon black, NMP etc [1,2]. In the present work thin films of LiMn$_x$Ni$_y$O have been prepared in a cost effective approach using powder sputtering on nickel coated stainless steel (SS 304) substrates. Powder sputtering is more convenient with the advantages like less material consumption, slightly higher deposition rates and cost effective approach compared to pellet sputtering. The advantage of utilizing powder sputtering for the deposition and electrochemical performance of Li$_x$MnO$_y$ thin films has been reported [3]. Post deposition annealing at 500 °C for one hour was carried out in air ambiance. XRD, XPS and electrochemical characterizations have been carried out to investigate the phase, surface atomic concentration and electrochemical performance. XPS analysis indicates the presence of manganese, nickel, oxygen, and lithium at the surface as shown in Figure. 1. Electrochemical investigations delivered a specific discharge capacity of 54 μAH. μm^{-1}.cm^{-2} in the potential window 2.0-4.4 V vs Li/Li$^+$ in the first discharge cycle. Charge discharge profile up to 40 cycles have shown in the Figure.2. Discharge capacity values are in good agreement with the literature achieved using pellet sputtering.

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8:20am TF+SE-TuM2 The Dynamics of Reactive Foil Ignition after Pulsed Laser Irradiation, *Ryan Murphy*, *R.V. Reeves,* Sandia National Laboratories, *J.P. McDonald,* Dow Corning Corporation, *D.P. Adams*, Sandia National Laboratories
It has been shown that forced mixing of reactive layers (foils) leads to an exothermic release of energy after initiation of mixing by forced impact or pulsed laser irradiation. In order to understand the ignition of foils initiated by laser irradiation, we study the interaction of laser pulses with Al/Pt multilayer reactive foils prepared by sputter deposition. It will be shown that the single-pulse ignition threshold and dynamics are dependent on the length of the laser pulse as the pulse length is varied from 100 fs to 100 ms. The dependence of the ignition threshold on pulse length is a combination of laser-material interactions such as the size of the heat affected zone, changes in reflectivity with pulse length, and the onset of ablation for ultrafast irradiation. The laser spot size is varied for each pulse length to explore the effects of heat confinement on the ignition threshold. The dynamics of foil ignition is further investigated by imaging ignition and the subsequent reaction with a high-speed camera. Varying the bilayer thickness and laser pulse length is shown to change properties such as mixing, ignition in the solid-state, and the onset time of reaction.

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8:40am TF+SE-TuM3 Probing Rapid Formation and Oxidation Reactions with Multilayer Films and Foils, *Timothy Weihs*, Johns Hopkins University **INVITED**
Vapor-deposited multilayer films and foils provide model structures for studying exothermic formation and oxidation reactions. These reactions can proceed at slow to moderate rates (10^{-1} to 10^5 K/s) using controlled heating or at very rapid rates (10^6 to 10^8 K/s) by initiating self-propagating mixing within the films or foils. In this presentation we will probe the sequence of intermetallic phase formation and the kinetics of rapid oxidation as a function of heating rate, chemistry, and concentration gradients using novel characterization tools such as nanocalorimetry, bomb calorimetry, dynamic transmission electron microscopy and synchrotron X-ray diffraction. The experimental results will be compared with analytical predictions and molecular dynamic simulations and controlling factors will be identified.

9:20am TF+SE-TuM5 Detonation in Vapor-deposited Explosive Films at the Micro-scale, *Robert Knepper*, *M.P. Marquez, A.S. Tappan*, Sandia National Laboratories
Recent advances in physical vapor deposition of explosive materials have led to films that are capable of detonating at thicknesses smaller than 100 microns. The critical thickness needed to sustain detonation can be reduced even further (down to a few tens of microns) by confining the explosive with thin layers of a dense, inert material. The ability to sustain detonation at such small length scales opens the potential for such films to be integrated into micro-scale systems using standard micro/nanofabrication methods for use in actuation, gas generation, or similar functions. In this work, we present vapor-deposited hexanitroazobenzene (HNAB) and copper films as a model system to study the effects of confinement on the detonation properties of secondary explosives. Both the HNAB and copper confinement layers are vapor-deposited to promote intimate contact between the explosive and confinement and to provide precise control over both layer thicknesses and microstructure. Confinement thickness is varied to determine the minimum necessary to behave as though the confinement was effectively infinite, and the effects on detonation properties are quantified. In addition to the practical impact of these experiments, identification of the minimum effectively infinite confinement condition can provide insight into the kinetics of the detonation reaction.

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9:40am TF+SE-TuM6 Investigating the Effect of Heating Rate on the Al/Ni Formation Reaction using *In Situ* Nanocalorimetry, *Michael Grapes*, Johns Hopkins University, *M.K. Santala, T. LaGrange, G.H. Campbell,* Lawrence Livermore National Laboratory, *D.A. LaVan,* National Institute of Standards and Technology (NIST), *T.P. Weihs*, Johns Hopkins University
The Al/Ni formation reaction is highly exothermic and of both scientific and technological significance. In particular, Al/Ni thin-film multilayers have been used as a model system to understand how steep concentration gradients and large heating rates affect the identity and sequence of phases that form at the interface between two materials. We have developed an *in situ* nanocalorimetry system that enables us to simultaneously measure the heat generated by the Al/Ni reaction and observe the phases formed. The added ability to controllably vary the heating rate from 1000 K/s to 100,000 K/s makes possible a systematic assessment of the phase transformation sequence with heating rate that we hope will shed light onto the relative effects of kinetic and thermodynamic phase suppression in determining the first phase to form. In this talk I will describe the experimental system, present the baseline results that are obtained at low heating rates, and provide an update detailing recent results and potential conclusions of the systematic study.

11:00am TF+SE-TuM10 The Role of Magnesium in Heat Generation from Al-Mg/Zr Laminate Foils, *Kyle Overdeep*, Johns Hopkins University, *D.J. Allen, N.G. Glumac,* University of Illinois at Urbana-Champaign, *K.J.T. Livi, T.P. Weihs*, Johns Hopkins University
This study examines the ability of reactive multilayer foils to generate heat as a function of magnesium composition. This is accomplished by comparing the heat generated from the reactions of three chemistries: Al:Zr, Al-8Mg:Zr, and Al-38Mg:Zr, which correspond to foils with alternating aluminum and zirconium layers where the Al is either pure, an 8 at.% Mg alloy, or a 38 at.% Mg alloy, respectively. We have found that Al-8Mg:Zr releases 53% more heat than the Al:Zr foils when reacted in air (from 2.5 kJ/g for Al:Zr to 3.8 kJ/g for Al-8Mg:Zr), and 28% more heat than Al-38Mg:Zr (3.0 kJ/g), based on measurements performed in a specially designed bomb calorimeter. This may be a result of the expulsion of particles and vapor which is unique to the Mg-containing foils, because the

increase in surface area enhances combustion. In order to understand this mechanism more thoroughly, the ejected particles, ejected vapor, and remaining foils were all characterized to understand the amount and composition of all species being ejected, and how that influences the combustion of each foil.

11:20am TF+SE-TuM11 Dynamics of the Inverse MAPLE Process for Deposition of Nanoparticles and Nanoporous Thin Films, *Matthew Steiner, P.J. Steiner, J.M. Fitz-Gerald*, University of Virginia

Matrix assisted pulsed laser evaporation (MAPLE) was developed in the late 1990s at the U.S. Naval Research Laboratory as a non-destructive method of thin film deposition for polymers that could potentially be damaged by the ultraviolet radiation utilized for pulsed laser deposition. Conventionally MAPLE starts with a dilute organic compound dissolved in a volatile solvent that serves as a solid matrix when frozen at liquid nitrogen temperatures. By choosing a solvent with a significant UV absorption coefficient, the frozen matrix can be heated by preferential photothermal excitation during irradiation, leading to evaporation and desorption of the less volatile solute molecules onto a substrate in thin film form. Since its conception, use of MAPLE has expanded from the deposition of molecular polymers and proteins to more macroscopic species such as carbon nanotubes, living cells, and recently a number of inorganic nanoparticles.

Inspired by the laser decomposition of metal-acetate based sol-gels to form nanoparticle networks, it is also possible to simultaneously synthesize and deposit well-dispersed nanoparticles or nanoporous films through an inversion of the conventional MAPLE process, utilizing weakly absorbing solvents and photo-sensitive chemical precursor solutes. The chain of events following the laser pulse first entering the target and culminating with observation of nanoparticles on the substrate has been principally interpolated backwards from the nanoparticles produced; suggesting photothermal decomposition of the acetate precursors and formation of nanoparticles within the target prior to and eventually driving ejection. The research presented represents major developments in the understanding of the underlying sequence of multi-scale events controlling the inverse MAPLE deposition process. Modeling addresses optical absorption via Mie theory and the role of matrix conduction in solving nanoparticle heat balance within the target, which in turn is shown to play critical role in the deposition process. New supporting evidence is offered through direct observation of irradiated targets via cryo-stage scanning electron microscopy, as well and conventional scanning and transmission electron microscopy of deposited films and nanoparticles.

11:40am TF+SE-TuM12 Structural, Optical and Electrical Properties of Fe-doped BiOCl, *Yoon Myung, S. Banerjee, F. Wu, P. Banerjee*, Washington University, St. Louis

BiOCl is an attractive p-type semiconductor with a wide band-gap of 3.4 eV. It has a unique layered structure of alternating $[Bi_2O_2]^{2+}$ layers, interleaved by double slabs of Cl^- ions. The ionic layering guides the growth of BiOCl along the c-axis to form a 2D nanosheet morphology, favoring rapid and efficient electron/hole separation. Thus, BiOCl nanosheets can be naturally exploited as a photoactive material in applications such as solar harvesting, photocatalysis and sensing. However, given the large band-gap of BiOCl strategies to sensitize the BiOCl to the visible spectrum must be made. Substitutional doping of transition metal ions is an attractive approach given that many of the transition metal oxides are earth-abundant and have their band-gaps in the visible spectrum.

In this study, we demonstrate the effect of Fe doping on the structural, optical and electrical properties BiOCl nanosheets. Fe-doped BiOCl were synthesized by a facile hydrolysis process. Next, the samples are subjected to various annealing temperatures. We show that anneal temperatures >200 ${}^{\circ}$C can initiate successful Fe incorporation in BiOCl crystal lattice. X-ray diffraction (XRD) shows a higher angle shift after thermal annealing, corresponding to decrease in the lattice constant as a result of Fe^{3+} substitution of the Bi^{3+} ions. Raman spectroscopy shows the E_g stretching mode of the Bi–Cl bond has lower frequency shift, which is consistent with the XRD analysis of Fe^{3+} substitution. Electrical property measurements including IV characteristics show a linear behavior with a resistance of (2.5×10^{11}, 9.8×10^{10} and 9.32×10^{10} Ω) for samples annealed at 200, 300 and 400${}^{\circ}$C respectively.

Finally, we demonstrate a highly sensitive O_2 sensor using Fe-doped BiOCl nanosheets, operating at room temperature. The interaction of vacancies and O_2 is explored in the context of the Fe-doping in BiOCl.

12:00pm TF+SE-TuM13 Cathodoluminescent and Photoluminescent Properties of Sr_2SiO_4:Dy^{3+} Thin Films Prepared by the Sol-gel Spin Coating Technique, *M.A. Tshabalala, H.C. Swart, O.M. Ntwaeaborwa*, University of the Free State, South Africa, *Bakang Mothudi*, University of South Africa, South Africa

Phosphor thin films have been attracting attention because they play important roles in high resolution devices such as cathode ray tubes, thin film electro-luminescent panels and field emission displays[1]. Displays based on thin film phosphors are characterized by high contrast and resolution, good thermal conductivity as well as high degree of uniformity and better adhesion to substrates[2]. Efforts have been made in the past years to develop various types of luminescent thin films via the sol–gel method by using either dip-coating or spin-coating[3]. However spin-coating has emerged as the preferred technique because it is more versatile than the dip-coating technique. Thin film phosphors based on oxide hosts have received considerable attention for use in flat-panel displays due to their outstanding luminescent properties, high chemical stability in high vacuum and lack of emission of corrosive gases under electron bombardment[4]. In this study we investigated the structure, particle morphology, surface topography, chemical composition and luminescent (photoluminescent (PL) and cathodoluminescent (CL)) properties of dysprosium (Dy^{3+}) doped oxide based strontium silicate (Sr_2SiO_4) thin-film phosphor prepared by the sol-gel spin coating technique. Several parameters including number of sol drops, deposition times and post-deposition annealing temperatures were varied. Both the PL and CL intensities were dependent on the deposition conditions and post deposition annealing temperature. Data from scanning electron microscope and atomic force microscope show that the major influence of the deposition conditions on the CL/PL intensity was through changes in the morphology and topography of the films, which affects light scattering and out-coupling. The chemical states and composition, and the depth profiles of the films were examined using the x-ray photoelectron spectroscopy and Auger electron spectroscopy. The influence of the various deposition conditions on the luminescent intensities and the quality of the films will be discussed.

Tuesday Afternoon, November 11, 2014

Thin Film
Room: 305 - Session TF+AS+EM-TuA

Thin Film: Growth and Characterization II
Moderator: Mark Davidson, University of Florida

2:20pm **TF+AS+EM-TuA1 A Statistical Optimization of Perpendicular Anisotropy and Damping for Ta-Inserted Double CoFeB/MgO Interface MTJ's**, *S. Gupta, Samuel Schwarm, B. Clark*, University of Alabama

A statistical Design of Experiments was conducted on double-interface Ta-inserted CoFeB-MgO magnetic tunnel junctions (MTJ's). These MTJ's were deposited using a Shamrock planetary sputtering system. The thicknesses of the inserted Ta and the CoFeB electrodes were varied using Response Surface Methodology. The responses measured using magnetometry and ferromagnetic resonance were a) effective magnetization, b) damping constant and c) perpendicular anisotropy. The effect of annealing on the perpendicular anisotropy was also observed for these devices. As the Ta thickness is increased for fixed CoFeB thickness, the M-H loops indicate that the anisotropy is becoming perpendicular. After annealing, both magnetometry and FMR results show that the MTJ's indicate full perpendicular anisotropy. Interfacial perpendicular anisotropy, which can be extracted from the FMR measurements, scales with the inserted Ta thickness for both as-deposited and annealed samples.

2:40pm **TF+AS+EM-TuA2 1D Matlab Modeling of the Reaction-Diffusion System during the Selenization Process in the Two-Step CIGS Solar Cells Production Process**, *Jurjen Emmelkamp, A. Mannheim*, TNO Technical Sciences, Netherlands

Introduction

In the two-stage fabrication process of CIGS thin-film solar cells first copper, indium and gallium precursor layers are deposited, followed by the selenization process where selenium vapor is provided at high temperature to form CIGS. Despite of the literature, many stages of the reaction-diffusion process are still a mystery. Several experimental techniques exist to analyze the selenization process, however, most of them are only useful to analyze the post-selenization product. In-situ XRD can be used to analyze the crystal structure during the selenization process, but the information is limited because depth profiles and amorphous intermediates are not measured. Modeling of the reaction-diffusion system during the selenization process can result in deeper understanding of the process and in a predictive model for the optimal process conditions that can lead to cheaper and more efficient CIGS solar cells.

The model

A relative simple 1D mathematical Matlab model is developed. Since many intermediate products and the CIGS end-product are crystals, and thus 3D systems, an 1D approach is very simplified. Intensive evaluation with experimental in-situ XRD and cross section EDX, as well as literature values, are used to tune the model specific parameters. Main parameters include diffusion and reaction constants of the different elements and binaries/ternaries, as well as the sticking factor at the surface for the uptake of selenium from the vapor phase. Using these parameters the (intermediate) reactions can be derived and fitted to the data from experiments and literature studies.

First the process temperature profile is calculated as function of time, followed by the calculating the uptake of selenium from the vapor phase. Additionally, the diffusion and reactions are modeled, using Fick's second law, error functions and multiple reflections at the solid interfaces. Based on phase diagrams the reaction kinetics of the most important reaction products are derived and are included into the model.

For reasons of memory limitations, the time and spatial mesh need to be relative coarse. For the spatial mesh this requires adaptive meshing, in order to adapt to small spatial variations and to mimic the overall and the specific layer growth well at small time changes.

Conclusions

The development of the model is still in progress, but the first results show good approximation of the selenium uptake and the formation of the first binaries and ternaries, such as $Cu_{11}In_9$, $Cu_{2-x}Se$, In_4Se_3 and InSe. This can be expanded easily to other intermediates, CIS, CGS and CIGS. However, further parameter fitting is required to mimic the experimental data better.

3:00pm **TF+AS+EM-TuA3 TiSiO Thin Films Deposited by Plasma Enhanced Chemical Vapor Deposition for Optical and Electrical Applications**, *Antoine Goullet, S. Elisabeth, D. Li, M. Carette, A. Granier*, IMN, France **INVITED**

TiO_2 thin films are good candidates for the development of passive optical or electrical integrated devices. They exhibit high optical refractive index ($1.8<n<2.7$ at 633 nm) in combination with high transparency in the visible range and high dielectric constant ($50<k<100$). They are compatible with semiconductor technologies and can be synthesized at low temperature by plasma processes such as plasma enhanced chemical vapor deposition (PECVD). This technique is very attractive to tune film composition and properties such as film refractive index. PECVD is also known for its ability to prepare good quality amorphous or partially crystalline films at low temperature.

Titanium-silicon mixed oxide (TiSiO) materials can overcome some of the limitations given by TiO_2 material, e.g. columnar morphology and relatively low band gap energy.

In this study, TiSiO thin films are prepared without any intentional heating in low pressure inductively coupled discharges from titanium tetraisopropoxide (TTIP- $Ti(OC_3H_7)_4$) and hexamethyldisiloxane (HMDSO - $SiO_2(CH_3)_6$) precursors mixed with oxygen.

Structure and chemical composition of the films are investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Information about film chemical bonds is also obtained from Fourier transform infrared spectroscopy (FTIR). Film morphology is characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Optical properties are mainly investigated by spectroscopic UV-Visible ellipsometry.

Capacitance-voltage (*C-V*) and current-voltage (*I-V*) measurements are performed by using MIS capacitors for evaluation of the mixed oxide film electrical performances.

TiO_2 thin films characteristics are investigated as a function of the plasma ion energy in the 25 – 175 eV range. Increasing the ion energy leads to more homogeneous and organized films with the transformation from anatase to rutile. To account for the columnar morphology of TiO_2 films, a gradient optical layer model was developed. The thin layer dispersion functions were described satisfactorily with the Tauc-Lorentz dispersion law.

TiSiO have been deposited by varying the HMDSO flow rate in the plasma operated in continuous or pulsed mode.

The thin films can be described as a mixture of silicon and titanium oxide at the atomic scale rather than two separate SiO_2 and TiO_2 phases. These mixed oxide layers are basically amorphous and exhibit good morphological properties provided the titanium content is lower than the silicon one.

On the whole these TiSiO layers offer a good compromise in terms of morphological, optical and electrical properties.

4:20pm **TF+AS+EM-TuA7 Kinetically-Limited Lattice Relaxation in Linearly- and Non-Linearly- Compositionally-Graded InxGa1-xAs/GaAs (001) Metamorphic Heterostructures**, *Tedi Kujofsa, J.E. Ayers*, University of Connecticut

Metamorphic buffer layers allow tremendous flexibility to design novel InGaAs/GaAs semiconductor heterostructures for application in various microelectronic and optical devices. However, device fabrication, reliability and performance are limited by dislocation defects associated with the growth of highly mismatched systems such as InGaAs on GaAs substrate. Thus, understanding kinetically-limited lattice relaxation and development of a plastic flow model applicable to multilayered and compositionally graded heterostructure is desirable to provide guidance in designing InGaAs/GaAs devices. Previously, we reported a plastic flow model for ZnS_ySe_{1-y}/GaAs (001) heterostructures which predicts the non-equilibrium strain relaxation as well as misfit dislocation and threading dislocation densities. Here, we have extended our model to $In_xGa_{1-x}As$/GaAs (001) metamorphic buffer layers with arbitrary compositional grading profile. In addition, we have investigated the evolution of the kinetically limited in-plane strain of $In_xGa_{1-x}As$/GaAs (001) heterostructures with an emphasis on grading schemes employing a step, linear-, S- and power-law- lattice mismatch compositional profile. For each structure, we have studied the thickness and grading coefficient dependence on the average and surface kinetically-limited in-plane strain. In addition, we show that the use of compositionally graded buffer layers enables the design of $In_xGa_{1-x}As$/GaAs (001) heterostructures with high surface strain values which enhance the

sweeping of threading defects and therefore yielding device structures with minimal defect.

5:00pm TF+AS+EM-TuA9 Superconducting Properties of NbN and NbTiN Thin Films, *Matthew Burton*, M.R. Beebe, R.A. Lukaszew, D. Beringer, College of William and Mary

Thin films of NbN and NbTiN are promising materials currently researched for improvements in superconducting radio frequency (SRF) technology and applications. At present, bulk niobium SRF accelerating cavities suffer from a fundamental upper limit in maximally sustained accelerating gradients; however, a scheme involving multi-layered superstructures consisting of superconducting-insulating-superconducting (SIS) layers has been proposed to overcome this fundamental material limit of 50 MV/m [1]. The SIS multi-layer paradigm is reliant upon implementing a thin shielding material with a suitably high Hc1 which may prevent early field penetration in a bulk material layer and consequently delay the high field breakdown. It has been predicted that for thin superconducting films — thickness less than the London penetration depth (~200 nm in the case of NbN) — the lower critical field Hc1 will be enhanced with decreasing thickness. Thus, NbN thin films with a high Hc1 value are possible candidates for such SIS structures. We note though that since the intrinsic resistivity of NbN is rather large, efforts are also devoted to NbTiN which has similar superconducting properties but much lower intrinsic resistivity which is preferable for this application. Here we present our study on the structure and superconducting properties of a series of NbN and NbTIN thin films and correlate the effects of film microstructure and surface morphology on relevant superconducting properties such as the critical temperature, Tc, the lower critical field, Hc1, and the residual resistance ratio.

[1] A. Gurevich, Appl. Phys. Lett., 88, 012511 (2006).

5:40pm TF+AS+EM-TuA11 High-Throughput Assessment of the Composition Dependence of Initial Passivating-Al_2O_3-Scale Establishment in $Al_xFe_yNi_{1-x-y}$ Alloy Thin Films, *Matthew Payne*, J. Miller, A.J. Gellman, Carnegie Mellon University, DOE - National Energy Technology Laboratory

AlFeNi-containing alloys capable of forming passivating Al_2O_3 scales are designed for high-temperature structural applications requiring robust oxidation resistance. Mechanical considerations typically dictate that Al content be minimized, but a critical concentration, N_{Al}*, is minimally required to promote the initial establishment of a continuous Al_2O_3 layer. Current understanding of how N_{Al}* evolves across multi-component composition spaces is limited, being based largely on experiments that are constrained by the need for meticulous preparation and characterization of large numbers of single-composition samples. The study of properties across alloy composition space can be greatly accelerated using composition spread alloy films (CSAFs), materials libraries comprised of continuous lateral composition gradients. Properly designed CSAFs can contain every possible composition of a ternary alloy. In this work, ~120 nm-thick $Al_xFe_yNi_{1-x-y}$ CSAFs spanning the entire ternary range ($x = 0 \rightarrow 1$, $y = 0 \rightarrow [1-x]$) over an area of ~1 cm^2 were prepared. A variety of spatially resolved techniques were developed for effective, high-throughput characterization of early oxidation behaviors in the CSAFs. Energy-dispersive X-ray spectroscopy was used to measure changes in CSAF oxygen content as a function of both alloy composition and oxidation time. Raman spectroscopy allowed specific oxide phases formed in different regions of the composition space to be identified. X-ray photoemission depth profiling was performed at select locations of interest to determine composition and chemical state in CSAF cross-sections. These methods were used to study oxidation across $Al_xFe_yNi_{1-x-y}$ composition space in both dry and moist air at 700 K, and have enabled the identification of continuous boundaries separating regions of phenomenologically unique oxidation behaviors, including the N_{Al}*(x,y) boundary for each environment. The results enhance fundamental understanding of early-stage $Al_xFe_yNi_{1-x-y}$ oxidation and can contribute to the accelerated design of next-generation alloys.

6:00pm TF+AS+EM-TuA12 Structural, Electrical, and Optical Characterization of Impurity-Dependent, Ultra-Low-Dislocation-Density Ge Epitaxially Grown on Si and Characterization of MOSFETs Fabricated on Ge-on-Si, *Swapnadip Ghosh*, S.M. Han, University of New Mexico

Building on a simple two-step MBE growth technique, we have investigated possible dislocation locking mechanisms by dopant impurities, coupled with artificially introduced oxygen (O). In the case of n-type Ge grown on Si, our materials characterization indicates that the dislocation density (DD) can reach the ~10^5 cm^{-2} level, compared to p-type and undoped Ge on Si (GoS). We note that our Ge film covers the entire underlying Si substrate at the wafer scale without mesas or limited-area growth. In this presentation, we will focus on the use of n-type impurity (phosphorus) diffusion from the Si

substrate and the introduction of O at the Ge-Si interface. The O is introduced by growing a thin chemical SiO_2 layer on top of the Si substrate before Ge epitaxy begins. Z-contrast cross-sectional TEM images suggest the presence of O precipitates in n-type Ge, whereas these precipitates appear absent in p-type Ge. These O precipitates are known to lock the dislocations. Supporting the argument of precipitate formation, the TEM shows Moiré fringes due to various phase boundaries that exist at the precipitate/Ge-crystal interface. We speculate that the formation of phosphorus (P) segregation resulting from slow diffusion of P through precipitates at the precipitate/Ge-crystal interface facilitates dislocation locking. Impurity segregation in turn suppress O concentration in n-type Ge leading to the reduced DD that appears on the top surface of n-Ge compared to p-Ge film. The O concentrations (10^{17} to 10^{18} cm^{-3}) in the n- and p-type GoS films are measured using secondary ionization mass spectroscopy. We have then compared the structural and electrical characteristics of n-type Ge films with its p-type counterparts. In n-type Ge, the DD decreases from ~10^9 cm^{-2} near the Ge-Si interface to ~10^5 cm^{-2} at the film surface. In contrast, we observe 5×10^7 cm^{-2} DD at the film surface in p-type Ge. The full width at half-maximum for our n-type Ge(004) XRD peak is 100 arcsec, compared to 230 arcsec of p-type Ge. As a stringent test of the dislocation reduction, we have also fabricated and characterized high-carrier-mobility MOSFETs on GoS substrates.We also report p- and n-MOSFETs with μ_{eff} of 401 and 940 cm^2/V-s and a subthreshold slope of 100 and 200 mV/decade, respectively.These effective mobilitiesshow an exceptional 82 and 30% improvement over that of conventional Si channel MOSFETs. We also investigate the optical quality of ultra-low DD GoS film by measuring photoluminescence (PL). Then-type Ge PL main peak shows pronounced tensile-strain (×0.8%) than that of p-type, which is an indicator of direct bandgap shrinking at the Γ band-edge.

Thin Film
Room: 307 - Session TF+EN+PS-TuA

ALD for Energy
Moderator: Erwin Kessels, Eindhoven University of Technology, Netherlands

2:20pm TF+EN+PS-TuA1 Li-Based ALD Solid Electrolytes for Beyond-Li-Ion Batteries, *Alexander Kozen**, A.J. Pearse, M.A. Schroeder, C. Liu, M. Noked, C.F. Lin, G.W. Rubloff, University of Maryland, College Park

Solid Li-based inorganic electrolytes offer profound advantages for energy storage in 3-D solid state batteries: (1) enhanced safety, since they are not flammable like organic liquid electrolytes; and (2) high power and energy density since the solid electrolyte can support interdigitated nanostructured electrodes, avoiding binders, separators, and much larger spacing (tens of mm's) between fully separated electrodes. The quality of thin solid electrolytes – even in planar form – is currently a major obstacle to solid state batteries[1] restricting electrolyte thickness to >100 nm to control electronic leakage, consequently slowing ion transport across the electrolyte and impeding interdigitated 3-D nanostructure designs that offer high power and energy. Furthermore, the ion-conducting, electron-insulating properties of solid electrolytes are promising for their use as passivation or protective layers on metal anodes (Li, Na, Mg) and on cathodes in proposed "beyond-Li-ion" battery configurations such as Li-O_2 and Li-S.

Atomic layer deposition (ALD) is well suited to the challenge of solid electrolytes, providing ultrathin, high quality films with exceptional 3-D conformality on the nanoscale. We have developed ALD processes for Li_2O, Li_3PO_4, and LiPON from LiO^{t}Bu, H_2O, and N_2, exploiting spectroscopic ellipsometry, downstream mass spectrometry, and XPS surface analysis, all *in-situ*. Post-ALD XPS reveals for the first time carbon-free electrolytes and their intrinsic surface chemistry. E.g., ALD Li_2O grown at 250C is reversibly transformed to LiOH upon exposure to H_2O, but transforms back upon annealing. LiOH is completely and irreversibly converted to Li_2CO_3 by CO_2 exposure. These kinds of observations are essential to developing process sequences for fabricating 3-D solid batteries.

We then demonstrate the impact of this solid electrolyte synthesis in several examples. For solid state batteries, we employ the electrolytes in planar and nanostructured battery configurations to determine their Li diffusivity and electrochemical performance. For beyond-Li-ion configurations with organic electrolytes, we show the use of ALD Li_2O at controlled mass loading in high aspect ratio Li-O_2 cathodes to elucidate the Li-O_2 charging

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* TFD James Harper Award Finalist

chemistry, and we demonstrate the use of the ALD solid electrolytes in passivating Li anodes in Li-S batteries.

[1] D. Ruzmetov, V. P. Oleshko, P. M. Haney, H. J. Lezec, K. Karki, K. H. Baloch, A. K. Agrawal, A. V. Davydov, S. Krylyuk, Y. Liu, J. Huang, M. Tanase, J. Cumings, and A. A. Talin, "Electrolyte Stability Determines Scaling Limits for Solid-State 3D Li Ion Batteries," *Nano Lett*, vol. 12, no. 1, pp. 505–511, Jan. 2012.

2:40pm **TF+EN+PS-TuA2   Engineering Lithium-Containing Ionic Conductive Thin Films by Atomic Layer Deposition for Lithium-ion Battery Applications**, *Jea Cho, T. Seegmiller, J. Lau, L. Smith, J. Hur, B. Dunn, J.P. Chang*, University of California at Los Angeles

Lithium (Li)-ion batteries have drawn much attention for their outstanding performance in portable electronics applications. These batteries have the potential to function as miniaturized power sources for microelectromechanical (MEMS) devices through the fabrication of 3-dimensional configurations. To fabricate a fully functional 3D Li-ion microbattery, however, an ultra-thin and highly conformal electrolyte layer is required to coat the 3D electrodes. The solid oxide Li-ion conductor, lithium aluminosilicate ($Li_xAl_ySi_zO$, LASO), synthesized by atomic layer deposition (ALD) is a promising electrolyte material for 3D battery applications owing its adequate ionic conductivity as well as improved electrode stability.

The self-limiting characteristic of ALD allows for precise control of thickness and composition of complex oxides and results in a highly conformal and pinhole-free coating even on highly complex structures such as high aspect ratio 3D electrodes. The metal precursors, lithium t-butoxide (LTB), trimethylaluminum (TMA), tris(tert-butoxy)silanol (TTBS), and tetraethylorthosilicate (TEOS) were used to form $Li_xAl_ySi_zO$ via ALD. *In-situ* FTIR was implemented to study the incubation time and growth mechanisms for each oxide deposited on the other to improve the controllability of the films. *In-situ* FTIR studies revealed that the growth mechanism of silicon oxide is strongly affected by the underlying oxide layer, exhibiting different surface reaction mechanisms during the incubation stage.

Li-ion conductivities and the activation energy for conduction of as-deposited LASO/LAO/LSO films were determined for different lithium contents and film thickness. The LASO ALD coating on 3D carbon array posts were confirmed to be conformal and uniform using transmission electron microscopy (TEM) imaging. A Li-ion half-cell consisting of LASO coated on 3D carbon array electrode showed reversible electrochemical behavior. Lithiation cycling tests of thin LASO/LAO/LSO films were found to be functions of both composition and thickness. The reversibility and kinetics of insertion as well as the effect on the cycling stability from the direct deposition of LASO/LAO/LSO on potential anode materials, SiNWs were also investigated using *in-situ*TEM observations during lithiation.

3:00pm **TF+EN+PS-TuA3   Applications of ALD for Li ion Batteries and Low Temperature Fuel Cells**, *Xueliang (Andy) Sun*, University of Western Ontario   **INVITED**

Atomic layer deposition (ALD) is a novel and unique coating technique with many applications in energy storage and conversion [1]. In this talk, I will present our recent work on exploring the applications of atomic layer deposition (ALD) in both fuel cells and Li ion batteries [2-7].

In the first part, we will report of use of ALD for Pt catalysts used in low temperature fuel cells. In particular, atomic Pt or clusters prepared by ALD show ten times higher methanol oxidation properties compared with ETK commercially-used catalysts [2].

In the second part, we will focus on employing ALD as a surface-modification method to enhance the performance of LIBs. Different materials for surface-modification (such as Al_2O_3, ZrO_2, TiO_2 and $AlPO_4$) [3,4] were first developed by ALD. Then systemic studies were carried out by using those materials to modify the anode ($Li_4Ti_5O_{12}$, SnO_2) [5] and the cathode (commercial $LiCoO_2$, NMC) [6]. The effects of different coating materials on the LIB performance of the anode and cathode were investigated in details. In addition, the potential application of ALD as a powerful technique for preparing solid-state electrolyte will be demonstrated [7]. We will discuss further development of ALD for fuel cells and Li ion batteries.

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[7]. J. Liu, M. Banis, X. Li, A. Lushington, M. Cai, R. Li, T.-K. Sham, X. Sun, **J. Phys. Chem. C** 117(2013)

20260-20267

4:20pm **TF+EN+PS-TuA7   ALD for a High Performance "All-in-One" Nanopore Battery**, *Chanyuan Liu, X. Chen, E. Gillette, A.J. Pearse, A.C. Kozen, M.A. Schroeder, K. Gregorczyk, S.B. Lee, G.W. Rubloff*, University of Maryland, College Park

A self-aligned nanostructured battery fully confined within a single nanopore presents a powerful platform to determine the performance and cyclability limits of nanostructured storage devices. We have created and evaluated such structures, comprised of nanotubular electrodes and electrolyte confined within anodic aluminium oxide (AAO) nanopores as "all-in-one" nanopore batteries. The nanoelectrodes include metal (Ru or Pt) nanotube current collectors with crystalline V_2O_5 storage material on top of them, penetrating part way into the AAO nanopores to form a symmetric full storage cell, with anode and cathode separated by an electrolyte region.

The unprecedented thickness and conformality control of atomic layer deposition (ALD) and the highly self-aligned nanoporous structure of anodic aluminum oxide (AAO) are essential to enable fabrication of precision, self-aligned, regular nanopore batteries, which display exceptional power-energy performance and cyclability when tested as massively parallel devices (~2billion/cm^2), each with ~$1\mu m^3$ volume (~1fL).

To realize these "all-in-one" nanopore batteries, we focused on the precise control of Ru and Pt thin film conformality inside very high aspect ratio (300:1) AAO nanopores by thermal ALD process. 7.5nm thick Ru and Pt are optimized to be 15μm deep at both sides of 50μm long AAO pores in order to provide fast electron transport to overlying V_2O_5 at both anode and cathode sides, while keeping them spatially and electrically isolated. Active storage layers of 23nm thick crystalline V_2O_5 were deposited inside the metal nanotubes to form core-shell nanotubular structures at low temperature (170°C) using O_3 as the oxidant, with <001> direction perpendicular to tube surface and RMS roughness ~4nm. Then the V_2O_5 was prelithiated at one end to serve as anode while pristine V_2O_5 without Li at the other end served as cathode, enabling the battery to be cycled between 0.2V and 1.8V and to achieve full theoretical Faradaic capacity of the V_2O_5. Capacity retention of this full cell at high power (relative to 1C rates) is 95% at 5C and 46% at 150C rates (i.e., 24 sec charge/discharge time). At 5C rate (12 min charge-discharge cycle), 81.3% capacity remains after 1000 cycles. These performance metrics are exceptional, exceeding those of most prototypes reported in the literature. These results demonstrate the promise of ultrasmall, self-aligned/regular, densely packed nanobattery structures as a building block for high performance energy storage systems.

4:40pm **TF+EN+PS-TuA8   Pseudocapacitive Manganese Oxide Grown by Atomic Layer Deposition**, *Matthias Young, C.D. Hare, A.S. Cavanagh, C.B. Musgrave, S.M. George*, University of Colorado, Boulder

Pseudocapacitive supercapacitors are a class of energy storage materials that are midway between lithium ion batteries and capacitors in terms of both power and energy densities. Manganese oxide is a well-known pseudocapacitive material with particular appeal due to its earth abundance and low cost. In previous work, we have demonstrated that MnO ALD produced using bis(ethylcyclopentadienyl)manganese ($Mn(CpEt)_2$) and water can be electrochemically oxidized to produce pseudocapacitive MnO_2 in aqueous electrolytes. However, recent results have shown that the electrochemical oxidation of MnO ALD films results in partial dissolution and delamination. To avoid these problems, we have worked to grow pseudocapacitive MnO_2 by ALD that requires no post-processing. We have grown manganese oxide ALD films using ozone as the coreactant with $Mn(CpEt)_2$. We have also used intermediate ozone doses during $Mn(CpEt)_2$ and water exposures during ALD growth. The use of ozone results in more oxidized manganese oxide films. Another issue is that the alpha-MnO_2 crystal structure of MnO_2 which exhibits high pseudocapacitance contains open channels that are only stable in the presence of cations such as Na^+ or K^+. Consequently, directing the ALD growth toward alpha-MnO_2 pseudocapacitive crystal structures requires the incorporation of an alkali metal into the MnO_2 ALD films.

5:00pm TF+EN+PS-TuA9 Excellent Chemical Passivation of p^+ and n^+ Surfaces of Silicon Solar Cells by Atomic Layer Deposition of Al₂O₃ and SiO₂/Al₂O₃ Stacks, *Bas van de Loo*, H.C.M. Knoops, Eindhoven University of Technology, Netherlands, *G. Dingemans*, ASM, Netherlands, *I.G. Romijn*, ECN Solar Energy, Netherlands, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Thin films of Al_2O_3 provide excellent passivation of heavily p-doped (p^+) silicon surfaces and are therefore often applied in silicon solar cells to reach high efficiencies. The high level of passivation by Al_2O_3 can be attributed to its low interface defect density and high negative fixed charge density Q_f. However, the negative fixed charge density of Al_2O_3 can be detrimental for the passivation of n^+ surfaces [1]. Furthermore, in advanced cell architectures such as interdigitated back-contact (IBC) solar cells, both n^+ and p^+ surfaces are adjacent and are preferably passivated simultaneously. To this end, we systematically study the surface passivation by SiO_2/Al_2O_3 stacks prepared by atomic layer deposition (ALD), which exhibit excellent chemical passivation while the effective fixed charge density can be tuned to zero by carefully tuning the SiO_2 thickness.

Al_2O_3 and SiO_2/Al_2O_3 film stacks with varying ALD SiO_2 thickness (0-12 nm) were prepared by plasma-enhanced ALD at 200°C, with $H_2Si(N(C_2H_5)_2)_2$ and $Al(CH_3)_3$ as metal-organic precursors and O_2 plasma as oxidant. Moreover, a SiO_2 ALD process using ozone was developed as this oxidant is more suitable for batch ALD. The relevant process parameters for surface passivation, such as ozone exposure time, were identified. The passivation of n^+ and p^+ doped surfaces was studied in detail, and results were compared with industrial passivation schemes, including PE-CVD SiN_x and similar SiO_2/Al_2O_3 stacks from a high-volume manufacturing ALD batch reactor.

A superior level of passivation of n^+ surfaces (R_{sheet} = 100 Ω/sq) was obtained by SiO_2/Al_2O_3 stacks as compared to single layer Al_2O_3, significantly reducing the recombination current density (J_0) from (81±10) to (50±3) fA/cm². On p^+ surfaces (R_{sheet}= 60 Ohm/sq), J_0 increases with increasing SiO_2 thickness. The results can be explained by an excellent level of chemical passivation, combined with a strongly reduced negative fixed charge density when increasing the SiO_2 thickness. To fully exploit the virtues of ALD, the concept of using SiO_2/Al_2O_3 stacks for the passivation of both the n^+ and p^+ doped surfaces in a *single* deposition run was demonstrated on (completed) n-type bifacial solar cells, reaching conversion efficiencies >19%. The results are promising for IBC solar cells, where n^+ and p^+ surfaces are adjacent and care must be to achieve a low surface recombination, high shunt resistance and industrial feasibility.

[1] B. Hoex *et al.*, *Phys. status solidi - Rapid Res. Lett.*, vol. 6, no. 1, pp. 4–6, (2012).

5:20pm TF+EN+PS-TuA10 Opportunities for Transparent Conductive Oxides Prepared by ALD for Silicon Heterojunction Solar Cells, *Bart Macco*, S. Smit, Y. Wu, D. Vanhemel, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

In silicon heterojunction (SHJ) solar cells, transparent conductive oxides (TCOs) serve as the top window layer which provides lateral charge transport to the metal contacts whilst maintaining a high optical transparency. Commonly-employed TCO materials include Sn-doped indium oxide (In_2O_3:Sn), Al-doped zinc oxide (ZnO:Al) and more recently also H-doped indium oxide (In_2O_3:H)[1], which are typically deposited by sputtering. In this work, atomic layer deposition (ALD) is explored as an alternative deposition technique for the abovementioned materials. Three salient features of the ALD process will be addressed. Firstly, the applicability of these ALD TCOs is evaluated in terms of their optoelectronic performance. It is shown that through controlled ALD doping cycles the carrier density can be accurately tuned and a low resistivity (<0.5 mΩcm) required for SHJ solar cells can be obtained. Secondly, it is shown that a thermal ALD process does not induce damage to the underlying a-Si:H passivation layers found in a SHJ solar cell. This is a distinct advantage over the conventional sputtering technique, in which plasma-related (UV, ions) damage is known to reduce the passivation level of the a-Si:H layers.[2] This perk of ALD is put to use in bilayers of ALD ZnO:Al/sputtered In_2O_3:Sn, where a thin ALD TCO layer (<15 nm) can very effectively protect the a-Si:H layers from sputter damage. TEM and *in-situ* spectroscopic ellipsometry measurements show that the protective properties are strongly correlated with the TCO surface coverage, as the initial ALD TCO growth on the a-Si:H layer suffers from a nucleation delay and associated island-like growth.[3] Finally, the accurate control over the doping (profile) of the TCO offered by ALD opens up ways to optimize the band alignment of a SHJ solar cell. At the interface of the TCO and the p-type a-Si:H, a high doping of the TCO is unfavorable for the band alignment and results in a reduced fill-factor.[3] On the other hand, the conductivity requirement of the TCO sets a lower bound to the doping level. In this respect, graded doping of the TCO by ALD allows for effective decoupling of the conductivity requirements of the TCO with the optimization of the interface contact formation.

[1] Barraud *et al.*, *Solar Energy Materials and Solar Cells*, **115**, 151–156 (2013)

[2] Demaurex *et al.*, *Applied Physics Letters*, **101**, 171604 (2012)

[3] Macco *et al.*, *Applied Physics Letters* (submitted)

5:40pm TF+EN+PS-TuA11 Study of the Surface Passivation Mechanism of c-Si by Al₂O₃ using *In Situ* infrared spectroscopy, *R.P. Chaukulkar*, Colorado School of Mines, *W. Nemeth, A. Dameron, P. Stradins*, National Renewable Energy Laboratory, *Sumit Agarwal*, Colorado School of Mines

The quality of Si surface passivation plays an integral role in the performance of c-Si-based solar cells. Recently, Al_2O_3 films grown by atomic layer deposition (ALD) have been shown to be an effective passivant for c-Si surfaces with surface recombination velocities (S_{eff}) that are <5 cm/s. The chemical passivation of the c-Si surface via Al_2O_3 is achieved by a reduction in the defect density at the interface, while field-effect passivation is attributed to the fixed negative charge associated with the Al_2O_3 films. However, a post-deposition annealing step is required to achieve this high level of passivation. We have investigated the mechanism of chemical passivation during the annealing step using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Specifically, we have studied the role of residual H- and O-atom migration from the ALD Al_2O_3 films to the c-Si/Al_2O_3 interface. Using $Al(CH_3)_3$ and O_3 as the ALD precursors, Al_2O_3 films were deposited directly onto high-lifetime float-zone c-Si internal reflection crystals (IRCs) followed by thermal annealing at 400 °C in different atmospheres. Specifically, we have used D-terminated c-Si IRCs to differentiate the residual H atoms that may migrate from ALD Al_2O_3 films versus the residual D atoms present at the Al_2O_3/c-Si interface after ALD. Within the sensitivity of the ATR-FTIR spectroscopy setup of ~10^{12} cm^{-2} for Si-H bonds, we do not detect any migration of H from Al_2O_3 to the c-Si interface. Therefore, we conclude that the migration of O, and the subsequent restructuring of the interface during the annealing step, primarily contributes towards the chemical passivation of the Al_2O_3/c-Si interface. The ATR-FTIR spectroscopy measurements are complemented by the minority carrier lifetime, interface defect density, and built-in charge density measurements on SiO_2/Al_2O_3 stacks on c-Si, which enable us to isolate chemical passivation from field-effect passivation. The stacks were annealed in different atmospheres to better understand the role of O versus H atoms in the chemical passivation mechanism.

6:00pm TF+EN+PS-TuA12 Low Temperature Plasma-assisted Atomic Layer Deposition of TiO₂ Blocking Layers for Flexible Hybrid Mesoscopic Solar Cells, *V. Zardetto*, Eindhoven University of Technology, Netherlands, *F. di Giacomo, T.M. Brown, A. di Carlo, A. D'Epifanio, S. Licoccia*, University of Rome "Tor Vergata", Italy, *W.M.M. Kessels, Mariadriana Creatore*, Eindhoven University of Technology, Netherlands

Atomic Layer Deposition (ALD) is widely acknowledged in the field of c-Si and thin film PV technologies, for the fabrication of ultra-thin, uniform and conformal layers.[1] Thermal ALD has been applied also in the case of more challenging interfaces, e.g. dye-sensitized solar cells (DSCs) and the novel hybrid organo-lead-halide perovskite solar cells. Particularly, TiO_2 blocking layers have been developed on glass/TCO substrates with the aim of decreasing the charge recombination processes at the interface between the ITO and the mediator. Recently, we have explored the benefit of plasma-assisted ALD (PA-ALD) in terms of low temperature processing applied to flexible DSCs for the development of highly transparent Pt counterelectrodes on ITO/PEN. [2] In this work, we further explore PA-ALD for the deposition of ultra-thin, highly compact TiO_2 blocking layers on ITO-polymer substrates for DSCs and perovskite solar cells. The layers were prepared in a remote plasma reactor (FlexAL™) at 150 °C using an heteroleptic alkylamido precursor $Ti(Cp^{Me})(NMe_2)_3$ alternated with an O_2 plasma. For DSCs with an iodide-based electrolyte, the introduction of the blocking layer is essential at low light intensity, in order to increase the indoor performance of the cell. It is found that the presence of ultra-thin (6 nm) TiO_2 layers slightly affects the performance of the cell under sun simulator, whereas it definitely improves the generated power (+40%) under low level illumination (300 lux). The blocking behaviour of the PA-ALD deposited TiO_2 towards the tri-iodide reduction has been investigated by electrochemical impedance spectroscopy and Tafel plot analysis. We pinpointed that an increase in the TiO_2 layer thickness above 6 nm leads to a decrease of the recombination processes at the TCO/electrolyte interface, as well as to a dramatic reduction of the electron collection at the TCO, accompanied by a decrease in cell performance. For mesostructured perovskite ($CH_3NH_3PbI_2Cl$- based) solar cells, the application of a TiO_2 blocking layer is essential for the performance of the device, due the higher

current exchange at the interface TCO-hole transport material, i.e. Spiro-OMeTAD, typically used in this architecture. The application of a 11 nm-thick TiO_2 layer resulted in an efficiency of 7.4%. In conclusion, ALD is a valid approach for controlling electrochemical charge-transfer processes in mesoscopic solar cells.

[1] J.A. van Delft, D. Garcia-Alonso , W. M. M. Kessels, Semicond. Sci. Technol., 27, 74002 (2012)

[2] D. Garcia-Alonso, V. Zardetto, A.J.M. Mackus, F. De Rossi, M.A. Verheijen, T.M. Brown, W.M.M. Kessels, M. Creatore, Adv. En. Mater. 4, 1300831 (2014)

2D Materials Focus Topic
Room: 310 - Session 2D+EM+NS+SS+TF-WeM

Novel 2D Materials
Moderator: Evan Reed, Stanford University

8:00am **2D+EM+NS+SS+TF-WeM1 Silicene and Germanene: Novel Graphene-like Artificial Silicon and Germanium Allotropes**, *Guy Le Lay*, Aix-Marseille University, France **INVITED**
Silicene, graphene's cousin, and germanene, a new born in Terra Plana, are predicted to combine the unique electronic properties of graphene associated to quasiparticles behaving as massless Dirac fermions to a character of two-dimensional topological insulators, and, even, possibly, high temperature superconductors. In this talk, I will present fundamental results on these novel synthetic 2D materials, which do not exist in nature, but which might open the way to practical applications, because of their expected direct compatibility with the current nano/micro electronic technologies.

8:40am **2D+EM+NS+SS+TF-WeM3 Silicon Growth at the Two-Dimensional Limit on Ag(111)**, *Andrew Mannix*, *B.T. Kiraly*, Northwestern University, *B.L. Fisher*, Argonne National Laboratory, *M.C. Hersam*, Northwestern University, *N.P. Guisinger*, Argonne National Laboratory
Bulk silicon has played a dominant role in the growth of microelectronics over the past 50 years. Considering the immense interest in two-dimensional (2D) materials (e.g., graphene, MoS_2, phosphorene, etc.), the growth of Si in the 2D limit is of high relevance to the evolution of electronic materials. Utilizing atomic-scale, ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have investigated the 2D limits of Si growth on Ag(111). In agreement with previous reports of sp^2-bonded silicene,[1,2] we observe the evolution of ordered 2D phases, which we attribute to apparent Ag-Si surface alloys. At sufficiently high Si coverage, we observe the precipitation of crystalline, sp^3-bonded Si(111) domains. These domains are capped with a √3 honeycomb phase that is indistinguishable from the √3 honeycomb-chained-trimer (HCT) reconstruction of Ag on Si(111).[3,4,5] Additional evidence suggests that silicon intermixing with the Ag(111) substrate is followed by the precipitation of crystalline, sp^3-bonded silicon nanosheets. These conclusions are supported by *ex-situ* atomic force microscopy (AFM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Even at the 2D limit, scanning tunneling spectroscopy shows that the sp^3-bonded silicon nanosheets exhibit semiconducting electronic characteristics.

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[2] Feng, B., *et al*. Evidence of silicene in honeycomb structures of silicon on Ag(111). *Nano Lett.*, *12*(7), 3507–11 (2012)

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9:00am **2D+EM+NS+SS+TF-WeM4 Growth, Structure, and Properties of 2D SiO_2 Polymorphs**, *Eric Altman*, *J. Götzen, X. Zhu, A. Sonnenfeld, U.D. Schwarz*, Yale University
Recently it has been shown that SiO_2 can form closed 2D bilayers; because the layers have no dangling bonds they are expected to interact solely through van der Waals interactions. Despite the expected weak interactions, hexagonal crystalline bilayers on Pd(100) are stretched 4% to match the lattice constant of the substrate. Both electron diffraction and STM reveal that the size of the crystalline domains is limited along Pd[011] and one of the other bilayer close-packed directions but was long along the third one. The formation of regular domain boundaries on the square Pd substrate is attributed to stress relief in the crystalline layer. Ab initio calculations indicate that much of the remaining strain energy can be relieved by allowing the film to relax along the incommensurate direction. In this way the square substrate actually aids the templating of the overlayer despite the severe geometric mismatch. The calculations also indicate that the bilayer is surprisingly compliant, explaining the lattice matching despite the weak interaction and poor match. Amorphous bilayers could also be prepared on Pd(100). Atomic-scale features in STM images of the amorphous film could be associated with 4-9 membered rings of corner-sharing SiO_4 tetrahedra. In addition to the structural heterogeneity, spectroscopic STM imaging revealed electronic heterogeneity with oxygen sites joining larger rings of corner-sharing SiO_4 tetrahedra fading at low bias; spectra revealed two distinct electronic states responsible for this phenomenon. MBE growth of silica bilayers on graphene layers grown on epitaxial Ru on sapphire will also be discussed.

9:20am **2D+EM+NS+SS+TF-WeM5 Layer-dependent Electronic and Vibrational Properties of $SnSe_2$ and SnS_2 2D Materials**, *Joseph Gonzales*, *R. Schlaf, I.I. Oleynik*, University of South Florida
Layered metal chalcogenides possess a wide range of unique electronic properties, which are currently explored for applications as novel two-dimensional electronic materials. SnS_2 and $SnSe_2$ layered materials consist of covalently bonded S-Sn-S (Se-Sn-Se) sheets bonded together by weak van der Waals interactions. The atomic, electronic and vibrational properties of SnS_2 and $SnSe_2$ thin films are investigated using first-principles density functional theory (DFT). The accurate prediction of electronic and optical properties of SnS_2 and $SnSe_2$ layered 2D materials is achieved by applying state of the art many-body perturbation theory in GW approximation followed by solving the Bethe-Salpeter equation (BSE) to take into account excitonic effects. The evolution of the thickness-dependent band structure, optical and Raman spectra are discussed. The strain effects due to interactions with the substrate are also considered. The first-principles results are compared with available experimental data.

9:40am **2D+EM+NS+SS+TF-WeM6 Synthesis and Properties of Large Scale, Atomically Thin Tungsten Diselenide (WSe_2)**, *Sarah Eichfeld*, *Y.C. Lin, L. Hossain*, The Pennsylvania State University, *A. Piasecki*, The Pennsyvania State University, *A. Azcati*, University of Texas, Dallas, *S. McDonnell, R.M. Wallace*, University of Texas at Dallas, *J.A. Robinson*, The Pennsyvania State University
Transition metal dichalcogenides (TMDs), such as tungsten diselenide (WSe_2) are of interest due to their intriguing properties including the transition from indirect gap to direct gap as the material is thinned to a single atomic layer. Stacking of these layered TMDs also allows for the possibility of bandgap tuning. These properties can suit a large range of flexible and low temperature electronic and optoelectronic devices. Current methods of WSe_2 research involve exfoliation or vaporization of WO_3 and Se powder, which limits industrial scalability. This work is focused on development of a metal-organic chemical vapor deposition process that can controllably produce highly-crystalline, atomically thin WSe_2 on large area substrates.

Growth of controlled monolayer tungsten diselenide (WSe_2) was carried out using chemical vapor deposition in a cold wall vertical reactor. Tungsten hexacarbonyl ($W(CO)_6$) and dimethylselenium (DMSe) served as the tungsten and selenium precursors, respectively. Use of MOCVD precursors provides a means to independently control the W and Se precursors allowing for more precise control of the individual species during growth. Process variables including temperature (500-950°C), pressure (100-700 Torr), and carrier gas, which were correlated with grain size, growth rate, and nucleation density of the WSe_2 to identify optimal parameters for atomically controlled synthesis. Increasing the growth pressure from 100-700 Torr results in a decrease in growth rate and nucleation density, leading to a >50x increase in grain size. Increased growth temperatures yield an increase in grain size, however, it was found that above temperatures of 800 °C the sapphire substrate begins to decompose in the growth environment, resulting in a degradation of WSe_2 above 800°C. Synthesis using 100% hydrogen, and also hydrogen/nitrogen mixtures was carried out. It was found that 100% hydrogen was necessary in order to achieve low carbon incorporation in the WSe_2 films. Characterization of these samples via Raman and photoluminescence spectroscopy verified that high quality, monolayer WSe_2 is readily achievable. Additional characterization (i.e. scanning electron microscopy, atomic force microscopy, etc.) verify the quality, grain size, and nucleation density of the atomic layers. Finally, we will discuss the impact of substrate choice on the quality of the WSe_2 atomic layers, as well as providing direct evidence that synthesis on graphene results in highly textured films, with nearly 100% commensurability to the underlying graphene.

11:00am 2D+EM+NS+SS+TF-WeM10 Growth of Transition Metal Dichalcogenides and their Alloys and on Flat and Patterned Substrates, *E. Preciado, A. Nguyen, D. Barroso, V. Klee, S. Bobek, I. Lu, S. Naghibi, G. Von Son Palacio, T. Empante, K. Brown, K. Yang, A. Nguyen, J. Mann,* **Ludwig Bartels**, University of California - Riverside

The use of organic chalcogen precursors permits the CVD growth of $MoS_{2(1-x)}Se_{2x}$ alloys of any composition between pure MoS_2 and $MoSe_2$ on SiO_2. Spatially resolved vibrational and photoluminescence (PL) spectroscopy is used to characterize our samples: while we observe a continuous transition of the PL maximum with S: Se ratio, the vibrational modes behave in a more complicated, 2-mode fashion. Depending on growth conditions, compositional homogeneous and heterogeneous films can be prepared.

We present details of our growth processes and show to which extend patterns on the substrates can affect the resultant structures. The patterns range from simple hole and pillar arrays to complex waveguide structures. We find that holes to an underlying reducing substrate (silicon) are effective in seeding growth. In contrast, protrusions on the substrate have little effect, so that complex devices can be overgrown.

Ref: Mann et al., 2-Dimensional Transition Metal Dichalcogenides with Tunable Direct Band Gaps: $MoS_{2(1-x)}Se_{2x}$ Monolayers, Advanced Materials 26, 1399 (2014)

11:20am 2D+EM+NS+SS+TF-WeM11 Synthesis, Characterization and Radiation Response of Boro-Carbon-Oxy-Nitride: A Heterogeneous 2D Material, *GaneshRahul Bhimanapati, M. Wetherington, M. Kelly, J.A. Robinson*, The Pennsylvania State University

Since graphene, there have been many other two-dimensional materials systems (e.g., boron nitride (hBN), borocarbon nitride (BCN), transition-metal dichalcogenides) that provide an even wider array of unique chemistries and properties to explore future applications. In fact, these other 2D materials, are sometimes far better suited for many optoelectronic and mechanical applications. Specifically, tailoring graphene/boron nitride heterostructures, which retain the character of single-atom thick sheets that can withstand large physical strains, are easily functionalized, and have entirely different optical and mechanical properties compared to graphene can provide the foundation for entirely new research avenues. In recent years, it has been shown that because of the similar crystal structure, carbon, boron, and nitrogen can coexist as atomic sheets in a layered structure. Thus, combining these materials to form a new heterogeneous material system known as boro-carbon-oxy-nitride (BCON) for potential nano-mechanical and electronic applications and to study its fundamental property relations is necessary. Here, we present the fundamental property relations of BCON and its structural response to various radiation sources such as alpha, beta and gamma particles thereby providing a means for potential radiation sensing applications.

We have developed a facile method of integrating boron nitride and graphene oxide (GO) via chemical exfoliation. Chemical exfoliation of graphene oxide and boron nitride powders is accomplished via oxidation in strong acids, as we find previous methods of sonication in polar solvents does not yield stable solutions of hBN .Upon exfoliation, GO and hBN are mixed, and the resulting BCON material can be suspended in DI water, with suspension stability depending on the pH of the GO. The study of the stability of this material at different pH conditions indicates a stable and a uniform solution is achievable at pH 4-7. Fourier transform infrared spectroscopy (FTIR) indicates the B-N-B bending in the BCON is decreased as an effect of parent GO. Further, radiation response of this material to various radiation sources such as alpha, beta and gamma radiation are studied using In-Situ X-Ray Photoelectron Spectroscopy (XPS). The structural changes of carbon 1s peak in the BCON even for very low doses of radiation energy indicate potential applications in radiation sensing.

11:40am 2D+EM+NS+SS+TF-WeM12 The Structure of 2D Glass, *Christin Büchner*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *L. Lichtenstein,* Lawrence Berkeley National Laboratory, *M. Heyde, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

For the first time, the structure of an amorphous network is imaged in real space.[1] Through a thin film approach, silica is made accessible for investigation with scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Physical vapor deposition with subsequent annealing is employed to create an atomically flat bilayer of SiO_2, supported on a Ru(0001) single crystal. Atomic positions of oxygen and silicon can be visualized, as well as ring structures with their distributions and local neighborhoods. All atomic species on the surface can be directly assigned with chemical sensitivity imaging.[2] This allows for statistical analysis of the building units, comparing amorphous to crystalline regions, as well as experiment to theory. Pair correlation functions of the 2D film structure are

set against diffraction data of bulk silica, revealing very similar bond distributions.

Coexisting crystalline and amorphous areas allow imaging of a topological transition region.[3] The understanding of glassy structures gained from these experiments is the starting point for more in-depth structural investigations[4], but also for investigating thin films with modified composition. Al-doping or Fe-doping can be employed to create 2D-Aluminosilicates or 2D-Clays, respectively.[5] Adsorption properties of the film can be probed using single metal atoms which migrate through the film, exhibiting ring-size-selectivity.[6]

[1] L. Lichtenstein, et al., Angew. Chem., Int. Ed. 51, 404 (2012)

[2] L. Lichtenstein, et al., J. Phys. Chem. C 116, 20426 (2012)

[3] L. Lichtenstein, et al., Phys. Rev. Lett. 109, 106101 (2012)

[4] C. Büchner, et al., Z. Phys. Chem., DOI: 10.1515/zpch-2014-0438 (2014)

[5] J. A. Boscoboinik, et al., Angew. Chem. Int. Ed. 51, 6005 (2012)

[6] W. E. Kaden, et al., Phys. Rev. B 89, 115436 (2014)

Thin Film
Room: 307 - Session TF+MS+PS-WeM

Applied ALD: Nanoelectronics and Emerging Applications
Moderator: Jesse Jur, North Carolina State University

8:00am TF+MS+PS-WeM1 ALD and Beyond CMOS Materials, *Robert Wallace*, University of Texas at Dallas **INVITED**
Two-dimensional layered materials, such as graphene and transition metal dichalcogenides (TMDs), have been recently proposed for a number of novel device concepts due to their interesting materials properties. For example, the possibility of low surface defect densities due to an anticipated dearth of surface defects and dangling bonds raises the prospect of improved performance for low power tunnel field effect logic devices that switch on and off very rapidly due to the anticipated steep subthreshold slope characteristic. However, for ALD processes, such surfaces present significant challenges for nucleation and growth. This talk will review our recent work on in-situ characterization of 2D materials for such device applications. This research is supported in part by the STARNet Center for Low Energy Systems Technology, sponsored by the Semiconductor Research Corporation (SRC) and DARPA, the SWAN Center sponsored by the SRC Nanoelectronics Research Initiative and NIST, and by an IBM Faculty Award.

9:00am TF+MS+PS-WeM4 Combining Gas Phase Aerosol Deposition with Atomic Layer Deposition for Fast Thin Film Deposition: A Case Study of Transparent Conducting ZnO, *Elijah Thimsen*, Washington University, St. Louis, *M. Johnson, A. Wagner, A. Mkhoyan, U.R. Kortshagen, E.S. Aydil*, University of Minnesota
Atomic layer deposition (ALD) has emerged as a powerful and scalable technique for a variety of applications where layer-by-layer control over film properties and conformal deposition in tight geometries are needed. One common criticism of ALD is that it is slow and may become uneconomical when thick films and high deposition rates are needed. In fact, deposition rate is often an issue even with physical vapor deposition methods such as sputtering and also chemical vapor deposition. One way to deliver material onto a substrate at high rates is through deposition of nanoparticles. Gas phase aerosol deposition is particularly attractive because rates as high as 100 nm/s are possible even at low temperatures. However, aerosol deposition often yields porous films unsuitable for optoelectronic applications. In this talk, we describe a new two-step strategy for depositing dense thin films at high rates. Our strategy combines the high rates of aerosol deposition with advantages of ALD. In the first step nanoparticles are synthesized in the gas-phase and deposited onto suitable substrates by aerosol deposition. In the second step, the space between the nanoparticles is infilled by ALD. This is a versatile approach since there are many material options for forming both the nanoparticle network and the ALD coating. In the specific example that will be discussed in this talk, the crystalline nanoparticles are synthesized in a nonthermal plasma containing the precursors that lead to nucleation and growth of the desired material. These nanocrystals are deposited on suitable substrates through supersonic expansion and inertial impaction. Using this approach, we demonstrate fast deposition of nanocrystalline ZnO films, an earth-abundant, nontoxic, low cost material that can be used as a transparent conducting oxide (TCO), from a plasma containing Ar, O_2 and diethylzinc. The space between the particles is filled either by Al_2O_3 or Al-doped ZnO (AZO) to give

continuous TCO films. After annealing in H_2 and coating with Al_2O_3, the ZnO nanocrystal network becomes conductive with Hall effect electron mobilities as high as 3.0 cm^2 V^{-1} s^{-1}. Depending on the combination of the nanocrystals, ALD coating, and post processing, we have obtained transparent films with resistivity values as low as 3.8 x10^{-3} Ohm cm. The lowest resistivity films were obtained with undoped ZnO nanoparticles coated with AZO. The resistivity can be improved by doping the nanocrystals, which has proven to be challenging. We will discuss the effects of nanocrystal size, doping of nanocrystals in the gas phase, and film porosity on electrical conductivity.

9:20am TF+MS+PS-WeM5 Detecting Order in the Molecular Layer Deposition of Polymer Films by X-Ray Diffraction, *David Bergsman, R.W. Johnson, R. Britto, S.F. Bent*, Stanford University

The deposition of highly ordered, thin, organic films is of great importance to a variety of fields. The development of biological sensors, organic solar cells, and optical devices relies on the ability to grow thin layers of organic material with various thicknesses, compositions, functionalities, and levels of crystallinity. One promising method of creating such films is molecular layer deposition (MLD), which uses an alternating sequence of self-saturating reactions by vapor-phase organic precursors at the substrate to grow films in a layer-by-layer fashion. This technique has been demonstrated with a variety of precursor chemistries and has been shown capable of growing films on high aspect ratio features with low surface roughness and high conformality. But despite the growing use of MLD, many questions still remain as to the orientation of the molecular chains within the deposited films and the packing of these chains. Many different factors may contribute to varying degrees of crystallinity during growth, such as chain-chain steric repulsion, Van der Waals forces, chain growth angle, and inter-chain hydrogen bonding. Here, we demonstrate that some MLD chemistries can form nanoscale organic films that exhibit well-ordered packing. Polyurea MLD films with different thicknesses and backbone chemistries were grown in an MLD reactor and then examined with x-ray diffraction (XRD) using synchrotron radiation at the Stanford Synchrotron Radiation Lightsource (SSRL). Spectroscopic ellipsometry was used to observe film thickness, while x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy monitored for film degradation. XRD results for the polyurea MLD films show peaks at q-values of 1.5/Å, corresponding to a d-spacing around 4.2 Å. Changing the precursor from a more rigid to a more flexible backbone leads to variations in d-spacing and diffraction intensity. Growth on substrates with different surface chemistries and roughness, as well as the effect of heating and re-cooling the films, is also explored. These results suggest that thin organic films with varying levels of packing order can be grown using MLD by tuning the precursor chemistry.

9:40am TF+MS+PS-WeM6 Native Oxide Diffusion and Removal During the Atomic Layer Deposition of Ta_2O_5 on InAs(100) Surfaces, *Alex Henegar, T. Gougousi*, University of Maryland, Baltimore County

The use of high-κ dielectrics on III-V semiconductors in place of Si/SiO$_2$ structures in metal oxide semiconductor devices has been perpetually hindered by poor quality native oxides at the substrate/film interface. A promising solution for the removal of these oxides is the atomic layer deposition (ALD) growth technique which has shown the ability to remove native oxides during deposition without additional processing for certain chemistries.[1–4]

In this work, Ta_2O_5 thin films were deposited on InAs(100) by ALD using pentakis dimethyl amino tantalum (PDMAT) and H_2O to study the effects of film deposition on the native oxides. 3 and 7 nm films were grown at 150-300 °C on InAs substrates covered with native oxides and substrates chemically etched in NH_4OH. Analysis of the film deposited on native oxide covered substrates by x-ray photoelectron spectroscopy (XPS) shows arsenic and indium oxides are readily removed during deposition of 3 nm Ta_2O_5 at 250 and 300 °C, temperatures very close to the optimal ALD temperature for the specific chemistry. At lower temperatures both oxides persist with indium oxides generally being harder to remove.

Depth profiling by argon-ion sputtering data of 7 nm films shows that indium oxides have diffused into the Ta_2O_5 film. The sharp decrease in oxide signal after the first sputter cycle indicates that the majority of the indium oxide is located near the surface suggesting the migration of indium oxides to the film surface during deposition. Arsenic oxides, however, are detected in smaller amounts and generally speaking remain at the interface. For depositions on etched InAs no arsenic oxides were detected but a small amount of indium oxides remain even at the optimal deposition temperatures. Films grown on etched substrates always contain less indium and arsenic oxides than their equivalents deposited on native oxide surfaces. Mixing of indium oxide in the films may have a significant negative effect on their insulating properties negating any gain from a sharper interface.

[1] P.D. Ye, G.D. Wilk, B. Yang, J. Kwo, S.N.G. Chu, S. Nakahara, H.-J.L. Gossmann, J.P. Mannaerts, M. Hong, K.K. Ng, and J. Bude, Appl. Phys. Lett. **83**, 180 (2003).

[2] M.M. Frank, G.D. Wilk, D. Starodub, T. Gustafsson, E. Garfunkel, Y.J. Chabal, J. Grazul, and D.A. Muller, Appl. Phys. Lett. **86**, 152904 (2005).

[3] M.L. Huang, Y.C. Chang, C.H. Chang, Y.J. Lee, P. Chang, J. Kwo, T.B. Wu, and M. Hong, Appl. Phys. Lett. **87**, 252104 (2005).

[4] C.-H. Chang, Y.-K. Chiou, Y.-C. Chang, K.-Y. Lee, T.-D. Lin, T.-B. Wu, M. Hong, and J. Kwo, Appl. Phys. Lett. **89**, 242911 (2006).

11:00am TF+MS+PS-WeM10 ALD in High Aspect Ratio Structures and Nanoporous Materials, *C. Detavernier, Jolien Dendooven*, University of Ghent, Belgium **INVITED**

Atomic layer deposition (ALD) is known to be an excellent technique for the deposition of thin films with uniform thickness over micro- and nanoscale 3D structures. The superior conformality of ALD is a direct consequence of the self-saturated surface reaction control and makes the technique increasingly useful in the rapidly growing field of nanotechnology. The successful ALD-based processing of nanostructured materials requires however a careful optimization of the growth parameters. In this work, we present an extensive study on the conformality of ALD in high aspect ratio structures and nanoporous materials.

A first experimental approach was based on the use of macroscopic, trench-like structures in combination with low precursor pressures. In this way, the transport of the precursor molecules in the test structures was governed by molecular flow, as in microscopic trenches under standard ALD conditions. This method allowed us to quantify the conformality of the trimethylaluminum (TMA)/H2O process as a function of the aspect ratio and the TMA exposure time. Our experimental data indicated that the sticking probability is a determining factor in the conformality of ALD [1]. A better understanding of the effect of this parameter on the conformality was obtained via kinetic modeling and Monte Carlo modeling.

As a second substrate, porous titania thin films with pore sizes in the low mesoporous regime (< 10 nm) were considered in order to get insights on the minimum pore diameter that can be achieved by ALD. Novel in situ characterization techniques were developed to monitor the pore filling by ALD. Synchrotron-based x-ray fluorescence and scattering techniques provided cycle-per-cycle information on the material uptake and densification of the porous film, while ellipsometric porosimetry was used to quantify the pore size reduction. This study nicely demonstrated the ability of ALD to tune the diameter of nanopores down to the molecular level [2].

Finally, we performed ALD of TiO2 into a 3D ordered silica powder with two types of mesopores [3]. By varying the Ti-precursor exposure time, we investigated the introduction of TiO2 into the differently sized mesopores. A TEM study revealed the diffusion limited nature of the TiO2 ALD process, leading to anisotropic penetration profiles in this specific pore structure. We observed a systematic deeper penetration of the deposition front along the main channels compared to the narrower mesopores. These results were corroborated by modeling work.

[1] J. Dendooven et al., J. Electrochem. Soc. 156, P63, 2009. [2] J. Dendooven et al., Chem. Mater. 24, 1992, 2012. [3] S. P. Sree et al., Chem. Mater. 24, 2775, 2012.

11:40am TF+MS+PS-WeM12 Pyrolysis of Alucone MLD Films to Form Electrically Conducting and Nanodomained Al_2O_3/C Composite Films, *J.J. Travis, J.W. DuMont, Steven George*, University of Colorado, Boulder

Alucone is an aluminum alkoxide polymer grown using molecular layer deposition (MLD) techniques with trimethylaluminum and organic diols or triols as the reactants. Alucone films can be pyrolyzed under inert atmosphere or vacuum to yield electrically conductive Al_2O_3/C composite films. This pyrolysis provides a pathway to deposit ultrathin, conformal and conducting Al_2O_3/C films on high surface area substrates. Our recent results have shown that the electrical conductance of the Al_2O_3/C films is dependent upon the amount of carbon in the film. The initial alucone films are non-conducting. After pyrolysis to 850°C, alucone films grown using glycerol, with three carbons, or hydroquinone, with six carbons, display high electrical conductivity of ~1-3 S/cm. In contrast, pyrolyzed alucone films grown using ethylene glycol, with only two carbons, remain non-conducting. In situ transmission Fourier transform infrared (FTIR) spectroscopy was used to monitor the pyrolysis of the alucone films. The C-H, C-O and C-C vibrational features were lost from the alucone films between 300-450°C. The vibrational spectra also showed prominent carboxylate features at 400-450°C. Carboxylate features are consistent with $COO^- – Al^{3+}$ complexes at the interfaces between the Al_2O_3 and carbon regions of the composite. High resolution transmission electron microscopy (HRTEM) images are consistent with a highly interfacial nanodomained

Al$_2$O$_3$/C composite. These Al$_2$O$_3$/C composite films may provide electrical conductivity and oxidation resistance during electrochemical processes on metal and carbon electrodes.

12:00pm **TF+MS+PS-WeM13 Atomic Layer Deposition of Metal Oxides on Ultra-High Aspect Ratio, Vertically Aligned Carbon Nanotube Arrays**, *Kelly Stano*, *M. Carroll, R.P. Padbury, J.S. Jur, P. Bradford*, North Carolina State University

Atomic layer deposition (ALD) is commonly used to coat high aspect ratio structures, including vertically aligned carbon nanotube arrays (VACNTs). Previous studies, however, have demonstrated precursor diffusion depths of only 60 μm for long exposure times, leading to a "canopy effect" where preferential coating takes place at the top of arrays. In this research we report the first example of conformal Al$_2$O$_3$ ALD on 1.5 mm tall VACNTs with uniform coating distribution from CNT base to tip. Large-scale CNT arrays with free volume aspect ratios ~15,000 were able to be uniformly coated by manipulating sample orientation and mounting techniques, as confirmed by cross-sectional energy dispersive x-ray spectroscopy. Conformal coating was achieved through modification of CNT surface chemistry via vapor phase techniques including pyrolytic carbon deposition and atmospheric pressure oxygen plasma functionalization. Thermogravimetric analysis revealed that arrays which were functionalized prior to ALD coating were more stable to thermal degradation compared to untreated, ALD coated arrays. Interestingly, CNTs could be easily removed during thermal oxidation to yield arrays of continuous, high surface area, vertically aligned Al$_2$O$_3$ nanotubes. Additionally, functionalized and ALD coated arrays exhibited compressive moduli two times greater than pristine arrays coated for the same number of cycles. Al$_2$O$_3$ coated arrays exhibited hydrophilic wetting behavior as well as foam-like recovery following compressive strain. These processing techniques have been successfully applied to other ALD precursors to yield CNT arrays uniformly coated with ZnO and TiO$_2$ as well.

Wednesday Afternoon, November 12, 2014

2D Materials Focus Topic
Room: 310 - Session 2D+AS+EM+MI+MN+NS+TF-WeA

Properties of 2D Materials
Moderator: Guy Le Lay, Aix-Marseille University

2:20pm 2D+AS+EM+MI+MN+NS+TF-WeA1 Tuning Excitons in Two-Dimensional Semiconductors, *Kirill Bolotin*, Vanderbilt University **INVITED**

Monolayer molybdenum disulfide (MoS2) is a two-dimensional crystal comprising a single layer of molybdenum atoms sandwiched between two layers of sulfur atoms. Monolayer MoS2 differs from its celebrated all-carbon cousin, graphene, by the presence of a direct band gap leading to robust light absorption and by strong electron-electron interactions leading to formation of rightly bound excitons. In this talk, we demonstrate that both electrical and optical properties of MoS2 can be widely tuned via external influences.

In the first part of the talk, we study changes in the bandgap and phonon spectra in strained MoS2. We investigate the transition from direct to indirect band gap in MoS2 under uniaxial strain. The experimental signatures of this transition include strain-induced changes in the PL wavelength and intensity.

Second, we examine the influence of the environment of MoS2 on its properties. We demonstrate substrate-induced scattering is suppressed in suspended MoS2 specimens. We use photocurrent spectroscopy to study excitons in pristine suspended MoS2. We observe band-edge and van Hove singularity excitons and estimate their binding energy. We study dissociation of these excitons and uncover the mechanism of their contribution to photoresponse of MoS2.

3:00pm 2D+AS+EM+MI+MN+NS+TF-WeA3 Electron-Phonon Coupling and Photoluminescence in Single Layer Transition Metal Dichalcogenides, *Neha Nayyar, V. Turkowski, D.T. Le, T.S. Rahman*, University of Central Florida

Single layer MoS_2 and other transition metal dichalcogenides have been the subject of numerous investigations because of their unusual optical, electronic and transport properties. To understand and thereby tune their photoluminescent properties, we have analyzed the role of electron-phonon interactions. Density functional perturbation theory is used to calculate the dispersion of system phonons, while electron-phonon coupling is obtained using the Eliashberg approach. Time-dependent density-functional theory based calculations using the density-matrix approach is employed to study the exciton and trion excitations which are found to appear as peaks in the absorption spectrum in the visible range with binding energy ~0.5 − 1 eV and ~0.02-0.03 eV, correspondingly. The emission peak is found to also lie in the visible spectrum and is sensitive to the value of the electron-phonon coupling, which depends on the nature and extent of doping. The position of the spectral peaks may thus be manipulated by doping. Calculations of the self-energy and spectral functions of doped systems show excitations to have 10-100 fs lifetime, which makes the system interesting for ultrafast applications. Comparison will be made of these optical properties of several single layer dichalcogenides and contact will be made with available experimental data. Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

3:20pm 2D+AS+EM+MI+MN+NS+TF-WeA4 Temperature Dependent Photoluminescent Spectroscopy of MoS2, *Michael Watson*, *J.R. Simpson,* Towson University & NIST, *R. Yan, H. Xing,* University of Notre Dame, *S. Bertolazzi, J. Brivio, A. Kis,* EPFL, Switzerland, *A.R. Hight-Walker*, NIST

We report temperature and power dependent photoluminescence (PL) of molybdenum disulphide (MoS₂). Mechanical exfoliation of MoS₂, from bulk provides single-layer flakes which are then transferred either to sapphire substrates or suspended over holes in Si/Si 3 N 4 . We measure temperature dependence from ≈ 100K to 400K and power dependence from ≈ 6μW to ≈ 7mW using an Argon laser at 514.5nm and a HeNe laser at 632.8 nm. The PL spectrum exhibits a main exitonic peak(A) at ≈ 1.87eV which consist of both neutral excitons and charged trions (A- or A+) [1]. The A exciton peak and the A- exciton peak redshift and broaden with increasing temperature and power. Along with the A peak, we observe a lower energy bound exciton (BE) that is likely related to defects. The BE,a broad peak centred at ≈ 1.7eV, linearly redshifts and narrows with increasing power. The power dependence of both the main and bound peak saturates above 0.5mW. Raman temperature and power dependence will also be discussed [2].

[1] KF. Mak et al. Nat. Mat 12,207(2013)

[2] R.Yan and J.R.Simpson, S. Bertolazzi and J. Brivio, M. Watson, X.Wu and A. Kis, T.Luo, H.G.Xing, A.R. Hight Walker, ACS Nano 8,1 (2013)

4:20pm 2D+AS+EM+MI+MN+NS+TF-WeA7 Effects of Dimensionality on the Raman and Photoluminescence Spectra of and TaSe₂ and TaS₂ Dichalcogenides, *Danilo Romero*, University of Maryland, College Park, *M. Watson, J.R. Simpson,* Towson University, *H. Berger,* Ecole Polytechnique Federale de Lausanne, Switzerland, *A.R. Hight Walker*, NIST

We investigate the effects dimensionality on the electronic properties through the optical spectra of the transition-metal dichalcogenides 2H-TaSe₂ and 1T-TaSe₂, and 1T-TaS₂. In bulk, these materials exhibit electronic states from Mott insulator, commensurate and incommensurate charge-density phases, and superconducting ground state as function of temperature. We explore the evolution of these properties as the materials approach a few layers, achieved via mechanical exfoliation of bulk single-crystals. Raman and photoluminescence spectroscopy of 2H-TaSe₂ and 1T-TaSe₂, and 1T-TaS₂, carried out over a wide-range of temperature, were used as a probe of the change of the electronic properties from the bulk to single-layer phases of the materials. Comparison of the phonon and excitonic transitions as a function of temperature and dimensionality will be presented.

4:40pm 2D+AS+EM+MI+MN+NS+TF-WeA8 Few-Layer and Symmetry-Breaking Effects on the Electrical Properties of Ordered CF₃Cl Phases on Graphene, *Josue Morales-Cifuentes, T.L. Einstein, Y. Wang, J. Reutt-Robey*, University of Maryland, College Park

An effective potential mechanism for breaking the inherent sublattice symmetry of graphene has been studied using DFT calculations on hexagonal boron nitride.[1] Electrical detection of CF3Cl phase transitions on graphene shows the existence of a commensurate ordered phase in which this can be tested.[2] We study the electronic properties of similar phases varying coverage and orientation of CF3Cl with respect of the graphene substrate using VASP ver 5.3.3, with ab initio van der Waals density functionals (vdW-DF1, vdW-DF2).[3][4] Consistent with a physisorbed phase, binding energies are calculated to be on the order of 280meV, and insensitive to coverage and orientation of the CF3Cl molecules. Charge transfer was calculated to be sensitive with coverage, but not orientation, which is qualitatively consistent with experiment. For low coverages, sub-lattice symmetry breaking effects are responsible for gap openings in the order of 4meV, whereas for large coverages it is the formation of ordered overlayers that opens gaps of 15meV. Furthermore, in bilayer graphene at low coverage we estimate an enhanced gap of 20meV.

[1] Gianluca Giovannetti et al. , PRB **76**, 073103(2007)

[2] Yilin Wang et al. , APL **103**, 201606 (2013)

[3] Jiri Klimes et al. , PRB **83**, 195131 (2011)

[4] Kyuho Lee et al. , PRB **82**, 081101(R) (2010)

5:00pm 2D+AS+EM+MI+MN+NS+TF-WeA9 Optical Anisotropies in Layered Nanomaterials, *Jon Schuller*, UC Santa Barbara **INVITED**

In nanomaterials optical anisotropies reveal a fundamental relationship between structural and optical properties. In layered materials, optical anisotropies may result from in-plane and out-of-plane dipoles associated with intra- and inter-layer excitations respectively. In this talk, I describe a novel method wherein we resolve the orientation of luminescent excitons and isolate photoluminescence signatures from distinct intra- and inter-layer excitations, respectively. We compare photoluminescence anisotropies in materials with weak or strong interlayer coupling, MoS₂ and the organic semiconductor PTCDA respectively. We demonstrate that photoluminescence from MoS2 mono-, bi- and trilayers originates solely from in-plane excitons, whereas PTCDA supports distinct in-plane and out-of-plane exciton species with different spectra, dipole strengths and temporal dynamics. The insights provided by this work are important for understanding fundamental excitonic properties in layered nanomaterials and designing optical systems that efficiently excite and collectlight from exciton species with different orientations.

5:40pm 2D+AS+EM+MI+MN+NS+TF-WeA11 Mechanical Properties of 2D-Materials, *J.M. Gonzales,* University of South Florida, *R. Perriot,* Los Alamos National Laboratory, *Ivan Oleynik*, University of South Florida

Graphene and other two-dimensional (2D) materials possess extraordinary mechanical properties, which are currently being explored in various novel applications. Atomic force microscopy (AFM) nanoindentation experiments

on both pristine and polycrystalline samples of 2D materials, while being successful in measuring overall mechanical performance of graphene, require some theoretical input to extract the important mechanical properties. Large-scale atomistic molecular dynamics simulations are used to predict the mechanical properties of 2D materials, such as the elastic moduli, breaking strength, stress/strain distributions, and mechanisms of fracture under conditions of AFM nanoindentation experiments. Perfect, defective, and polycrystalline samples are investigated using large-scale molecular dynamics simulations with a screened environment-dependent bond order (SED-REBO) potential. The mechanisms of crack propagation in both perfect and defective samples will also be presented.

6:00pm EM+AS+EM+MI+MN+NS+TF-WeA12 Mechanical Control of Structural Phase Transitions in Two-Dimensional Mo- and W-Dichalcogenide Monolayers, *Evan Reed*, K.-A.N. Duerloo, Y. Li, Stanford University

Mo- and W- dichalcogenide compounds have a two-dimensional monolayer form that differs from graphene in an important respect: it can potentially have more than one crystal structure. Some of these monolayers exhibit tantalizing hints of a poorly understood structural metal-to-insulator transition with the possibility of long metastable lifetimes. If controllable, such a transition could bring an exciting new application space to monolayer materials beyond graphene. Here we discover that mechanical deformations provide a route to switching the thermodynamic stability between a semiconducting and a metallic crystal structure in these monolayer materials. We employ density functional and hybrid Hartree-Fock/density functional calculations including vibrational energy corrections to discover that single layer MoTe$_2$ is an excellent candidate phase change material. We identify a range from 0.3% to 3% for the tensile strains required to transform MoTe$_2$ under uniaxial conditions at room temperature. We elucidate the appropriate thermodynamic constraints for monolayers, which can differ from bulk materials. The potential for mechanical phase transitions is predicted for all six studied compounds. The potential application space ranges from catalysis to information storage and nanoscale electronics.

Electronic Materials and Processing
Room: 311 - Session EM+EN+TF-WeA

Thin Films and Materials for Energy Storage
Moderator: Christopher Hinkle, University of Texas at Dallas

2:20pm EM+EN+TF-WeA1 Investigation of Composite Dielectric Materials for Energy Storage, *Kimberly Cook-Chennault*, U. Sundar, W. Du, Rutgers, the State University of New Jersey

Electrical energy storage plays a key role in electronics, stationary power systems, hybrid electric vehicles and pulse power applications. Traditionally, bulk ceramic dielectric oxides are used for these applications, though they suffer from inherently low breakdown field strength, which limits the available energy density and increases the dielectric loss. On the other hand, polymers have high break down field strengths, low dielectric losses and can be readily processed into thin films, but suffer from relatively low dielectric permittivity, and thus low energy densities. As a result, contemporary materials have become a limiting factor to the realization of miniaturized devices, due to Moore's Second law, in terms of size, cost and parasitic impedances. Realization of micrometer to sub-micrometer scale commercial and industrial devices such as, high density DRAM (dynamic access memory), non-volatile memory (NRAM) and capacitors, require advanced materials that can both accumulate and deliver vast amounts of energy nearly instantaneously with minimal dielectric losses. This work focuses on examination of piezoelectric-epoxy based composites for dielectric materials, and explores the interrelationship processing plays on realized electrical and dielectric properties. Materials under investigation include lead-zirconate-titanate, and barium titanate – epoxy composites.

2:40pm EM+EN+TF-WeA2 Preparation and Characterization of ZnO Nano Rods, *P. Thamaraiselvan*, Selvam Arts and Science College, India, *M. Saroja*, M. Venkatachalam, P. Gowthaman, Erode Arts and Science College, India, S. Ravikumar, Sengunthar Arts and Science College, India, S. Shankar, Erode Arts and Science College, India

ZnO nano rods were prepared using chemical bath deposition technique. ZnO seed layer thin films were deposited on glass substrates by dip coating method . Subsequently, ZnO seed-coated glass substrates were immersed in aqueous solution of zinc nitrate and hexamethylenetetramine (HMT) at three different growth time of 3, 4 and 5 hours at low temperature of 90°C.

0.02 mol of Zinc nitrate and 0.2 mol of Hexamethylenetetramine (HMT) on 1:10 molar concentration were used for the growth of Zinc oxide nano rods. The structure and surface morphology of the ZnO nano rod were studied using X-ray diffraction Scanning Electron Microscopy (SEM), respectively.

3:00pm EM+EN+TF-WeA3 Rational Design of Energy Storage Materials from Earth Abundant Elements, *Kyeongjae Cho*, UT Dallas **INVITED**

As a part of global scale renewable energy technology solutions, large scale energy storage system (ESS) would be critical in mediating the gaps between cycles of energy demands and intermittent solar and wind energy generations. Furthermore, electric vehicles (EV) require significantly larger energy storage capacity compared to the batteries used electronic device applications. There are significant challenges in extending the current Li ion battery (LIB) technology (based on graphite anode, organic liquid electrolyte, and Co oxide cathode) to EV and ESS applications. Many different approaches are currently investigated to overcome the capacity, safety and cost issues of LIB in EV and ESS applications, and new battery technology researches include Si anode, Na and Mg batteries, metal-air batteries, over-lithiated-oxide (OLO) [1] and silicate cathodes [2] for LIB. OLO and silicate cathode materials provide two times larger charge storage capacity (~300 mAh/g) compare to current commercial LiCoO$_2$ (LCO) or Li(Ni,Co,Mn)O$_2$ (NCM) cathodes. Both Li$_2$MnO$_3$ and Li$_2$FeSiO$_4$ are based on earth abundant transition metals of Mn and Fe so that a successful development of these cathode materials would improve cathode capacity and cost problems. In order to achieve the short term goal of OLO and silicate cathode development and the long term goal of EV and ESS material development, we have applied the rational material design and development framework developed for pollution control technology in which Pt catalysts are replaced by PdAu alloy and Mn-mullite catalysts. [3-5] In this talk, we will discuss the current status of OLO and silicate cathode material research based on the integrated material design-synthesis-characterization framework.

This work was supported by Samsung GRO project.

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4:20pm EM+EN+TF-WeA7 Transferring Environmentally Sensitive Battery Materials between GloveBox and UHV Surface Analysis Chamber: Composition Study of Model Battery Interfaces and their Controlled Oxidation, *Hugo Celio*, University of Texas at Austin

Environmentally sensitive battery materials prepared in an inert environment (e.g., Argon filled glovebox containing trace levels of water and oxygen at ~1 part-per-million) are often difficult to transfer to an ultra-high vacuum (UHV) chamber for surface analysis. While minimizing additional oxidant(s) exposure, three challenging factors arise from transferring environmentally sensitive materials: 1) Engineering a pump-down load-lock to transition from atmospheric pressure to UHV regime, 2) developing a method to generate a set of figures of merit (FOMs) that allows a user to evaluate transfer reliability, and 3) evaluating of the amount of material that subsequently undergoes, due to reaction with trace ppm levels of oxidants in the Argon gas, oxidation during transfer . To target these issues a novel transfer load-lock/capsule was built and directly coupled to a UHV surface analysis chamber, equipped with X-ray photoelectron spectrometer (XPS). This new load-lock/capsule has lead to a new capability to study the composition of model battery materials (e.g., silicon anode and metal oxide cathode) at the solid electrolyte interfacial (SEI) layer, including their controlled oxidation post-transfer.

4:40pm EM+EN+TF-WeA8 Development of Thin Film Si-C Based High Temperature Microsupercapacitor Devices, *J.P. Alper*, C.-H. Chang, C. Carraro, *Roya Maboudian*, University of California at Berkeley

On-chip integrated energy storage and delivery at high power is an important aspect in realizing the full potential of microsystems technology such as remote mobile sensor platforms. One promising high power device which has garnered much attention is the supercapacitor. Energy is stored in

SC's at the electrode-electrolyte interface, making the high specific surface area of thin films of 1-d materials particularly attractive for application to these devices. However many operations such as in the chemical process industries which could benefit from remote sensor deployment reach temperatures beyond current electrode and electrolyte material constraints. Here we report on the use of bottom-up chemical vapor deposition based silicon carbide (SiC) nanowires and top-down chemically etched SiNWs passivated with an ultrathin carbon sheath as thin film micro-SC electrodes. The electrochemical performance of the two nanowire types in high temperature compatible electrolytes such as ionic liquids and yttria stabilized zirconia (YSZ) are presented. The materials are stable during cycling and achieve specific capacitance values comparable to or better than previously reported carbon electrodes. Operation at temperatures above those attainable with standard electrode-electrolyte systems is also demonstrated. Current challenges for the methods presented and strategies for overcoming them are discussed.

5:00pm EM+EN+TF-WeA9 Rate Capability of Silicon Carbon Nanotube Anodes for Lithium Ion Batteries, *Lawrence Barrett, R. Fan, R.C. Davis, K. Hinton, R.R. Vanfleet*, Brigham Young University
Research has shown stable high capacity lithium ion battery anodes can be made from silicon deposited on carbon nanotubes (CNTs). However, rate capability remains a challenge. We have explored two potential limiting factors: diffusion from the top of the forest down and diffusion into the silicon coating. To probe top down diffusion, we compared a uniform CNT forest to a forest with an array 10 um holes spaced 10 um apart to allow channels for faster top down diffusion and found rate capability was unaffected, indicating top down diffusion is not a limiting factor. We also probed diffusion through the silicon coating by changing the thickness and morphology of the coating.

5:20pm EM+EN+TF-WeA10 Characterization and Optimization of Interface Engineering on Li Metal Anode Using Atomic Layer Deposition and *In Situ* Electrochemical AFM, *Chuan-Fu Lin, A.C. Kozen, A.J. Pearse, M. Noked, M.A. Schroeder, S.B. Lee, G.W. Rubloff*, University of Maryland, College Park
Rechargeable Li-metal anode batteries could be considered the holy grail of energy storage systems because Li offers extremely high theoretical specific capacity (3860 mAh/g), low density (0.59 g/cm^3), and the lowest negative electrochemical potential (-3.040 V vs. standard hydrogen electrode). However, Li is thermodynamically unstable with organic solvents, inviting serious capacity degradation as well as safety concerns such as Li dendrite growth. The prognosis for Li anodes would be profoundly enhanced for next generation batteries if suitable passivation schemes could be developed to protect Li anodes without significantly reducing ion transport between Li and electrolyte.

In our laboratory, we use atomic layer deposition (ALD) to precisely deposit very thin layer of aluminum oxide (Al_2O_3) on Li foils, using glove box and UHV environments to avoid air exposure while depositing passivation layers on the Li metal surface. We then characterize the surface morphology of the passivated Li by AFM at varying stages of electrochemical reaction and as a function of time and film thickness. We observed the growth of defects on ALD-passivated Li metal surface, decorated by AFM structures indicative of localized electrochemical reactions. The resulting defect density decreased as the film thickness increased.

For thinner ALD protection layers, EC-AFM showed bubble-like structures decorating the steps and boundaries of ALD/Li metal surface in electrochemical system, suggesting mechanisms associated with volatile products. While thin ALD layers suppress charge transfer processes which lead to electrolyte decomposition and formation of solid electrolyte interphase (SEI) [1-2], defects in the ALD passivation layer may cause localized SEI formation, which in turn involves volatile products (e.g., C_2H_4, CO). Alternatively, trace H_2O in the propylene carbonate electrolyte may react with Li metal through pinholes in the ALD layer, leading to LiOH and volatile H_2 products. We are working to differentiate between these by applying in-situ mass spectroscopy to monitor the gas formation in the cell as a function of controlled water content and ALD film thickness. The identification of passivation layer degradation mechanisms and the development of robust approaches to metal anode protection have profound benefit to a variety of beyond-Li-ion batteries.

References:

1. Kevin Leung, J. Phys. Chem. C, 2012, 117, 1539-1547.

2. Kevin Leung et al., JACS, 2011, 133, 14741-14754.

5:40pm EM+EN+TF-WeA11 The Road to Next-Generation Energy Storage is Paved with Zinc, *Joseph Parker, C.N. Chervin*, Naval Research Laboratory, *I.R. Pala*, National Research Council postdoc working at Naval Research Laboratory, *E.S. Nelson*, Pathways Student working at Naval Research Laboratory, *J.W. Long, D.R. Rolison*, Naval Research Laboratory
While Li-ion batteries presently dominate the energy-storage landscape, zinc-based batteries offer a compelling alternative due to the earth-abundance of zinc, innate safety and cost advantages that arise from using aqueous electrolytes, and device-realized specific energy that is comparable to or higher than Li-ion. Yet the performance of present-day Zn-based batteries is hindered by suboptimal Zn utilization (typically <60% of theoretical capacity) and poor rechargeability—a consequence of the complex dissolution/precipitation processes that accompany Zn/Zn^{2+} cycling and the ad hoc construction of conventional powdered-bed Zn anodes. We address these limitations by designing and fabricating highly conductive, porous, and 3D-wired Zn "sponge" electrodes from emulsion-cast, consolidated Zn powders that are thermally treated to produce rugged monolithic forms. With this 3D Zn architecture, we achieve >90% Zn utilization when discharged in primary Zn–air cells with retention of the 3D framework of the Zn sponge and uniform deposition of charge/discharge products at the surfaces of the Zn sponge, as verified by scanning electron microscopy and impedance spectroscopy. We further show that the structural characteristics of the Zn sponge promote greater rechargeability when cycled in prototype Ag–Zn and Ni–Zn cells. Our results demonstrate that all Zn-based chemistries can now be reformulated for next-generation rechargeable batteries.

Manufacturing Science and Technology
Room: 302 - Session MS+TF-WeA

Overview: Applications and Manufacturing of Devices on Paper and Textiles
Moderator: Liangbing Hu, University of Maryland, College Park, Bridget R. Rogers, Vanderbilt University

2:20pm MS+TF-WeA1 Challenges and Opportunities in the Production of Cellulose Nanomaterials, *Junyong Zhu*, USDA Forest Products Lab **INVITED**
Callulose nanomateruals has attracted great attention in the scienticific community due to its unique optical and mechancal properties along with its renewablility and abundance. However, the production process is very costly using current technologies, which limited its use to high value products. This created a market mismatch, i.e., a very large amount natural cellulose are available. In this presenttaion I will outline the challenges in reducing the cost of cellulose nanomaterials. At the sametime, I provide some opportunities to reduce the cost. I will specifically outline a few process innovation in our laboratory for both cellulose nancrystal and cellulose nanofibril productions

3:00pm MS+TF-WeA3 Engineering Cellulose Nanomaterial Substrates for Flexible Electronics, *Y. Zhou, C. Fuentes-Hernandez, T. Khan*, Georgia Institute of Technology, *J.-C. Liu, J. Diaz*, Purdue University, *J. Hsu, J. Shim, A. Dindar*, Georgia Institute of Technology, *Robert Moon*, US Forest Service-Forest Products Laboratory, *J. Youngblood*, Purdue University, *B.J. Kippelen*, Georgia Institute of Technology **INVITED**
Fabrication of flexible electronics (e.g. solar cells) on recyclable and biodegradable substrates are attractive for the realization of a sustainable technology, but significant advances are required to make the technologies economically viable and, from a life-cycle perspective, environmentally friendly, and consequently scalable. One of the key areas of research for making this a reality is in the design/engineering of suitable substrate materials that can: mechanically and chemically support the given electronics, have sufficient surface features (low roughness, surface chemistry, etc) to facilitate the process of the electronics, have similar thermal expansion characteristics of the electronics to minimize stress at the substrate-device interface, have the desired optical transmittance for device performance or application of product, and facilitate the recovery of the electronic components during the recycling process, to name a few. Our recent work has focused on the development cellulose nanocrystals (CNCs) based substrates for such applications. Cellulose nanomaterials (CNM) are emerging high-value nanoparticles extracted from plants that are abundant, renewable, and sustainable. CNCs are rod-like nanoparticles of about 4-10 nm in diameter and 50-400 nm in length and through solvent casting of aqueous suspensions, transparent substrates suitable for electronic devices can be produced. By adjusting the suspension composition, pH, application of shear (control CNC alignment), drying conditions and heat treatment,

have been identified as relevant factors affecting the final film/substrate properties.

This talk will provide a general introduction and review of the current state of art in cellulose nanomaterials, their use as substrate materials for flexible electronics, and summarize our work on the measurement of thermo-mechanical properties of CNC-based substrate materials and the development of efficient polymer solar cells fabricated on optically transparent CNC substrates.

4:20pm MS+TF-WeA7 Circuits on Cellulose: From Transistors to LEDS, from Displays to Microfluidics on Paper, *Andrew Steckl*, University of Cincinnati **INVITED**
Organic electronics is a rapidly growing field due to a combination of strong performance from improving materials with the low fabrication cost associated with large area printing technology. Recently, the incorporation into organic electronic technology of natural biomaterials that are renewable and biodegradable is being increasingly investigated with the goal of producing "green" electronics that is environment-friendly.

In this presentation, a review is given on the use of cellulose-based paper as a material in a variety of electronic (and related) applications, including transistors, light emitting diodes, displays, microfluidics. Paper is a very attractive material for many device applications: very low cost, available in almost any size, versatile surface finishes, portable and flexible. From an environmental point of view, paper is a renewable resource and is readily disposable (incineration, biodegradable). Applications of paper-based electronics [1,2] currently being considered or investigated include biochips, sensors, communication circuits, batteries, smart packaging, electronic displays. The potential advantages of paper-based devices are in many cases very compelling. For example, lab-on-chip devices fabricated on paper for bio/medical applications [3] use the capillary properties of paper to operate without the need of external power sources, greatly simplifying the design and reducing the cost. Specific examples of paper-based devices will be discussed, including organic light emitting diodes [4] (OLED) and field effect transistors [5] (OFET) on flexible and transparent paper, medical diagnostic devices utilizing lateral capillary flow on paper.

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5:00pm MS+TF-WeA9 Cellulose Nanostructures for Energy Devices and Flexible Electronics, *H.L. Zhu, W. Bao, F. Shen, Y. Li, Z. Fang, Liangbing Hu*, University of Maryland, College Park **INVITED**
I will discuss our recent results and the fundamental science of novel transparent paper with tailored optical and mechanical properties, and applications in flexible electronics, origami devices and solar cells. I will also discuss the fundamental advantages of using mesoporous, soft wood fibers for low-cost Na-ion batteries.

5:40pm MS+TF-WeA11 Designing Functional Paper for Emerging Electronics and Energy Devices, *Hongli Zhu, L.B. Hu*, University of Maryland, College Park
The natural wood fiber has a hierarchical structure with one regular fiber consisting of numerous smaller fibers, and these small nanofibers can be disintegrated from the microfiber with chemical and mechanical treatment. By integrating electronically conductive material, we apply the low cost and sustainable biomaterial in the electronics and energy storage devices. In the first part, we will introduce a novel transparent paper made of wood fibers that displays both ultrahigh optical transparency (~96%) and ultrahigh haze(~60%), thus delivering an optimal substrate design for solar cell devices. We will also introduce the flexible transparent organic field-effect transistors (OFETs) and organic light emitting diode (OLED) device fabricated on nanopaper. These studies are important for the future development of flexible electronics based on new transparent substrates made from sustainable cellulose instead of plastic. In the second part, we will discuss wood fiber based batteries. The wood fibers are intrinsically porous and soft. Thin film Sn anodes deposited onto wood fibers sustain

more than 400 charging/discharging cycles, a new record for Sn anodes in Na-ion batteries. Additionally, dual ion transport pathways within the mesoporous structure of wood cellulose fibers significantly improve the traditionally slow ion transport in Na-ion batteries.

6:00pm MS+TF-WeA12 Transparent Films of Cellulose Nanocrystals Derived from Waste Cotton T-shirts, *Nasim Farahbakhsh*, *J.S. Jur, R.A. Venditti*, North Carolina State University
The hierarchical structure of cellulosic materials is a renewable building block for a wide range of novel applications, including electronic devices. In this work we present on the fabrication of the transparent cellulose nanocrystal (CNC) thin films for flexible electronic applications. The CNC platforms were manufactured from waste cotton T-shirts fibers using sulphuric acid at optimum reaction temperature and acid concentration. The derivation of nanocellulose from cotton fibers beneficial due to a high cellulose content (~95%) and high crystalline structure which results in high yield without any intensified purification process. The resultant CNC particles, with an average diameter of 25 nm with average length of 200 nm, are used to produce transparent free-standing films and spun-cast films on silicon. Opportunities related device fabrications are presented.

Thin Film
Room: 307 - Session TF+EM+EN-WeA

Thin Film and Nanostructured Coatings for Light Trapping, Extraction, and Plasmonic Applications
Moderator: Tansel Karabacak, University of Arkansas at Little Rock

2:20pm TF+EM+EN-WeA1 Enhanced Light Trapping by Glancing Angle Deposited Semiconducting and Metallic Nanostructure Arrays, *Hilal Cansizoglu*, *R. Abdulrahman, M.F. Cansizoglu*, University of Arkansas at Little Rock, *M. Finckenor*, NASA Marshall Space Flight Center, *T. Karabacak*, University of Arkansas at Little Rock
Management of light trapping in nano materials has recently got attention owing to altering optical properties of materials commonly used in potential applications such as photovoltaics and photonics. Trapping the light inside the semiconducting nanostructure coating can increase optical absorption capacity of the material dramatically. Meanwhile, metallic nanostructures can serve as individual back reflectors if the light is achieved to be trapped among metallic nanostructures, which results in enhanced optical absorption of the possible surrounding absorber material around metallic structures. In this study, we examine light trapping in arrays of zig-zags, springs, screws, tilted rods, and tapered vertical rods of indium sulfide (In_2S_3) and aluminum (Al) as the model semiconducting and metallic materials, respectively. Nanostructures of different shapes were produced by glancing angle deposition (GLAD) technique. We investigated the effect of size and shape of the arrays on light trapping properties using ultraviolet–visible-near-infrared (UV-VIS-NIR) spectroscopy and finite difference time domain (FDTD) simulations. Optical characterization results show that light trapping by GLAD nanostructures can strongly depend on their shapes. Under normal incidence of light, 3D geometries of semiconducting nanostructures such as springs, screws, and tapered vertical rods can provide an enhanced optical absorption compared to zigzags, and tilted rods. In addition, total reflectance measurements reveal that reflectance is inversely proportional to metallic nanorod length in the wavelength range of 200-1800 nm. Meanwhile, FDTD optical modelling indicates an enhanced diffuse light scattering and light trapping through uniform distribution of diffracted light within the 3D In_2S_3 nanostructure geometries such as springs, screws and vertical rods. On the other hand, zigzags and tilted rods show light absorption at relatively low level similar to the experimental results. In addition, simulations reveal that average reflectance of Al nanorods can drop down to as low as ~50%, which is significantly lower than the ~90% reflectance of conventional flat Al film at similar wavelengths. Our results demonstrate that GLAD nanostructures can provide efficient light trapping through the control of their shapes and size.

2:40pm TF+EM+EN-WeA2 Enhanced Photoresponsivity of Conformal TiO₂/Ag Nanorod Arrays Fabricated via (Successive) Glancing Angle and Atomic Layer Deposition, *Ali Haider*, *N. Biyikli, A.K. Okyay*, Bilkent University, Turkey, *T. Karabacak, H. Cansizoglu*, University of Arkansas at Little Rock, *B. Teckcan*, Bilkent University, Turkey, *M.F. Cansizoglu*, University of Arkansas at Little Rock
Improved charge carrier collection and optical absorption are two main techniques to enhance the photocurrent of a nanostructured photodetector. In a nanostructured photodiode, longer carrier life time and shorter transit

time of the photo-generated carriers provides efficient charge carrier collection while the nanostructured device architecture contributes towards trapping the light by diffuse light scattering and enhancing optical absorption. However, efficient charge carrier collection is limited by the random and non-uniform nano-network. For nanostructured Schottky photodetectors, uniform nanostructured geometries with larger aspect ratio can enhance the interface of the Schottky junction which in turn decreases the transit time of generated carriers. In addition, most of the nanofabrication methods that can produce uniform nanostructure geometries are limited to certain materials. Therefore, it is an overwhelming demand to develop innovative low-cost nanostructured photodetector fabrication methodologies which enables the use of a variety of semiconductor alloy families with uniform and optimized geometries for improving photoresponsivity performance. In this work, we demonstrate a proof-of-concept nanostructured Schottky photodiode fabrication method combining glancing angle deposition (GLAD) and atomic layer deposition (ALD) to fabricate metal-semiconductor radial junction nanorod arrays, which offers significantly enhanced photoresponse compared to conventional planar counterpart. Firstly, silver (Ag) nanorod (NR) arrays were deposited on Ag thin film/Si templates by utilizing glancing angle deposition (GLAD) technique. A conformal and thin titanium dioxide (TiO_2) coating was deposited on silver nanorods via ALD. ALD emerge as highly attractive deposition technique for coating of nanorods due to its remarkable conformality and uniformity on the densely packed NR structures. Moreover, ALD also facilitates the ultra-precise control of deposited film thickness in the sub-nm scale. Following the growth of TiO_2 on Ag NRs, aluminum (Al) metallic top contacts were deposited by thermal evaporation to complete the fabrication of NR-based Schottky photodiodes. Due to the improved charge carrier collection and optical absorption, the resulting nanostructured detector exhibits a more-than two orders of magnitude photoresponsivity enhancement factor (3.8×10^2) under 3V reverse bias when compared to the corresponding thin film counterpart device with the same TiO_2 thickness. Our preliminary structural, optical, electrical, and photoresponse characterization results are presented.

3:00pm TF+EM+EN-WeA3 Nanostructured Photonic Materials for Light-Trapping and Photon Management in Solar Energy Conversion, *Koray Aydin*, Northwestern University **INVITED**
Nanophotonics, the emerging field of photon-material interactions at the nanoscale, poses many challenges and opportunities for researchers both in the basic and applied sciences. In this talk, I will describe our efforts in designing, realizing and characterizing nanostructured photonic materials including metals, transparent conductive oxides and inorganic semiconductors. By shaping materials at the nanoscale, one can drastically increase absorption in and/or scattering from nanostructures that could provide significant performance enhancements in solar energy conversion processes including photovoltaics and photocatalysis. First, I will discuss our research efforts on realizing broadband plasmonics absorbers enabled by nanophotonic light-trapping approaches in metal-insulator-metal resonators. By using reflective metals and transparent dielectrics, we have achieved significant absorption enhancement in the metallic parts opening routes for spectrally and spatially selective light-absorbing devices that could find use in thermophotovoltaics and hot-electron collection devices. Then, I will describe light-trapping in nanostructured inorganic silicon ultrathin films which results in drastic absorption enhancement over the entire solar spectrum and over the wide range of incident angles. This approach does not involve any plasmonic components and based solely on localized and delocalized resonances in semiconductor nanostructures. This novel resonant light absorption phenomenon in semiconductors could find use in photocatalytic and photovoltaic applications of inorganic semiconductors. Finally, I will talk about our results on nanostructured transparent conductive oxide contacts, which is capable of light trapping over broad range of wavelengths. Nanostructured TCO contacts could benefit both organic and inorganic photovoltaic materials, offering significant absorption and short circuit enhancements.

4:20pm TF+EM+EN-WeA7 Porous Solid Phase Microextraction (SPME) Fibers by Oblique Angle Deposition, *Anubhav Diwan, B. Singh,* Brigham Young University, *M. Kaykhaii,* Sistan & Balouchestan University, Iran (Islamic Republic of), *B. Paul, P. Nesterenko,* University of Tasmania, Australia, *M.R. Linford,* Brigham Young University
Solid phase microextraction (SPME) is a solvent-free technique used for extracting organic compounds from matrices such as air or wastewater. It involves a fiber coated with a liquid or solid stationary phase that extracts target compounds directly from a solution or from the head space above a solution or material. Solid stationary phases provide faster extraction than liquid phases, but exhibit lower capacities. Porous solid phases have been able to overcome these issues by providing large surface areas for analyte adsorption. Commercial SPME fibers are rather expensive, swell in many solvents, and often extract limited numbers of compounds (show limited

selectivity). Herein, we discuss the preparation of porous SPME fibers by oblique angle deposition (OAD) of sputtered silicon or other materials onto a fiber. OAD involves deposition of materials onto substrates placed at steep angles with respect to the direction of the incoming species, creating porous structures. The resulting nanoporous coatings can be modified with different functional groups to enhance selectivity of the phase towards target compounds. If normalized for thickness, our fibers show ca. three times the capacity of a commercial, 7 μm PDMS fiber. To confirm their morphologies, new OAD-based fibers have been characterized by scanning electron microscopy (SEM). Various silane coatings can be applied to our fibers, which will offer a range of selectivities. These coatings, e.g., a C18 silane, have been characterized on model planar substrates by X-ray photoelectron spectroscopy (XPS) and contact angle goniometry (wetting).

4:40pm TF+EM+EN-WeA8 Chiral Patchy Particle Arrays: A Simple Fabrication Method to Achieve Plasmonic Circular Dichroism in the Visible Region, *George Larsen, Y. He, W. Ingram, Y.P. Zhao*, University of Georgia, Athens
An object is said to be "chiral" if it cannot be made superimposable upon its mirror image solely by rotations and translations. That is, chiral objects do not exhibit reflective symmetry. By combining self-assembled colloid monolayers and glancing angle deposition (GLAD), we can create chiral patchy particle thin films that exhibit plasmonic activity in the visible region. Due to their chirality, these patchy particle films exhibit circular dichroism, i.e., they absorb right- and left-circular polarized light to different degrees. Interestingly, we find that the GLAD method relaxes requirements on the template quality, allowing for the production strongly chiral films from polycrystalline colloidal monolayers with randomly oriented domains. It is determined that the rotation direction during GLAD breaks the racemic symmetry of the templates by creating a chiral distribution of material which enhances the chirality of one set of enantiomers relative to the other. Microscopic analysis and geometric chirality calculations confirm that the optical chirality of the bulk film results from incomplete cancellations of even stronger local chiralities. By improving the quality of the colloidal monolayers and intentionally creating a chiral material distribution, we seek to use these chiral patchy particle arrays as plasmonic biosensors that are sensitive to the handedness of the target molecule.

5:00pm TF+EM+EN-WeA9 Tunable Three-Dimensional Helically Stacked Plasmonic Layers on Nanosphere Monolayers, *Yizhuo He*,* *G.K. Larsen, W. Ingram, Y.P. Zhao*, University of Georgia, Athens
Chiral metamaterials are artificial materials designed to interact with left- and right-handed circularly polarized light in different ways. Such a unique optical property enables applications such as negative refractive index, circular polarization, enantiomer sensing, etc. Practical applications usually require the fabrication of large-area chiral metamaterials on substrates with tunable chiroptical properties, especially in visible to near infrared wavelength region. We report a simple and scalable method to fabricate three-dimensional chiral metamaterial combining glancing angle deposition and self-assembled colloidal monolayers. Ag and SiO_2 are deposited alternatingly on colloidal monolayers. By controlling the azimuthal rotation of substrates between depositions, Ag and SiO_2 layers can be helically stacked in left-handed and right-handed fashions to form continuous helices. These helically stacked plasmonic layers (HSPLs) exhibit localized surface plasmon resonances (LSPR) and strong chiroptical responses in visible to infrared region, which is also confirmed by finite-difference time-domain simulations. The most important feature of HSPLs is the great tunability of chiroptical spectra. By increasing the nanosphere diameter from 200 nm to 500 nm, the HSPL structure can be scaled up and thus the LSPR peak redshifts from 520 nm to 1000 nm. Since the chiroptical response originates from the strong interaction of metal layers with light, i.e. LSPR, the chiroptical spectra also redshifts accordingly without a significant change in magnitude. With such flexibility in the design, HSPLs may act as tunable chiral metamaterials, as well as serve as different building blocks for chiral assemblies.

5:20pm TF+EM+EN-WeA10 Co-deposition of Mixed-Valent Oxides of Molybdenum and Germanium ($Mo_xGe_yO_z$): A Route to Tailored Optical Absorption, *Neil Murphy,* Air Force Research Laboratory, *L. Sun,* General Dynamics Information Technology, *J.G. Jones,* Air Force Research Laboratory, *J.T. Grant,* General Dynamics Information Technology
Mixed-valent oxides of molybdenum and germanium were deposited simultaneously using reactive magnetron co-deposition within an oxygen-argon environment. The films' stoichiometry, optical and physical properties were varied through changes in oxygen partial pressure induced by systematic variation of the potential applied to the molybdenum cathode.

∗ TFD James Harper Award Finalist

The oxygen partial pressure was determined from the drop in pressure as measured by a capacitance manometer, assuming constant argon partial pressure. To facilitate deposition, a constant power of 100 W DC was applied to the germanium cathode, while power was applied to the molybdenum target using a modulated pulse power supply. Modulated pulse power magnetron sputtering was used due to its ability to generate high target power densities, allowing for rapid reduction of oxygen on the surface of the "oxygen poisoned" molybdenum cathode, as well as for its highly metallic plasma resulting in increased oxygen-gettering capability. Changes in the modulated pulse power supply's capacitor bank charge, stepped from settings of 300 to 380 V, resulted in films ranging from mixtures of transparent GeO_2 (Ge^{4+}) and MoO_3 (Mo^{6+}) to the introduction of various absorptive ionic species including Mo^{5+}, Mo^{4+}, Ge^{2+} and Ge^0, as determined from X-ray photoelectron spectroscopy. The presence of each of the aforementioned ions results in characteristic changes in the films' band energies and optical absorption, measured using UV-VIS-NIR optical spectroscopy. As deposited $Mo_xGe_yO_z$ thin films grown using this method have been shown to have band gaps that are able to be tailored between 2.8 eV and 0.6 eV, spanning useful ranges for devices operating in the visible and near-infrared.

5:40pm **TF+EM+EN-WeA11 Permanent Optical Tape and Solid State Data Storage Devices**, *Hao Wang*, *R. Gates, N. Madaan, J. Bagley, A. Diwan, A. Pearson, S. Jamieson, K. Laughlin,* Brigham Young University, *Y. Liu,* Lehigh University, *B. Lunt, M. Asplund,* Brigham Young University, *V. Shutthanandan,* Pacific Northwest National Laboratory, *R.C. Davis, M.R. Linford*, Brigham Young University

Recently we have prepared novel write–once–read–many (WORM) optical stacks on Mylar for archival data storage in an optical tape format.[1] Here, a nanoscale, co-sputtered bismuth–tellurium–selenium (BTS) alloy was employed as the write layer with carbon protective layers on both the top and bottom of the BTS film. We have successfully written information (matrix of marks) on the C/BTS/C optical stack using a 532 nm laser. Both the optical stack structure (film thickness) and writing conditions (laser power and laser spot size) have been optimized. Films were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, scanning electron microscopy, spectroscopic ellipsometry, and atomic force microscopy.[2, 3]

We have also recently developed novel WORM solid-state memory elements. These consisted of nanoscale, bowtie-like sputtered carbon films to which a voltage (ca. 10 V) is applied. These fuses have been successfully blown, and the carbon fuse shape, thickness of the carbon layer, and writing voltage have been optimized. Other aspects of the device are currently being optimized.

References

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[3] Wang, H.; Lunt, B.M.; Davis, R.C.; Linford, M.R. Simulation of laser writing on Bi-Te-Se alloy/carbon/Mylar pemanent optical storage tape, ISOM 2013 International Conference, Incheon, South Korea, 2013.

Manufacturing Science and Technology
Room: 302 - Session MS+PS+TF-ThM

Processes for Mesoscale Structure on Paper and Textiles
Moderator: Jesse Jur, North Carolina State University

8:00am **MS+PS+TF-ThM1 High-Performance Composites Based on Wood Cellulose Nanofibrils**, *Qi Zhou*, KTH Royal Institute of Technology, Sweden **INVITED**
With increasing concerns for the climate and environment, it has been recognized globally that paradigm-shifting research is required to improve the performance of materials based on renewable resources. Attempts to develop very high performance natural cellulosic fibers based composite materials using intact cells from hemp, flax and cotton have failed mainly due to the inherent imperfections of the secondary cell walls of natural fiber cells. These issues have been recently addressed by replacing with cellulose nanofibrils (CNFs), which are three orders of magnitude smaller than the intact fiber cells. The extraction process of CNFs from renewable resource has been extensively investigated in the past decade. A critical challenge in the fabrication of high performance products based on CNFs is to tailor their surface structure and functionality in an efficient and environmentally friendly fashion, thus to accommodate a wider range of applications and sustainability requirements for the next generation of materials. In this talk, I will present our recent work on the fabrication of functional composite materials based on CNFs. In particular, several novel surface modification techniques of CNFs and their effects on nanostructure and material properties of CNFs based composites will be discussed.

8:40am **MS+PS+TF-ThM3 Manufacturing and Applications of Carbon Nanotube Textiles**, *Philip Bradford*, North Carolina State University **INVITED**
Carbon nanotubes (CNTs) are short nanofibers that are usually produced in the form of a black powder. This powder is then incorporated into other materials to produce a wide array of multifunctional products. Processing raw CNTs into materials that look and behave like traditional textiles is a growing area of interest, however the CNTs are often processed in solution and the end products look more like papers than textiles. There are currently only a couple of options for creating fabrics out of CNTs which preserve the high surface area of the individual tubes and retain high porosity. This presentation covers the work of my research group to make this type of fabric from a special type of CNT structure called drawable CNT arrays. These arrays are synthesized in a low pressure chemical vapor deposition process and then utilized for CNT nonwoven fabric formation. My group is also exploring many novel applications for the use of these unique fabrics.

The nonwoven CNT fabrics produced in our lab contain millimeter long CNTs, have a preferential CNT alignment, low CNT bundling and high porosity. These features make them attractive for use in: composites reinforcement, battery electrodes, sensing, filtration and barrier fabrics. Of particular interest to the AVS community may be our recent work with collaborator Dr. Jesse Jur at NC State, to study the atomic layer deposition (ALD) of thin inorganic layers into CNT arrays and fabrics. Through optimization of CNT pretreatment, ALD parameters and sample orientation, we have been able, for the first time, to uniformly coat CNT structures whose characteristic aspect ratios are extremely large. Due to the un-bundled nature of the CNT fabrics we have the ability to uniformly coat CNTs along their entire millimeter length, making for some very unique hybrid CNT structures.

9:20am **MS+PS+TF-ThM5 Carbonized Cellulose Fibers for Low-Cost Energy Storage**, *Fei Shen*, *L.B. Hu*, University of Maryland, College Park
A low-cost but scalable carbon film was successfully obtained via cellulose fiber carbonization. This cellulose derived film can be also applied as an alternative anode for lithium or sodium ion battery due to its natural mesoporous structure of the starting material which was excellent for ion storage. Furthermore, this new type of carbonized cellulose possesses electrically interconnected three-dimensional framework with advanced dual properties of anode material and current collector, afford to result in a higher energy density by eliminating the extra mass of inactive materials such as binder and carbon black in conventional designs. Electrochemical studies showed the film achieved a high capacity of 800mAh/g for lithium ion battery and a moderate capacity of 200mAh/g for sodium ion battery at C/10.

9:40am **MS+PS+TF-ThM6 Traditional, 20th, and 21st Century Strengthening Techniques for Cultural Heritage Papers Weakened by Cellulose Depolymerization**, *L. Pei*, *M. McGath*, **John Baty**, Johns Hopkins University
Cellulose depolymerization leading to paper brittleness can occur throughout the sheet, or be localized to where a corrosive substance is present. Uniform brittleness is associated with mass-produced, inexpensive, and acidic papers. Rendering millions of books and unbound papers useless, paper brittleness impairs scholarly communication and destroys historic and artistic works. Localized brittleness is most commonly associated with corrosive pigments and inks, including iron gall ink. It visually alters and can also physically destroy paper-based works. In the absence of techniques to restore the cellulose polymer to its initial condition, diverse techniques have been developed to strengthen paper. Traditional conservation techniques vary from conceptually simple ones, such as backing the sheet with a reinforcing layer, to complex ones, such as splitting the sheet into two plies to adhere a reinforcing sheet in-between. 20th century techniques include the widespread lamination of documents with a cellulose acetate film, the present condition of which we have studied and discuss along with its successor, the encapsulation of papers within a polyester film envelope to which the sheet is only electrostatically attracted. Both of these techniques involve the addition of a visible film, altering the look and feel of the artifact. Therefore, we are studying chemical vapor deposition (CVD) using Parylene to deposit a thin, conformal, barely perceptible coating to add strength to brittle papers. We conclude that, here as elsewhere, scientific research can improve traditional conservation techniques by making additional tools available to the conservator; that both cellulose acetate lamination and polyester film encapsulation have achieved a greater preservation benefit than they are credited for; and that CVD is a useful tool for both single-item as well as batch treatments to preserve cultural heritage papers weakened by cellulose depolymerization.

11:00am **MS+PS+TF-ThM10 Visualizing the Interface in Strained Cellulosic Nanocomposites**, *Chelsea Davis*, *J. Woodcock*, *A.M. Forster*, *M. Zammarano*, *I. Sacui*, *N. Chen*, *SJ. Stranick*, *J.W. Gilman*, National Institute of Standards and Technology (NIST)
In fundamental composite theory, the nature of the interface is often the key parameter which determines the strength of the resulting composite structure. While it is possible to observe interfacial failure and characterize the areal coverage of the matrix on the surface of the reinforcement phase in conventional composite materials, directly quantifying interfacial strength and contact area in a nanocomposite becomes far more difficult. A novel solution developed at NIST has been to utilize Förster resonance energy transfer (FRET) imaging[1,2] by preferentially labeling the interface within a nanocomposite system, allowing direct imaging of the interface with an optical microscope.[3] Zammarano et al. have shown that the incorporation of a FRET dye pair onto the surface of a cellulosic nanoreinforcement phase (dye 1) and within a polymer matrix (dye 2) allows visualization of the nanoscopic interphase region as the two dyes transfer energy on the same scale as the interphase depth (1 nm-100 nm).[3,4]

Building upon this FRET-based interfacial characterization technique, our goal is to develop a globally nondestructive measurement system that allows the quantitative characterization of key interfacial properties; first, the wetting and surface contact formed between the nanocellulose and an epoxy matrix and second, the deformation of the interface on the nanoscale upon application of small mechanical strains. We are constructing a suite of mechanical strain tools to enable *in situ* mechanical interrogation with simultaneous FRET imaging. The development of the first of these tools, uniaxial tensile test will allow a preliminary observation of small strain effects on the interphase region regarding the fluorescent response of the FRET dye pair. As a first proof of concept, it has been shown that FRET can be used to observe nanoscopic interfacial fracture and to determine local (microscopic) stress concentration zones before macroscopic failure of the nanocomposite is observed.

This *in situ* FRET/mechanical deformation approach allows the use of an optical microscope to probe nanoscale features in a powerful way, enabling characterization of nanomaterials which will complement measurements made by electron microscopy and standard mechanical property testing methods.

Topic Area: Novel nanocomposites, Multi-technique characterization of nanostructured materials

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[2] E. a Jares-Erijman, T. M. Jovin, *Nat. Biotechnol.***2003**, *21*, 1387.

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11:20am MS+PS+TF-ThM11 SERS-based Chemical and Biological Analytics on Inkjet-fabricated Paper Devices, *Ian White*, University of Maryland
SERS-based chemical and biological analytics on inkjet-fabricated paper devices

Abstract. As a bio/chemical sensing technique, surface enhanced Raman spectroscopy (SERS) offers sensitivity comparable to that of fluorescence detection while providing highly specific information about the analyte. The high sensitivity of SERS detection results from the localized plasmons generated at the surface of noble metal nanostructures upon excitation by resonant electric fields at optical frequencies. Although single molecule identification with SERS was demonstrated over a decade ago, today a need exists to develop practical solutions for point-of-sample and point-of-care SERS systems. Recently, we demonstrated the fabrication of SERS substrates by inkjet printing silver and gold nanostructures onto paper and other similar membranes. Using a low-cost commercial inkjet printer, we deposited silver nanoparticles with micro-scale precision to form SERS-active biosensors. Using these devices, we have been able to achieve detection limits comparable to conventional nanofabricated substrates. Furthermore, we have leveraged the fluidic properties of paper to enhance the performance of the SERS devices while also enabling unprecedented ease of use, which is critical for extending chemical and biological analytics from central labs out into the field.

In this presentation we will review the capabilities of inkjet-fabricated paper SERS devices as chemical and biological sensors. We will introduce the fabrication of paper-based fluidic SERS devices using inkjet printing, and we will review results for chemical detection with paper SERS devices, including the use of the paper substrates as swabs and dipsticks for pesticide detection, as well as chromatography SERS on PVDF membranes for the detection of melamine in infant formula. We will then present the results of the fluidic paper SERS devices for biomolecule detection, including paper SERS dipsticks that leverage the chromatographic separation properties of paper to distinguish the outcome of multiplexed TaqMan PCR from a single reaction. In particular, we have utilized this technique to detect the presence of two drug resistance biomarkers for methicillin-resistant *S. Aureus* (MRSA).

11:40am MS+PS+TF-ThM12 NSF Scalable Nanomanufacturing (SNM) Program, *Khershed P. Cooper* **INVITED**
Abstract: Nanomanufacturing involves the fabrication of nano-scale building-blocks (nanomaterials, nanostructures), their assembly into higher-order structures such as nanodevices and nanosystems, and the integration of these into larger scale structures and systems such that both heterogeneity and complexity are possible with manipulation and control at nano-scale. In 2010, following a review of the NNI, PCAST recommended greater emphasis be put on commercialization of nanotechnologies by doubling Federal Government investment in nanomanufacturing R&D. In 2011, the inter-Agency NNI Signature Initiative (NSI) in Sustainable Nanomanufacturing was announced. In response to the NSI, the NSF Scalable Nanomanufacturing (SNM) Program was launched. SNM's emphasis is on research to overcome the key scientific and technological barriers that prevent the production of useful nanomaterials, nanostructures, devices and systems at an industrially relevant scale, reliably, and at low cost and within environmental, health and safety guidelines. The SNM program's objective is to address challenges presented at the various stages of the nanomanufacturing value chain of nano-scale building-blocks to nano-enabled products. It sponsors fundamental scientific research in well-defined technical areas that are strongly justified as approaches to overcome critical barriers to scale-up and integration. It seeks discovery of scalable processes and methods for large-area or continuous manufacturing at the nano-scale. It encourages the study of design principles for production systems leading to nanomanufacturing platforms, identification of metrology, instrumentation, and standards, and development of methodologies needed for process control and assessing quality and yield. SNM encourages an inter-disciplinary approach, industry collaboration and integration of research and education. SNM projects are studying a variety of building-blocks—CNT, graphene, membranes, BCPs, DNA, nanowires, nanofibers, QDs, etc., a variety of top-down and bottom-up processes—thermal, vapor-based, solution-based, lithography, patterning, bio-inspired, etc., targeting applications across the board—energy, environmental, electronics, sensors, structural, etc. Many projects are investigating roll-to-roll processing systems, some are studying in-line metrology and quality control. Moving ahead, SNM seeks to explore new research opportunities in processing (hierarchical nanomanufacturing, cyber-enabled nanomanufacturing, etc.), in materials (graphene, MoS2, etc.), in devices (plasmonics, ultrafine vias, etc.), and in manufacturing platforms (3D printing, bio-enabled assembly, etc.). SNM encourages an inter-disciplinary approach involving the disciplines of engineering, physical sciences and mathematics. The ultimate goal is to create a knowledge base for the reliable production of nano-enabled systems and products.

Plasma Science and Technology
Room: 305 - Session PS1+TF-ThM

Plasma Deposition and Plasma Assisted ALD
Moderator: Sumit Agarwal, Colorado School of Mines

8:00am PS1+TF-ThM1 Sputtering Growth of High-Quality ZnO-based Semiconductors for Optoelectronic Applications, *Naho Itagaki*, Kyushu University, Japan **INVITED**
ZnO and its related semiconductors are remarkable multi-functional materials with a huge range of existing and emerging applications including transparent conducting oxides (TCO) and light emitting diodes (LED). In order to obtain physical properties required for such applications, control of the crystallinity (grain size, crystal axis alignment, crystal defects) is of great importance. We have recently developed a new fabrication method based on magnetron sputtering, "Impurity mediated crystallization (IMC)", where crystal nucleation and the growth are controlled by impurity atoms adsorbed on the film surface [1,2]. Here we demonstrate sputtering deposition of two kinds of ZnO films by utilizing buffer layers fabricated via IMC method. One is polycrystalline TCO films fabricated on glass substrates, and the other is single crystalline films on sapphire substrates for LED applications. Effects of impurity during the crystal growth of ZnO are studied by observing the evolution of film morphology by means of atomic force microscopy (AFM).

IMC-ZnO buffer layers have enabled fabrication of single-crystalline ZnO films even on large lattice-mismatched (18%) sapphire substrates by a conventional sputtering method. The ZnO films have atomically-flat surfaces with steps of 0.26nm-hight, corresponding to a half of c-axis length of ZnO. AFM observation of IMC-ZnO buffer layers revealed that impurity atoms inhibit the crystal growth and thus increase in the grain density, which reduce the strain energy caused by the large lattice mismatch between ZnO and sapphire. IMC-ZnO buffer layers have also improved the film quality of ZnO based TCO fabricated on glass substrates. The most remarkable effect is a reduction in the resistivity of the films thinner than 100 nm. The resistivity of ZnO:Al films fabricated by conventional sputtering increases substantially from 6.3×10^{-4} W×cm to 1.5×10^{-3} W×cm with decreasing the film thickness from 100 nm to 20 nm, while the resistivity of ZnO:Al films with IMC buffer layers is low of 2.8-3.2×10^{-4} W×cm in the thickness range 20-100 nm. The role of impurity here is to suppress the nucleation and allow the crystal growth with larger grains from the very early stage of deposition.

We believe that IMC method will not only accelerate the commercialization of ZnO in optoelectronic devices but also open up a new pathway for development of other oxide semiconductors, some examples of which including In_2O_3:Sn will be presented at the conference.

[1] N. Itagaki, et al., Appl. Phys. Express 4 (2011) 011101. [2] K. Kuwahara, et al., Thin Solid Films 520 (2012) 4507.

8:40am PS1+TF-ThM3 Novel Composite Materials Fabricated by Plasma-enhanced CVD of Carboranes and Pyridine or Benzene, *Robinson James, U. Chiluwal*, University of North Texas, *E. Echeverria*, University of Nebraska-Lincoln, *R. Gapfizi, J. Tae*, University of North Texas, *P.A. Dowben*, University of Nebraska-Lincoln, *J.A. Kelber*, University of North Texas
Altering the electronic structure of carborane-derived boron carbides by incorporating aromatic compounds is of scientific and technological interest in neutron detection and microelectronics. The fabrication of novel composite materials derived from ortho-carborane or meta-carborane with benzene or pyridine by plasma enhanced chemical vapor deposition (PECVD) at room temperature may lead to improved device performance over conventional boron carbides. The chemical composition and electronic structure of the resulting films were studied using in-situ x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) respectively. XPS of composite films of carboranes with pyridine shows the evidence of B-N bond formation during the PECVD process. Pyridine incorporation in the boron carbide materials resulted in the improved adhesion of physical vapor deposited Cu (PVD Cu) overlayers on the surface. XPS indicates that no thermal induced diffusion/dewetting of Cu was observed in the ortho-carborane and pyridine composite films even after annealing up to 1000K in UHV. In contrast, pure boron carbide films exhibited poor adhesion of Cu overlayers on the surface resulted in the significant dewetting during 400-

600 K annealing although no diffusion of Cu was observed even after annealing up to 1000 K. Composite films of ortho-carborane or meta-carborane with benzene were also grown on Si substrates by PECVD. These carborane: benzene composite films exhibit augmented B-C bond formation due to linking of benzene with the icosahedral carborane units as evidenced by XPS.

9:00am PS1+TF-ThM4 Engineering High-k Dielectric Gate Stacks using *In Situ* Spectroscopic Ellipsometry, *Yuanxia Zheng*, Penn State University, *G.B. Rayner,* Kurt J. Lesker Company, *A. Agrawal, S. Datta, R. Engel-Herbert*, Penn State University

The development of Ge-based field effect devices requires the integration of a high quality dielectric that forms an electrically well behaved semiconductor dielectric interface. Although GeO_2/Ge has been found promising, the thermodynamic instability as well as the relatively low dielectric constant of GeO_2 requires an alternative approach. The utilization of an ultrathin Si layer to move the semiconductor/dielectric interface from Ge into Si has been successfully demonstrated; however, the introduction of a planar thin layer into the gate stack is incompatible with a 3D FinFET manufacturing process flow. It is thus desirable to develop a multilayer gate stack by atomic layer deposition process, where an ultrathin GeO_2 layer can be thermodynamically stabilized and combined with a high-k dielectric film to meet the stringent requirement of low interface trap density and large capacitance density while maintaining a low gate leakage.

In this talk, we will present an approach of developing a multilayer gate-stack of HfO_2/Al_2O_3/GeO_2 for Ge using in-situ processing control in plasma-enhanced atomic layer deposition (PEALD) by utilizing real-time monitoring capabilities of in-situ spectroscopic ellipsometry (SE). Pristine Ge-surface is obtained by removing native GeO_x using H-plasma and an ultrathin GeO_2 layer is grown thereafter by O-plasma anneal; in-situ SE is used to monitor the process and to control GeO_2 thickness. An ultrathin bilayer of alumina and hafnia is subsequently grown using thermal ALD and large capacitance densities with equivalent oxide thicknesses (EOT) below 1 nm and gate leakages below 1×10^{-4}A/cm^2 at -1V (EOT=0.7 nm) are demonstrated. The impact of the thickness of the individual dielectric layers on interface trap density, determined by the conductance and the Terman method, leakage current and EOT is discussed. We will further discuss how in-situ SE is used to optimize process-relevant parameters for native oxide etching, intentional oxidation and deposition of high-k dielectrics. The potential of this in-situ real-time process metrology is projected for the development of high quality high-k dielectrics on other high mobility low band gap semiconductor materials.

9:20am PS1+TF-ThM5 Impact of Low Frequency Addition to RF Power in PECVD Process: Case of TiN and GeTe, *Christophe Vallee*, *F. Piallat, M. Aoukar, P.D. Szkutnik*, LTM - CEA/LETI, France, *R. Gassilloud, P. Noé, P. Michallon*, CEA, LETI, MINATEC Campus, France

In Dual Frequency plasma etching, one frequency is chosen to be much higher than the other in order to achieve an independent control of ion bombardment and electron density (i.e. ion flux). It is assumed that high frequency control the density and low frequency (LF) the energy. Recently, many groups have simulated the effect of LF addition to RF source. Depending on the model, it has been reported that the plasma density may be reduced due to sheath width variation as well as it may be increased due to highly energetic secondary electrons. Donko *et al* have shown how the γ coefficient of the secondary electrons may be used to interpret contradictory published papers [1] and they concluded that there is only a small pressure process window for which the effect of secondary electrons on the ionization compensates the effect of the frequency coupling.

The interest of adding LF to RF plasma in order to enhance the deposition reaction mechanisms is demonstrated here. An in depth investigation of plasma by Optical Emission Spectroscopy shows that the plasma density increases when adding LF (350 Khz) in a RF (13.56 Mhz) metal deposition process. In this case, the plasma enters a γ-mode due to secondary electron heating. This mode is not obtained when depositing semiconductors (GeTe) or dielectric, i.e. depending on the biased nature of the surface of showerhead electrode during the process. Adding LF to RF also modifies the sheath thickness of the plasma and increases the electron temperature of the gas [2]. In our experiments, all the deposited materials show different properties and new emission peaks are observed by OES for all precursors. Carbon content, density and growth rate are strongly modified by adding LF. For example, in case of TiN we found that the deposition rate is increased by a factor of two while in the same time the resistiviy is strongly reduced (50%) and the density is going from 3.4 to 3.8 g.cm^{-3}[3]. We also studied the plasma impact on the Equivalent Oxide Thickness (OET) regrowth of a TiN/HfO_2 integrated MOS capacitors. For phase change material (PCM) applications, very different cycles (amorphous to crystalline) are observed for devices with RF GeTe or LF+RF GeTe. All the deposition processes are performed in 200 (GeTe) and 300 mm (TiN)

pulsed liquid injection PEMOCVD chambers from AltaCVD Advanced Materials™, located in CEA-LETI cleanroom.

[1] Z. Donkó, *et al*, Appl. Phys. Lett. **97** (2010) 081501

[2] W-J Huang *et al*, Phys. Plasmas **16** (2009) 043509

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11:00am PS1+TF-ThM10 Surface Reactions during Ammonia-Plasma-Assisted Atomic Layer Deposition of Silicon Nitride, *Dennis Hausmann*, Lam Research Corporation, *R. Ovanesyan, S. Agarwal*, Colorado School of Mines

The advent of FinFETs with high-aspect-ratio 3-D geometries increases demands on conformality of the SiN_x films. These stringent requirements on conformality and low thermal budget can be simultaneously met using atomic layer deposition (ALD). While there are a few reports in the literature that show that SiN_x can be conformally deposited via ALD at <400 °C, these films are not sufficiently dense to serve as moisture or oxidation barriers. Hence, improvements in this area are needed via a fundamental understanding of the surface reaction processes. Recently, we have developed a novel ALD processes for the growth of Si_3N_4 thin films using trisilylamine (Si(NH_3)_3, TSA) and silane precursors, and an NH_3 plasma. This ALD process with TSA provides dense films with a conformal coverage over aspect ratios typical for the applications; 10:1. To understand the underlying film growth mechanism, the specific surface reactions involved during each half-reaction cycle of this ALD process were monitored with *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. ZnSe internal reflection crystals were used as substrates since ZnSe is transparent in the infrared up to 700 cm^{-1}. This spectral range, combined with the high sensitivity achieved with ATR-FTIR spectroscopy, allows us to identify and monitor in real time the different surface species generated and consumed due to sequential exposure of the growth surface to Si-containing precursors and an NH_3 plasma. The vibrational modes that were monitored include the surface SiH_x and NH_x stretching modes in the 2100 and 3400 cm^{-1} region, respectively, and Si_3N_4 phonon modes, which appear in the 800-900 cm^{-1} region. The corresponding surface reaction products were monitored using quadrupole mass spectrometry. Further, these films were extensively characterized using a suite of *ex situ* diagnostic tools.

11:20am PS1+TF-ThM11 Plasma Assisted Atomic Layer Epitaxy of III-N Ternaries for Next Generation Devices, *Neeraj Nepal*, *J.K. Hite, V.R. Anderson, V.D. Wheeler, S. Qadri, C.R. Eddy*, Naval Research Laboratory

III-Ns (InN GaN and AlN) and their alloys have been attractive semiconductor materials for application in a wide range of device technologies. The most common growth methods of this material system are CVD and MBE, but these conventional growth techniques have challenges in achieving alloys without phase separation over the entire stoichiometric range, ultimate thickness control at the atomic level, and the ability for *in situ* growth of complete device structures. Plasma-assisted atomic layer epitaxy (PA-ALE) is a promising method to grow III-N alloys and incorporate them into device structures as it allows low temperature growth and precise control of thickness, stoichiometry and uniformity. Recently, PA-ALE has been used for the growth of III-N binaries at low temperatures (≤500°C)[1,2]. Ternary growth at these low temperatures could eliminate miscibility gaps, which has been an issue for conventional growth methods.

We present the growth and characterization of III-nitride ternaries by PA-ALE over a wide stoichiometric range including the range where phase separation has been an issue for MBE and CVD. Using our previously reported optimal growth conditions for GaN, InN [1], and AlN [2], $Al_xGa_{1-x}N$, $In_xAl_{1-x}N$ and $In_xGa_{1-x}N$ (0≤x≤1) alloys were grown at 250–500 °C. Group III-B metal contents in these alloys were varied with binary cycle ratios and the alloy compositions were determined by XPS and XRD and reflectivity measurements. Since the growth rate (GR) of InN is slower than that of AlN, a digital alloy produced from 3 cycles of InN for every cycle of AlN results in an $Al_{0.83}In_{0.17}N$ film. The GaN GR, however, is slower than InN, and $In_{0.54}Ga_{0.46}N$ alloy was grown for every alternating cycle of GaN and InN. Additionally, 4 cycles of GaN for every cycle of AlN gave $Al_{0.5}Ga_{0.5}N$ alloy and the measured concentration was confirmed optically. By this digital alloy growth method, we are able to grow In containing ternaries by PA-ALE in the spinodal decomposition region (15-85%). The surface roughness of III-N alloys on GaN were the same as the starting roughness of 0.4 nm. Optimal ternary growth conditions were used to synthesize III-N based device structures on GaN and demonstrated 2DEG at the interface. We will present electrical and optical data on ALE III-N heterojunctions on GaN templates.

These early efforts suggest great promise of PA-ALE for addressing miscibility gaps issue encountered with conventional growth methods and realizing high performance optoelectronic and electronics devices involving ternary/binary heterojunctions, which are not currently possible.

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[2] N. Nepal et al., APL **103**, **0**82110 (2013).

11:40am PS1+TF-ThM12 Plasma-enhanced Atomic Layer Deposition: Prospects and Challenges, *Hyungjun Kim*, Yonsei University, Korea
INVITED

Due to various benefits such as atomic level thickness control and excellent conformality, atomic layer deposition (ALD) is expected to play an important role in future device fabrication. Especially, plasma enhanced ALD (PE-ALD) allows deposition at significantly lower temperatures with better film properties than conventional thermal ALD. This low temperature process makes PE-ALD more attractive for emerging nanoscale device fabrication. In addition, since ALD is surface-sensitive deposition technique, surface modification by plasma exposure can be used to alter nucleation and adhesion. In this presentation, the basic characteristics and several examples of PE-ALD processes for various applications such as semiconductor/display devices fabrication will be presented. The PE-ALD is a valuable tool to deposit very thin metal layers with good properties including little nucleation delay and high purity. Co, Ni, Ru films with good conformality was deposited by PE-ALD using NH3 plasma. Film properties as well as applications for emerging electronic devices of the metal PE-ALD will be discussed. Also, the use of plasma for ALD enables improvements in electrical properties of next generation semiconductor devices. Various high k oxides including HfO2, CeO2, La2O3 and doped high k oxides were deposited by PE-ALD from metal organic precursors and oxygen plasma. Especially, comparative study between PE-ALD and thermal ALD has shown that the interface defect density and leakage current are better for PE-ALD. Also, PE-ALD of ZnO thin films was investigated for thin film transistors. We studied the modulation of device parameters of PE-ALD ZnO based TFTs using UV light exposure. Finally, PE-ALD TiO2 thin films have shown high photocatalytic effects on various substrates. These indicate that the PE-ALD processes are versatile methods enabling nano scale manufacturing in emerging applications.

Plasma Science and Technology
Room: 308 - Session PS2+TF-ThM

Atomic Layer Etching (ALE) and Low-Damage Processing

Moderator: Geun Young Yeom, Sungkyunkwan University, Republic of Korea

8:00am PS2+TF-ThM1 Fluorocarbon Assisted Atomic Layer Etching of SiO$_2$ and Selectivity over Si Using Cyclic Ar/C$_4$F$_8$ Plasma, *Dominik Metzler**, University of Maryland, College Park, *S.U. Engelmann, R.L. Bruce, E.A. Joseph,* IBM T.J. Watson Research Center, *V.A. Godyak,* University of Michigan, *G.S. Oehrlein*, University of Maryland, College Park

There is great interest in establishing directional etching methods capable of atomic scale resolution for fabrication of highly scaled electronic devices. Recently, controlled etching of SiO$_2$ at the Angstrom-level based on steady-state Ar plasma, periodic injection of a defined number of C$_4$F$_8$ molecules, and synchronized plasma-based Ar$^+$ ion bombardment has been shown [1]. Controlled etching is based on deposition of a thin (~ several Å) reactive fluorocarbon (FC) layer on SiO$_2$ enabled by precise C$_4$F$_8$ injection. For low energy Ar$^+$ ion bombardment conditions, the physical sputter rate of SiO$_2$ vanishes, whereas SiO$_2$ can be etched when FC reactants are present at the surface. In this work, plasma conditions have been characterized in real time during cyclic exposure using a Langmuir probe. Changes in plasma potential, electron density, and electron temperature are measured throughout each cycle and compared to continuous precursor addition. Continuous precursor addition has a higher C$_4$F$_8$ concentration than periodic injection. The C$_4$F$_8$ injection has a short, significant impact on the plasma properties within each cycle and a small impact for longer time scales, i.e. from cycle to cycle. Observed trends in plasma properties agree with continuous precursor addition. Additionally, this cyclic approach was used to investigate the transition from SiO$_2$ to Si etching employing SiO$_2$-Si-SiO$_2$ layers. Si etching and the selectivity of SiO$_2$ over Si is investigated as a function of FC surface coverage, ion energy (20 to 30 eV), and etch step length using *in situ* ellipsometry. Time-dependent etch and deposition rates are compared for Si and SiO$_2$. The etch behavior during the cyclic approach is compared to continuous precursor addition etching of SiO$_2$ and Si. X-ray

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* Coburn & Winters Student Award Finalist

photoelectron spectroscopy is used to investigate surface chemistry at various stages of the cyclic etching and will be reported.

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8:20am PS2+TF-ThM2 Highly Selective Atomic Layer Etching of Silicon Dioxide Using Fluorocarbons, *Eric Hudson, V. Vidyarthi, R. Bhowmick, R. Bise, H.J. Shin, G. Delgadino, B. Jariwala, D. Lambert, S. Deshmukh*, Lam Research Corporation

As microelectronics advancements require smaller device features, masking layers are becoming thinner. Additionally, there are tighter requirements on allowable loss of films during processing. This leads to exacting requirements for etch, where a target film must be removed with very high selectivity to a mask and/or substrate film. For etching of SiO2 or similar materials, this high selectivity is typically achieved using very polymerizing fluorocarbon-based combinations of gases. However this approach can introduce problems with etch rate loading, such that the oxide in features with larger critical dimension (CD) tends to etch more slowly due to excessive passivation.

A novel approach for oxide etching has been developed which addresses this tradeoff between selectivity and etch rate loading. The etch process is based on repeated cycles of fluorocarbon deposition and etch reaction activation, similar to the process described by Metzler et al [1]. In each cycle there are two different phases of plasma conditions in which (1) a thin film of fluorocarbon polymer is deposited and (2) the polymer film is bombarded by noble gas ions to activate the etch reaction. Under the right conditions, oxide films are incrementally etched in each cycle. This atomic layer etch approach is less susceptible to etch rate loading because under properly adjusted conditions, the oxide etch front remains clear of polymer buildup after each cycle. Under the same conditions, polymer can build up on the mask or substrate surface with successive cycles, protecting the film and resulting in minimal loss. The process times for the deposition and activation phases of the cycle are the primary parameters for process control. A comparison of model and experiment is presented to characterize the effect of these two time parameters upon process results.

[1] Metzler, et al JVST A 32, 020603 (2014).

8:40am PS2+TF-ThM3 Electron Beam Plasma Tool for Atomic Precision Etching, *Leonid Dorf, S. Rauf, M.-F. Wu, Y. Zhang, F. Tavassoli, K. Ramaswamy, K. Collins*, Applied Materials Inc.

As the node size diminishes, microelectronics fabrication progressively requires atomic layer precision, so it becomes critical to accurately control ion energy during plasma processing. Damage caused by conventional plasma technologies (capacitively or inductively coupled plasmas) is becoming unacceptable for critical etch and clean applications. Using electron sheet beam parallel to the substrate surface to produce plasma in a processing chamber provides an order of magnitude reduction in electron temperature T_e (~ 0.3 eV) and ion energy E_i (< 2 eV without applied bias) compared to conventional plasma technologies, thus making electron beam plasmas an ideal candidate for processing features at 5 nm and below. In this presentation, we report processing results for a range of advanced plasma etching applications tested using the electron beam generated low T_e plasma. Using patterned wafers, we have developed low-bias power (0 – 10 W) processes resulting in infinite selectivity (as per high-resolution TEM images) of silicon nitride to silicon oxide and poly-silicon in fluorocarbon based chemistries. Such high selectivity can be attributed to the two phenomena: (1) at very low bias power, ion energy is sufficiently small to allow processing near the etch threshold, and (2) plasma ions and radicals in the electron beam generated plasma are produced by highly energetic (~ 2000 eV) electrons, such that the ratio between dissociation and ionization cross-sections for most gases differs considerably from that in conventional tools with chemical processes determined by 10-15 eV electrons. The latter results in weak dissociation of the fluorocarbon gas (CH$_2$F$_2$) and relatively low free fluorine concentration, which in turn leads to very low silicon etch rate. We have also investigated a nitride spacer application, in which 20 nm nitride layer deposited conformly over a silicon fin needs to be etched away to produce straight side walls for further double patterning (as one application). Our results indicate that using the electron beam plasma provides suitably small footing with a reasonably small slant angle of the shoulder, at the same time being selective to the underlying silicon layer. Accurate analysis of several time-series of TEM images allowed characterization of lateral and vertical etch processes over a range of operating conditions, such as the bias power and the beam current. Initial studies also indicate excellent loading characteristics, even at high bias

power, which again can be attributed to unique chemical composition of the processing gas in the electron beam generated plasma.

9:00am PS2+TF-ThM4 Precise Theoretical Calculation of Neutral Beam Generation Efficiency by Collision of Chlorine Against Graphite Surface, *Tomohiro Kubota*, Tohoku University, Japan, *N. Watanabe, S. Ohtsuka, T. Iwasaki, K. Ono, Y. Iriye,* Mizuho Information & Research Institute, Japan, *S. Samukawa*, Tohoku University, Japan

We investigated the generation mechanism of neutral particles in high efficiency neutral beam source developed by Samukawa et al [1], by collision of positive and negative chlorine ions against graphite surface. It is already known experimentally that neutralization efficiency of negative ion (Cl⁻) is much higher than that of positive ion (Cl_2^+) [2]. However, the mechanism has not been clarified. Recently we investigated the neutralization mechanism by using numerical simulations based on quantum mechanics [3] and succeeded in explaining higher neutralization efficiency of negative ions than positive ions.

In this study, collision process of a chlorine particle (Cl, Cl⁻, Cl_2, or Cl_2^+) against graphite surface was simulated by calculation based on time-dependent density functional theory (TD-DFT). Neutralization efficiency was calculated from the number of the valence electrons on the particle after the collision. By using a unit cell with enough size, dispersion of electron density into vacuum was suppressed and quantitative interpretation became possible.

Also, dependence on incident angle and energy of the particle was investigated. It was found that experimental result of energy dependence of the neutralization efficiency was quantitatively reproduced by the calculation. It suggests we have achieved a precise simulation of the neutralization process.

A part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

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9:20am PS2+TF-ThM5 Achieving One Tenth of a Nanometer Precision in Etching of SiO₂ Over Silicon: Challenges and Opportunities, *Gottlieb Oehrlein*, University of Maryland, College Park **INVITED**

We discuss use of low pressure plasma surface interaction mechanisms aimed at achieving atomic scale precision in etching materials. Using a steady-state Ar plasma in conjunction with periodic injection of a defined number of C_4F_8 molecules and synchronized plasma-based Ar⁺ ion bombardment, we have shown that one tenth of a nanometer precision in etching of SiO_2 is possible.[1] For low energy Ar⁺ ion bombardment conditions giving a maximum ion energy of about 20eV, the physical sputter rate of SiO_2 vanishes whereas for an FC-coated SiO_2 surface, chemical modifications of the SiO_2 surface take place and SiO_2 etching is initiated. Precise management of C_4F_8 supply enables control of the deposited fluorocarbon (FC) layer thickness in the 1 to several Ångstrom range. We will discuss the temporal variation of the chemically enhanced etch rate of SiO_2 for Ar⁺ ion energies below 30 eV as a function of fluorocarbon surface coverage which enables controlled removal of Ångstrom-thick SiO_2 layers per process cycle. We will also discuss silicon underlayer etch rate measurements and challenges connected with this approach.

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* Based on collaborations with D. Metzler, C. Li, S. Engelmann, R. Bruce, E. Joseph, E. Godyak, and M. Kushner. We gratefully acknowledge funding from National Science Foundation (CBET-1134273) and US Department of Energy (DE-SC0001939).

11:00am PS2+TF-ThM10 Numerical Simulation of Atomic Layer Etch via FPS3D, *Paul Moroz*, Tokyo Electron US Holdings

Atomic layer etching (ALE) and atomic layer deposition (ALD) are becoming more attractive processing methods primarily due to their higher control of profiles and less induced damage to materials. They require multi-step processing, with each time-step having its own chemistry, incoming fluxes, and energy distribution of species. In this work, we simulated ALE of Si by employing a cycle of two main steps: chlorination of Si surface layer by Cl2 gas and then removal of the chlorinated layer with Ar neutral beam of low energy and narrow energy spectrum, so the sputtering of Si could be neglected. Feature scale simulator FPS3D [1,2] is

well designed for the multi-step operations and allowed us to replicate main results of the corresponding experiments [3]. Each step in ALE processing was self-limiting, and we have used the same conditions and parameters as reported for the experiment. The intermediate gas-purge steps were excluded, as simulations allow instantaneous change of chemistry and fluxes, which is not possible in actual processing. We will demonstrate simulation of ALE processing with clear time resolution of chlorination and removal steps and with etch rate corresponding to experiments.

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11:20am PS2+TF-ThM11 Low Damage Etch Residue Removal of CoFeB Material using CO/NH₃ Reactive Ion Beam for STT-MRAM Device, *MinHwan Jeon*, K.C. Yang, D.H. Yun, J.Y. Youn, G. Yeom, Sungkyunkwan University, Republic of Korea

Spin transfer torque magnetic random access memory (STT-MRAM) is a promising candidate for the next generation memory device due to high density, nonvolatile storage, fast switching speed, etc. comparing to conventional memory devices. For the nano scale STT-MRAM device fabrication, the dry etch process is one of the critical issues due to difficulty in the formation of volatile compounds between MTJ materials such as CoFeB, CoPt, MgO, NiFe and etch gases. The MTJ materials have been etched using conventional reactive ion etching (RIE) system with noncorrosive gases such as CO/NH₃, CH₃OH so as to increase the volatile compounds. However, the relatively low etch selectivity over hard mask material and etch residue still remain on the etched pattern sidewall. In this study, reactive ion beam etching (RIBE) system has been applied to effectively remove the etch residues remaining after the main etch of CoFeB material in the conventional ICP system. The CO/NH₃ gas mixtures was also used for the removal of the etch residues on the sidewall of etched MTJ features. After the optimized RIBE, the etch residue was effectively removed, the surface composition was restored, and the surface roughness of the etched CoFeB thin film after the etching in the RIBE system was decreased indicating the effective removal of redeposited etch residue by the RIBE. The other characteristics of CoFeB substrate after the residue removal by the RIBE were also investigated and will be reported in the presentation.

11:40am PS2+TF-ThM12 Effects of Cryogenic Cooling on Gallium Nitride Film in Argon Plasma, *Daisuke Ogawa*, Y. Nakano, K. Nakamura, Chubu University, Japan

We have developed the technique to reduce the damage that is induced by argon plasma to the surface of a gallium nitride (GaN) film. Our technique especially reduces the damage relating to the band gap more than 2.5 eV. Our in-situ monitoring showed that a GaN film cooled with liquid nitrogen (LN₂) has a different pattern of the damage induced by the plasma.

In order to make the in-situ monitoring of the GaN surface, we made real-time measurements with photoluminescence (PL) spectrum emitted from the GaN film. Here, the GaN film was excited with a light illumination generated from a xenon lamp passing through a 313 nm band pass filter. This configuration allows us to monitor the volume-averaged material condition from the surface to ~75 nm depth. M. Chen previously found that the ratio of the blue luminescence (BL) band over the near-band edge (NBE) band is effective to make the in-situ monitoring of the damage induced by plasma.[1] The ratio basically gets larger as the film gets more damages. However, our result showed that the ratio stayed almost constant only when the film was cooled with LN₂. This means that the damage induced by the argon plasma was likely avoided by using LN₂ cooling.

To find the effect of the cooling with LN₂, we made X-ray photoelectron spectroscopy (XPS) measurements for three samples (pristine, LN₂, and no LN₂) after the plasma exposures. We sputtered the film with argon ion beam for 3 minutes in vacuum every cycle of the XPS measurements to obta in the depth profile. The XPS spectrum from the GaN film that was exposed in argon plasma *with LN₂ cooling* was matched well with the spectrum from the pristine GaN film after the first sputtering. On the other hand, the XPS spectrum from the GaN film that was exposed in argon plasma *without LN₂ cooling* showed a chemical shift at the gallium line and a decrease at a nitrogen line. All three spectra matched well after the second sputtering. This profile indicates that the plasma-damaged layer thicker than ~30 nm was formed in the case of no LN₂ cooling. (Assumed the sputtering rate at 5 nm/min.)

Our in-situ temperature monitoring on the GaN surface that was exposed in the argon plasma showed that the temperature stayed below 150 ° C with LN₂ while the temperature exceeded over 300 ° C without LN₂. This is the indication that we should be able to reduce the damage by controlling the GaN film temperature during the plasma processing.

In this presentation, we will show the evolution of the PL spectrum, connecting with the surface temperature, XPS results supporting with more details.

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Surface Science
Room: 309 - Session SS+TF-ThM

Organic Layers on Surfaces
Moderator: Edmund Seebauer, University of Illinois at Urbana Champaign

8:00am **SS+TF-ThM1 Orbital Tomography: Imaging the Wavefunctions of Adsorbed Molecules with Angle Resolved Photoemission**, *Michael Ramsey*, University of Graz **INVITED**
Here it will be shown that the apparently complex angular distribution of valence band photoemission can be simply and quantitatively predicted from a Fourier transform of initial state wavefunctions. This will be demonstrated for a variety of orbitals of the proto-typical pi conjugated molecules pentacene, sexiphenyl and PTCDA on a number of substrate surfaces. For adsorbate monolayers it will be shown how this orbital tomography can be used to determine molecular geometries, unambiguously determine the orbital energy ordering, gain insight into the nature of the surface chemical bond and image the orbitals in real space.

8:40am **SS+TF-ThM3 Chemical Pathways for Surface Functionalization: From Surface-"Stapled" Nanostructures to Layered Materials**, *Andrew Teplyakov*, University of Delaware
One of the important venues in designing novel interfaces and materials is based on the complementary functionalization of surfaces, modified molecules, and nanostructures, so that combining them would lead to layers and materials with novel chemical and physical properties. This presentation will focus of the molecular-level view of surface functionalization and extending the molecular approach to nanostructures and nanostructured layers with three-dimensional control. Classical organic reactions will be used to first build a nearly perfect layer of chemically functionalized nanoparticles on a flat surface and then the approach will be extended into the third dimension. The work will combine "click chemistry" with chemical functionalization approach and utilize surface analytical techniques including XPS, infrared spectroscopy, microscopic techniques combined with focused ion beam (FIB) sample preparation and will be complemented with the DFT studies. The spectroscopic techniques combined with DFT modeling will support the chemistry of deposition, while the electron microscopy techniques will confirm the growth of layered structures.

9:00am **SS+TF-ThM4 Observation and Trapping of Organic Reaction Intermediates for the Reaction of $O(^3P)$ with Oligo(Phenylene Ethynylene) Thiolate Self Assembled Monolayers on Au(111)**, *Wenxin Li*, G. Langlois, N.A. Kautz, S.J. Sibener, The University of Chicago
We have taken steps to develop a methodology for observing and trapping organic reaction intermediates by exposing well-ordered self assembled monolayers (SAM) to supersonic beams of atomic oxygen. The use of a SAM stabilizes highly energetic intermediates formed from bimolecular reactions at the interface due to rapid thermal equilibration with the SAM matrix. In this presentation we will discuss the elucidation of the mechanistic details for the fundamental reaction between $O(^3P)$ and alkyne bonds by monitoring chemical and structural changes in an oligo(phenylene ethynylene) SAM reacting with $O(^3P)$ under collision conditions having specified initial reaction orientation. Utilizing time-resolved reflection-absorption infrared spectroscopy (RAIRS) and scanning tunneling microscopy (STM) under ultrahigh vacuum conditions, we have directly observed electrophilic addition of $O(^3P)$ onto the alkyne moieties, resulting in formation of a ketene intermediate via phenyl migration. Under single-collision conditions in the gas phase the vibrationally-excited ketene intermediate cleaves to release CO. In contrast to this, herein we have directly observed the formation of the condensed-phase stabilized singlet ketene by RAIRS. Moreover, we have also observed that the phenyl ring at the vacuum/film interface significantly cants towards the substrate plane as a result of this reaction. STM images of the SAM taken before and after $O(^3P)$ exposure show an expansion of the ordered lattice resulting from formation of the new nonlinear molecular structures within the adsorbed film. This approach of using pre-oriented reactive molecules in ordered self assembled monolayers in combination with angle and velocity selected energetic reagents provides a general approach for probing the geometric constraints associated with the reaction dynamics for a wide range of chemical reactions.

9:40am **SS+TF-ThM6 Relative Stability of S-Au and Se-Au Bonding in Aromatic and Aliphatic Self-Assembled Monolayers – Exchange and Ion Desorption Experiments**, *Jakub Ossowski*, *A. Noworolska*, Jagiellonian University, Poland, *S. Schuster*, University of Heidelberg, Germany, *J. Rysz*, Jagiellonian University, Poland, *A. Terfort*, University of Frankfurt, Germany, *M. Zharnikov*, University of Heidelberg, Germany, *P. Cyganik*, Jagiellonian University, Poland
Self-assembled monolayers (SAMs) are considered a model system in many areas on nanotechnology.[1] However, potential use of SAMs strongly depends on stability of their chemical bonding to the substrate. Most of the studies of SAMs have been performed using S-Au bonding.[1] More recently the Se-Au bonding is considered as an interesting alternative. However, as documented by the recent review,[2] there is still missing information which of these head group provides higher stability binding to the Au(111) substrate and whether or not this relative stability depends on the type of molecular backbone i.e. aliphatic or aromatic. A meaningful comparison of S-Au and Se-Au stability requires that respective molecules not only have the same carbon backbones, but also should form ordered structures with very similar molecular packing. Only under such conditions, not fulfilled by the most of previous studies, the contribution of the molecule-substrate bonding on the film stability can be elucidated. Following this idea, we will present a new data obtained for naphthalene based SAMs bound to the Au(111) substrate via S or Se atoms.[3] After presenting detailed microscopic (STM) and spectroscopic (XPS, NEXAFS) characterization of these SAMs, which exhibit very similar well-ordered structure, we will show results of two independent experiments probing the stability of their bond to the Au(111) substrate using an exchange method as well as ion-induced desorption (SIMS). We will compare these results with our previous exchange[4] and recent ion-desorption experiments[5] of aliphatic based systems. Irrespective of the type of molecular backbone our results clearly demonstrate much higher stability of the Se-Au bond as compared to the S-Au bond.

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11:00am **SS+TF-ThM10 CuPc:C_{60} Composite Films: From Sub–Monolayer to Multi-Layer Growth**, *Taylor Stock*, *J. Nogami*, University of Toronto, Canada
CuPc:C_{60} composite films of various compositions and thicknesses grown on the Cu(111) surface have been studied using room temperature scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). At coverages below two monolayers (ML), phase segregated, ordered films, or well mixed, disordered films can be produced depending on the particular deposition sequence. This compositional variability is achieved by exploiting the differences in the relative strengths of the various molecule-substrate and molecule-molecule interaction forces. In thicker films, the CuPc-C_{60} intermolecular interaction dominates the growth, and for a range of concentrations these films are found to be well mixed, amorphous and thermally stable. These results provide a rationale for improvements that have been seen for organic light emitting diode (OLED) performance associated with C_{60} doping of CuPc molecular layers. [1]

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11:20am **SS+TF-ThM11 2D Co-Crystallization of Organic Ferroelectrics**, *Axel Enders*, *D.A. Kunkel, A. Sinitskii*, University of Nebraska-Lincoln, *S. Simpson*, University at Buffalo-SUNY, *J. Hooper*, Jagiellonian University, Poland, *E. Zurek*, University at Buffalo-SUNY
We will present an experimental study on the self-assembly and electronic properties of the organic ferroelectrics, croconic acid (CA), 3-hydroxyphenalenone (3-HPLN), and the related compound rhodizonic acid (RA) on crystalline metal surfaces. Importantly, the bond polarization of the selected organics is highly planar. This provides the foundation for the development of 2D polarization patterns by design, including rather complex ones like the honeycomb pattern recently discovered by our group [1]. What is remarkable about those honeycomb networks of CA, is that the

interaction with the substrate is key to ferroelectric switching barriers. Also the structurally related 3-HPLN forms linear chains on surfaces that are expected to exhibit 2D polarization ordering within the plane of the 2D organic layer. The molecular arrangement can be manipulated through the use of the substrate and growth conditions, and we have also identified a new, chiral phase of hydrogen-bonded trimers of 3-HPLN. This surface-science approach was key to the first reported synthesis of RA crystalline structures [2]. Here we present an overview over the structural phases of select organic ferroelectrics on surfaces and how ordered 2D polarization states can emerge. Importantly, we discovered by co-deposition of CA and 3-HPLN that they form ordered 2D co-crystalline phases.). The structure of the resulting networks can be tuned by varying the relative concentration of the organics. Namely, for equal ratios of CA and 3-HPLN two polymorphs are observed, while for 2/1 CA/3-HPLN ratio, only a single structure is found. Transitions from CA rich structures to CA poor structures can be induced through weak annealing, in which the smaller CA desorbs before 3-HPLN. We expect that important ferroelectric properties of organic ferroelectrics, such as their ordering temperature and switching fields, can be manipulated through co-crystallization. We will highlight how surface science studies, specifically STM, can help accelerate co-crystal discovery.

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11:40am **SS+TF-ThM12 Phenol Adsorption on TiO$_2$(110): Evidence for Temperature Dependent Radical Formation**, *Matthew Patterson, M.F. DiTusa, C.A. Thibodeaux,* Louisiana State University, *RW. Hall,* Dominican University of California, *O. Kizilkaya, R.L. Kurtz, E.D. Poliakoff, P.T. Sprunger*, Louisiana State University

We have examined the electronic structure of phenol on rutile TiO$_2$(110) using angle resolved photoelectron spectroscopy (ARPES), electron energy loss spectroscopy (EELS), and density functional calculations on model phenoxy/TiO$_2$ clusters. Previous electron paramagnetic resonance studies have shown that exposure of titania powder to phenol at 250°C results in the formation of environmentally persistent free radicals(EPFRs), which have lifetimes on the order of dozens of hours and have been shown to exacerbate negative health effects caused by particulate matter. The proposed chemisorption model of radical formation from aromatic species on metal oxides involves electron transfer from the adsorbed organic to the metal oxide, locally reducing the oxide. Resonant ARPES shows direct evidence of charge transfer from high-temperature adsorbed phenol to electronic states of TiO$_2$ (110) usually associated with the accumulation of charge at surface oxygen vacancies, providing direct evidence of the hypothesized reduction mechanism. Electronic EELS reveals there is an associated decrease of phenol HOMO-LUMO gap. Electronic structure calculations using model phenoxy-TiO$_2$ clusters give insight into the changes induced in the occupied molecular orbitals of the chemisorbed phenoxyl radical. Results will be discussed in light of other metal oxide systems

12:00pm **SS+TF-ThM13 Adsorption behavior of Zinc Tetraphenylporphyrin Molecules on a Au(111) Surface**, *Charles Ruggieri, S. Rangan, R.A. Bartynski, E. Galoppini*, Rutgers, the State University of New Jersey

The interaction between Zinc Tetraphenylporphyrin (ZnTPP) molecules and the Au(111) surface is investigated using scanning tunnel microscopy (STM), from initial adsorption sites to monolayer organization, with a particular emphasis on its relation to the surface atomic structure and reorganization. When adsorbed at room temperature, ZnTPP molecules initially decorate step edges at low coverage. As the coverage approaches 0.5 monolayer (ML), ZnTPP molecules self-organize into islands of molecules in a rectangular array that is in registry with the underlying Au(111) lattice. The molecules are oriented with their macrocycles parallel to the surface, and form islands in areas delimited by herringbone reconstruction domain walls. As the coverage approaches one ML, the adsorption geometry of the self-organized molecular layer can be fully characterized with respect to the atomic structure of Au(111) surface atoms. Moreover, ZnTPP adsorption alters the Au(111) herringbone reconstruction domain size, most likely caused by anisotropic adsorbate-induced surface stress. However, when a monolayer is prepared from desorption of a ZnTPP multilayer, a different molecular organization is observed at the surface. It is proposed that this reconstruction is enabled by the particular reconstruction of the Au(111) surface. In this configuration, the domain size of the Au reconstruction is closer to that of clean Au, due to smaller adsorbate-induced surface stress.

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

Advanced CVD and Chemical Vapor Infiltration Methods
Moderator: Robert Davis, Brigham Young University

8:00am **TF+PS-ThM1 Industrializing Single Wall Carbon Nanotubes by Water-Assisted CVD**, *Don Futaba*, AIST, Japan **INVITED**
Since the discovery of the carbon nanotube (CNT) 20 years ago, extensive effort has been made to utilize their exceptional intrinsic properties toward industrial applications. However, availability has significantly thwarted these endeavors. In one section of my presentation, I will describe our efforts toward the economical mass-production of single-walled carbon nanotubes (SWCNT) based on the water-assisted chemical vapor deposition technique, from which highly efficient synthesis of vertically aligned SWCNTs grow from substrates (SWCNT forests). These SWCNT forests form through the self-assembly of individual SWCNTs when grown in sufficient density and have been shown to be useful templates for various applications from energy device electrodes to MEMS materials due both the continuous nature and high porosity. Further, I will describe the forest, and present a few examples of how we have infiltrated these material to create a new material with enhanced properties.

8:40am **TF+PS-ThM3 Organoboranes as Single Precursors for Low Temperature CVD of Boron Carbide Thin Films for Neutron Detectors**, *M. Imam,* Linköping University, Sweden, *C. Höglund,* European Spallation Source (ESS AB), *J. Birch, Henrik Pedersen*, Linköping University, Sweden
The world-wide shortage of the ^{3}He isotope has led to a need for novel designs of neutron detectors. A detector based on the isotope ^{10}B, in the form of thin films, has been suggested by the European Spallation Source (ESS). The detector design uses ^{10}B$_4$C films, ≥1 μm, deposited on both sides of neutron transparent substrates such as Al blades.[1] The melting point of Al (660 °C) sets a strict upper temperature limit for CVD of the ^{10}B$_4$C films. Also, metallic Al will be badly affected by corrosive by-products, like HCl. This means that traditional B$_4$C CVD routes based on BCl$_3$ and CH$_4$ cannot be used. An alternative CVD route is to use oragnoboranes, i.e. molecules with direct B-C bonds, as such molecules are very reactive and do not produce corrosive by-products.

We have demonstrated the synthesis of thin, X-ray amorphous, boron-carbon films at low temperature (400-600 °C), by thermally activated CVD using triethylboron, B(C$_2$H$_5$)$_3$, (TEB) as single precursor on both single crystalline Si (100) and Al substrates.[2] Films with B/C-ratio of 4.6 with density 2.42 g/cm^3 (bulk B$_4$C density 2.52 g/cm^3) and 3.6 with density 2.14 g/cm^3 were deposited at 600 °C in hydrogen and argon ambient respectively, the impurity levels in the films was about 4 at.% of H at 600 °C. Further studies of TEB as precursor at higher temperatures (700-1200 °C) on Si substrates show that films with a B/C ratio of 4.5 and 3 were obtained from films deposited at 700 °C in hydrogen and argon ambient respectively with < 0.24 at.% of H. A threshold temperature of 1000 °C for the deposition is identified above which the B content decreases dramatically. Based on our results, a chemical mechanism for boron-carbon films from TEB, where the TEB molecule is decomposed to BH$_3$ and hydrocarbons, is suggested.

Plasma Enhanced CVD using trimethylboron, B(CH$_3$)$_3$, (TMB) is also explored to further lower the deposition temperature. Results from CVD and PECVD will be compared with state of the art PVD of ^{10}B$_4$C.

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9:00am **TF+PS-ThM4 High-Quality ZnO Thin Films Grown by a New CVD Method using Catalytically-generated High-energy Precursors**, *T. Nakamura, Y. Ohashi, N. Yamaguchi, E. Nagatomi, T. Kato, Kanji Yasui*, Nagaoka University of Technology, Japan
ZnO is useful for many applications, and various growth techniques, including MBE [1-2], PLD [3, 4], and MOCVD [5], have been used to prepare ZnO films. Despite the advantages of MOCVD in industry, ZnO deposition by conventional MOCVD consumes a lot of electric power to react the source gases and raise the substrate temperature. To overcome this, a more efficient means of reacting oxygen and metalorganic source gases is needed.

In this paper, a new CVD method for ZnO film growth using the reaction between dimethylzinc (DMZn) and high-temperature H$_2$O produced by a catalytic reaction on Pt nanoparticles is presented [6]. H$_2$ and O$_2$ gases were admitted into a catalyst cell containing a Pt-dispersed ZrO$_2$ catalyst, whose

temperature increased rapidly to over 1300 K due to the exothermic reaction of H_2 and O_2 on the catalyst. The resulting high-temperature H_2O molecules were ejected from a fine nozzle into the reaction zone and allowed to collide with DMZn ejected from another fine nozzle. ZnO epitaxial films were grown directly on a-plane sapphire substrates at substrate temperatures of 773-873 K with no buffer layer. Growth rates were 0.02-0.13 μm min^{-1}, and film thicknesses were 2-8 μm. X-ray diffraction patterns exhibited intense (0002) and (0004) peaks. The smallest FWHM value of the ω-rocking curve of ZnO(0002) was less than 0.1° (194 arcsec). The Hall mobility and residual carrier concentration of the epilayers were in the ranges 140-197 cm^{2}V^{-1}s^{-1} and 5.8×10^{16}-6.0×10^{17} cm^{-3} at 300K, respectively. This Hall mobility is very large compared with ZnO films grown directly on sapphire by other deposition methods. PL spectra at 10 K showed a strong emission peak at 3.360 eV, attributed to the neutral donor-bound exciton D^o_x. The FWHM was as low as 0.9 meV, which is smaller than that previously reported for ZnO obtained by MBE (5.5 meV) [4], and by PLD on a sapphire(0001) substrate (1.7 meV at 2K) [3]. .

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9:20am **TF+PS-ThM5 Filling High Aspect Ratio Features: A Ballistic Transport Model**, *Wenjiao Wang*, *J.R. Abelson*, University of Illinois at Urbana-Champaign

The ability to fill a high aspect ratio feature with a thin film material enables the fabrication of many nanoscale devices. Examples include shallow trench isolation or inter-metal dielectric in microelectronics. One approach is to use chemical vapor deposition under conformal coating conditions. However, as film builds up on the sidewalls the width of the feature shrinks and the aspect ratio increases sharply. This often results in incomplete filling, leaving a narrow void or 'seam' of low-density material along the central axis. One solution is to taper the feature into a 'V' shape, such that uniform deposition causes the apex of the V to move smoothly upwards.

To achieve complete filling, the flux of deposition precursor down the axis of the feature must be sufficient to maintain a uniform growth rate. Precursor transport is typically modeled using the diffusion equation under quasi-static conditions. We show that for high aspect ratio features, *the diffusion equation significantly under-estimates the flux of material that is deposited deep in the feature*. This occurs because the diffusion formalism assumes a mean transport distance between collisions that is proportional to the feature size. However, in molecular flow some of the transport events occur at glancing angles to the feature sidewall and afford very long flight paths. These events move precursor species to the bottom of the feature, an effect that enhances filling.

We have developed a ballistic transport model based on computing the emission/capture probability between all points on the surface and coding the result as a matrix. Species transport from a starting distribution is found by matrix multiplication to afford the distribution of final positions. We first show how the results of this model compare with the diffusion formalism: the bulk of the transport is similar, but the ballistic model predicts a 'tail' of long-range events. We then simulate the filling of V-shaped features as a function of the apex angle and sticking coefficient. The result is a prediction of regimes that can afford complete filling.

Finally, we consider the effect of growth rate saturation under high precursor flux, an effect that is physically significant and vastly improves conformal growth. We derive from the ballistic model the total flux arriving at each position, and self-consistently calculate the effective sticking probability. We simulate the coating profiles on rectangular and V-shaped features and determine that rate-saturated growth conditions, in combination with long-range precursor transport, greatly expand the regime that affords complete filling.

9:40am **TF+PS-ThM6 Ozone Pretreatment's Effect on Infiltration of Carbon Nanotube Forests**, *Richard Vanfleet*, *L. Barrett, J. Rowley, K. Hinton, R.C. Davis, D.D. Allred*, Brigham Young University

Thin films deposited on carbon nanotubes (CNTs) appear to be enabling materials for a variety of applications including: capacitive and electrochemical energy storage, chromatography and filtration chemical separations media, chemical sensing, and MEMS. Using CNT forests as a substrate creates new challenges to traditional thin film deposition techniques because of the need to penetrate into the forest and the chemical inertness of the CNT surface. We have explored the effect ozone pretreatment has on film morphology in two different deposition regimes: amorphous silicon deposited by low pressure chemical vapor deposition and nickel deposited by electroplating. TEM and SEM images of the forests

after deposition show increased nucleation density on forests that were pretreated with ozone.

11:00am **TF+PS-ThM10 A Novel Gap Fill Technology to Address the Current and Future Scaling Challenges of the Semiconductor Industry**, *A. Mallick*, *Jingmei Liang*, *B. Underwood, K. Thadani, N. Ingle, T. Mandrekar*, Applied Materials Inc.

Gap fill has been a continuous challenge for the semiconductor industry driving innovation in the field of chemical vapor deposition. Applied Materials has continuously met this challenge by developing and refining CVD technologies to address the challenges of void-free gap fill in features of narrowing opening dimension and increasing aspect ratio. Technologies including Applied's HARP™ sub-atmospheric CVD and Ultima™ high density plasma established themselves as workhorses of the semiconductor industry. These technologies enabled dielectric materials including silicon dioxide, nitrides, carbides, and carbon in narrow gap. While these technologies see continued use in the manufacture of Logic and Memory device at <20nm node and below, gap fill of the narrowest and highest aspect ratio features required a new technical approach. As structure CD drops below 30nm, the sidewall angle approaches or exceeds 90° presenting a shape that promotes void or seam formation with conventional gap fill approaches including CVD and ALD.

To address these challenges Applied Materials has developed a new CVD technology we call FCVD™ to enable synthesis of high quality dielectric films including silicon oxides, silicon nitrides, silicon carbo-nitrides, silicon, low-k dielectrics, and carbon with a mechanism of film growth that promotes void-free fill irrespective of structure dimension and shape; this technology demonstrates capability to fill re-entrant structures with opening size <5nm and aspect ratio >20, flexibility to address multiple material systems and has been productized to address volume manufacturing requirements. In this paper we will demonstrate that we can achieve a void-free, profile-insensitive gap fill with multiple materials in a CVD reactor.

11:20am **TF+PS-ThM11 Comparison of Carbonaceous Thin Films Deposited on Ru-capped Multilayer Mirrors via Extreme-Ultraviolet Light and Electrons**, *Michael Barclay*, Johns Hopkins University, *N.S. Faradzhev, S.B. Hill, T.B. Lucatorto*, National Institute of Standards and Technology (NIST), *D.H. Fairbrother*, Johns Hopkins University

This presentation focuses on comparing growth characteristics of carbonaceous thin films produced by irradiation of Ru-capped multilayer surfaces with either extreme-ultraviolet light or electrons in the presence of hydrocarbon vapors. This work is motivated by the likelihood that extreme-ultraviolet lithography (EUVL) will be the next step in improving chip production for the semiconductor industry. Using a shorter (13.5 nm) wavelength of light, manufacturers can mass-produce microchips with feature sizes (< 10nm) that are impossible to achieve with current lithographic techniques. Since all materials strongly absorb 13.5 nm light, EUVL must be carried out under vacuum. Ultimately, this makes certain that the delicate multilayer optics and chemical photoresists, used in the EUVL process, cannot be completely isolated from one another. As a corollary, volatile organics released from resist-outgassing have the ability to be deposited via EUV- induced reactions, resulting in degradation of the multilayer optics. To protect the delicate optics, industry has established a resist-outgas testing protocol to determine the outgas-contamination risk of each resist before introducing it to the EUVL tool. This qualification procedure determines a resist's rate of contamination as well as the cleanability of its outgas products. Unfortunately, a key component of this protocol is the use of a dedicated, bright, EUV source. To mitigate the large capital investment necessary for such a source, electron beams are often used as a proxy. It is therefore important to correlate the carbon deposition processes induced by electron and EUV irradiation. To this end, we have exposed Ru-capped multilayer optics to both electron and EUV irradiation in the presence of admitted hydrocarbon vapors of two model species: benzene and tetradecane. Multiple exposures were performed with varying doses of EUV and electron irradiation for various hydrocarbon partial pressures; then subsequently characterized using scanning X-Ray Photoelectron Spectroscopy and small-spot spectroscopic ellipsometry. Electron exposures utilized the electron beam from a Perkin-Elmer 10-155 Cylindrical-Auger Electron Optics System; calibrated and characterized using a ThorLabs DCC1645c camera in conjunction with a Ce:YAG scintillator. EUV exposures utilized the Synchrotron Ultraviolet Radiation Facility at NIST. We find that the carbon growth rates for both exposure methods have sub-linear pressure dependence at low irradiance which transitions to linear scaling at higher irradiance. The growth rates at which this transition occurs, however, are different for EUV and e-beam irradiation.

11:40am TF+PS-ThM12 Production and Characterization of Thin Film Group IIIB, IVB and Rare Earth Hydrides by Reactive Evaporation, *James Provo*, J.L. Provo Consulting

A recent short history of reactive evaporation by Mattox (1) described various methods for producing oxides, nitrides, carbides, and some compound materials using this special process. However, no mention was made producing hydrides using this method. A study was performed in the mid 1970's at the General Electric Company (GE) Neutron Devices Department (GEND) in Largo, FL, by the author to study preparation of thin film hydrides using reactive evaporation and to determine their unique characteristics and properties.

Films were produced of scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), and the rare earth praseodymium (Pr), neodymium (Nd), gadolinium (Gd), dysprosium (Dy) and erbium(Er) hydrides by hot crucible filament evaporation in atmospheres of deuterium and tritium gas. All metal vacuum systems were used and dedicated for this special processing. Thin film test samples ~ 5,000Å thick were prepared on half-inch diameter molybdenum disk substrates for each occluder material.

Loading characteristics (i.e., gas –to-metal atomic ratios), oxidation characteristics, film structure, and stress properties were determined and showed near maximum gas-to-metal atomic ratios, variable oxidation properties, platelet type film structures and minimum film stress levels as determined by a double resonator technique. Also, stress aging characteristics were determined for some hydride films prepared in a radioactive tritium gas atmosphere.

The timeless data obtained showed gas-to-metal atomic ratios varied from 1.8 to 2.0, surface oxide levels varied from ~ 80Å to over 1,000Å, and initial normalized differential (tensile) stress levels were (1.0 to 4.0) x 10^8 dyne/cm^2 for tritium loaded samples and (1.0 to 2.0) x 10^9 dyne/cm^2 for deuterium loaded samples. Tritium loading, however, had the undesirable characteristic of having to dispose of the internal processing system fixtures, but the method generally produced desirable thin films.

† Formerly, Principal Member of the Technical Staff at Sandia National Laboratories,

Albuquerque, NM (Retired).

(1) Mattox, D.M., "History Corner- A Short History of Reactive Evaporation", SVC Bulletin, p.50 –

51, Spring 2014.

12:00pm TF+PS-ThM13 Cathodic Cage Plasma Deposition of TiN and TiO$_2$ Thin Films on Silicon Substrate, *R.R.M. de Sousa,* IFPI, Brazil*, P.S. Sato,* UFSCar, Brazil*, B.C. Viana,* UFPI, Brazil*, C. Alves Jr,* UFRSA, Brazil*, A. Nishimoto,* Kansai University, Japan*, **Pedro Nascente**,* UFSCar, Brazil

A new technique called cathodic cage plasma deposition (CCPD) was used for growing TiN and TiO$_2$ films on silicon substrate. In this technique, the samples are positioned inside a cage having uniformly distributed round holes with fixed diameter, and onto an alumina insulator disk, so that the plasma acts on the cage and not on the sample surface, eliminating possible defects usually formed during the conventional plasma deposition. The CCPD technique produces films with high uniformity and permits a good control of roughness and crystallinity. The main advantages of this technique are the uniformity, tri-dimensionality, and high rate of deposition of the deposited films, as well as low cost of production.

TiN coatings increase the surface hardness and decrease the friction coefficient, thus enhancing the lifetime of components and tools employed in the metalworking industries. Thin films of TiO$_2$ have attracted considerable attention because of different applications on many fields due to their unique properties, such as chemical stability, no toxicity, low cost, high refraction index, high permittivity, wide valence band, etc. The TiO$_2$ main crystalline phases are: anatase, brookite, and rutile. The TiO$_2$ thin films can have a mixture of these phases showing hybrid properties. Many studies have focused on relationship of the different phases as dependent of the deposition method and parameters. Each one of these phases has its own characteristic properties, leading to different applications.

In this work, the influence of the parameters (temperature and gas atmosphere) in the characteristics of the deposited films was investigated. The TiN and TiO$_2$ thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy in order to identify their crystalline phases and estimate their thicknesses. The combination of XRD and Raman spectroscopy results indicates that only a TiN crystalline phase was detected for the TiN films, and mainly the anastase phase was detected for the TiO$_2$ film. High crystallinity and uniformity of the films were observed by XRD, Raman, and SEM, confirming that this low cost technique is effective in producing high quality TiN and TiO$_2$ films.

Thursday Afternoon, November 13, 2014

2D Materials Focus Topic
Room: 310 - Session 2D+EM+MI+MN+NS+SS+TF-ThA

Novel Quantum Phenomena in 2D Materials
Moderator: Alexander Sinitskii, University of Nebraska-Lincoln

2:20pm 2D+EM+MI+MN+NS+SS+TF-ThA1 Optoelectronics of Two-Dimensional Semiconductors, *Xiaodong Xu*, University of Washington **INVITED**
Two dimensional transition metal dichalcogenides are a recent addition to the 2D electronic materials family. They have shown outstanding electrical and optical properties for new optoelectronic device concepts. In this talk, we will first discuss the unique interplay between spin, valley, and layer pseudospins in bilayer WSe_2. Such coupling effects lead to electrical control of spin states and optical generation of valley coherence through interlayer trions, where electrons and holes are localized in different layers. We will then talk about optoelectronic devices based on monolayer WSe_2, including p-n junctions as light emitting diodes and hybrid monolayer semiconductor/photonic crystal cavity devices. We will conclude the talk with a discussion of the optoelectronic properties of $MoSe_2$-WSe_2 heterostructures.

3:00pm 2D+EM+MI+MN+NS+SS+TF-ThA3 Theory of Graphene Transport Barriers in the Specular Limit, *Daniel Gunlycke*, C.T. White, Naval Research Laboratory
Offering room-temperature ballistic electron transport well over one micron, while being atomically thin and planar, graphene is undeniably a promising material for future nanoelectronic devices. Presently, however, switchable devices have normally low on-off ratios, a reflection of the challenge of selectively blocking electron and hole carriers from propagating across the graphene surface. This has stimulated a lot of research on different methods for making graphene nanoribbons that exhibit suitable band gaps. An alternative way to obtain a controllable gap takes advantage of resonant tunneling across a pair of transport barriers. For the latter approach, the key is to find a barrier that is fairly reflective but not so much as to effectively cut off all transport across it.

In this presentation, we present a model for straight transport barriers in graphene in the specular limit. Using the Lippmann-Schwinger equation, we obtain the wave function, from which we derive the reflection and transmission probabilities, as well as the local density of itinerant states. This local density of states exhibits fluctuations arising from quantum interference between incoming and outgoing matter waves that allow the transport properties of a barrier to be estimated without explicitly probing the current across the barrier. Our model is tested against exact multi-channel, tight-binding quantum transport calculations for graphene with weak local potentials, local strain, local adsorption, and a locally defective structure. As the model parameters are related to observable quantities, they could be obtained from theory and/or experiment, allowing the model to be adopted even when the precise details of the barrier are unknown.

3:20pm 2D+EM+MI+MN+NS+SS+TF-ThA4 Tip-induced Potential Confinement on Graphene in Scanning Tunneling Microscopy Measurement, *Yue Zhao*, J. Chae, J.E. Wyrick, NIST/CNST, *F.D. Natterer*, Ecole Polytechnique Fédérale de Lausanne (EPFL), France, *S. Jung*, Korea Research Institute of Standards and Science (KRISS), *A.F. Young, C.R. Dean, L. Wang, Y. Gao*, Columbia University, *J.N. Rodrigues*, Graphene Research Centre, NUS, Singapore, *K. Watanabe, T. Taniguchi*, National Institute for Materials Science (NIMS), Japan, *S. Adam*, Graphene Research Centre, NUS, Singapore, *J.C. Hone, K. Shepard, P. Kim*, Columbia University, *N.B. Zhitenev, J.A. Stroscio*, NIST/CNST
Graphene is a two-dimensional-electron-gas(2DEG) system with exposed surface, which allows scanning tunneling microscopy(STM) to investigate the electron-electron interaction associated with the Dirac nature on a local scale, with a variety of tuning knobs, such as carrier density, spatially varying disorder potential, and applied magnetic field. However, the electron-electron interaction in graphene is sensitive to the disorder details. Moreover, tip induced potential confinement can significantly complicate the interpretation of STM experiment. Utilizing a high mobility graphene device with low residual disorder, we can minimize the effect of local potential fluctuation, to better understand the role tip-induced potential plays in the measurement. We observed the emergency of large spectra gaps, modification to graphene Landau levels (LLs), and quantum dots with changing size due to the spatially inhomogeneous tip gating.

4:00pm 2D+EM+MI+MN+NS+SS+TF-ThA6 Topological Phase Transitions and Spin-orbit Density Waves, *Hugo Dil*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**
In recent years systems where the spin-orbit interaction (SOI) is not just a perturbation but the main energy scale have received increasing attention. In combination with a broken inversion symmetry in the crystal structure or at interfaces, SOI will lift the spin degeneracy and induce a complex Fermi surfaces and spin textures with spin momentum locking [1,2]. Furthermore, the SOI can drive the system through a phase transition to a so-called topological insulator. Being an insulator in the bulk these systems are characterized by spin-polarized, topologically protected interface states.

After a short introduction to the role of topology in the band structure of solids I will give an overview of our main spin- and angle-resolved photoemission (SARPES) results on a variety of non-interacting topological insulators [3]. One of the questions is how the spin texture evolves around a topological transition. We explored the occurrence of spin polarized states around a SOI driven topological transition [4] and around a structure driven topological transition [5]. In both cases we observe spin-polarized precursor states, which indicate that although the topological transition is sharp, the response of the system is more gradual.

From a fundamental point of view the truly interesting aspect of non-trivial spin textures lies in their combination with other interactions. This can result in a variety of phenomena, cumulating in the creation of the elusive Majorana Fermion. An example of a combination of interactions is our recent verification with SARPES of SmB_6 as a topological Kondo insulator [6]. In topologically trivial systems, interactions can lead to the formation of a so-called spin-orbit density wave. I will show how the combination of a large spin-splitting and Fermi nesting leads to the formation of such a state and can explain the anisotropic behavior of Pb nanowires [7]. Furthermore, I will present our recent SARPES results for transition metal oxide surfaces where a subtle interplay between ferroelectricity and magnetic order results in the formation of a single spin-polarized energy contour. The occurrence of superconductivity in such systems could render it a 2D Majorana platform.

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4:40pm 2D+EM+MI+MN+NS+SS+TF-ThA8 The Symmetry Dependent Band Structure of MoS₂, *Duy Le*, University of Central Florida, *T. Komesu*, University of Nebraska-Lincoln, *Q. Ma*, University of California, Riverside, *E.F. Schwier, H. Iwasawa*, Hiroshima University, Japan, *M. Shimada*, Higashi-Hiroshima, Japan, *T.S. Rahman*, University of Central Florida, *L. Bartles*, University of California, Riverside, *P.A. Dowben*, University of Nebraska-Lincoln
We will present results of density functional theory (DFT) based calculations of symmetry dependent band structures of single crystal MoS_2(0001) surface together with symmetry-polarized angle resolved photoemission spectroscopy (ARPES) derived experimental band structure. The good agreement of the DFT band structure with the experimentally derived bands with even and odd symmetries, attests to the reliability of the results. We performed ARPES at the Hiroshima Synchrotron, determining the MoS_2 band structure separately for both p-, and s-, polarized to distinguish even and odd symmetry, and the experimentally determined dispersion, in accordance with expectations and experimental confirmation of C_{3v} symmetry, argues in favor of an experimental band structure obtained from single domains. The comparison of theory and experiment provides strong indications that the bands at the top of the valence band are dominated by Mo 4d states. These states and indeed placement of the valence band can be perturbed by adsorbates. Indeed, we find that, under the effect of Na adsorption, the changing placement of the valence band structure of MoS_2 clearly indicate the Na atoms donate electrons to MoS_2 and that the Fermi energy level shifts as much as 0.5 eV with respect to the top of MoS_2's valance band. Surprisingly, Na adsorption does not perturb the MoS_2 band dispersion significantly. We will discuss these results in the light of those obtained for single layer MoS_2 for insights and clarity.

5:00pm 2D+EM+MI+MN+NS+SS+TF-ThA9 CuIn$_{III}$P$_2$S$_6$ - Room Temperature Layered Ferroelectric, *Alex Belianinov, P. Maksymovych,* Oak Ridge National Laboratory, *A. Dziaugys,* Vilnius University, Lithuania, *Q. He,* Oak Ridge National Laboratory, *E. Eliseev,* National Academy of Sciences of Ukraine, *A,. Borisevich,* Oak Ridge National Laboratory, *A. Morozovska,* NAS of Ukraine, *J. Banys,* Vilnius University, Lithuania, *Y. Vysochanskii,* Uzhgorod University, Ukraine, *S.V. Kalinin,* Oak Ridge National Laboratory

We have utilized ambient and Ultra High Vacuum Scanning Probe Microscopy tools to explore ferroelectric properties in cleaved 2D flakes of copper indium thiophosphate, CuIn$_{III}$P$_2$S$_6$ (CITP), and report on size effect and presently achievable limits of ferroelectric phase stability. CITP is an unusual example of a layered, anti-collinear, uncompensated, two-sublattice ferroelectric system. These are the only materials known to display "2-D" ferroelectric semiconductor behavior in a van-der-Waals crystal. The material exhibits a first-order phase transition of order–disorder type from the paraelectric to the ferrielectric phase at T$_c$ = 315 K. Our observations suggest the presence of stable ferroelectric polarization as evidenced by domain structures, rewritable polarization, and hysteresis loops. These observations suggest that flakes above 100 nm have bulk-like polarization and domain structures, whereas below 50 nm polarization disappears. Furthermore, the materials have measurable ionic mobility, as evidenced both by macroscopic measurements and by formation of surface damage above tip bias of 4 V, likely due to copper reduction. We ascribe this behavior to well-known instability of polarization due to depolarization field, along with internal screening by mobile Cu ions, as suggested by their high ionic mobility.

Acknowledgement:

5:20pm 2D+EM+MI+MN+NS+SS+TF-ThA10 Doping Efficiency and Mechanisms of Single and Randomly Stacked Bilayer Graphene by Iodine Adsorption, *Hokwon Kim, A. Tyurnina,* Univ. Grenoble Alpes/ CEA, LETI, France, *J.-F. Guillet, J.-P. Simonato, J. Dijon,* Univ. Grenoble Alpes/ CEA, LITEN, France, *D. Rouchon, D. Mariolle, N. Chevalier, O.J. Renault,* Univ. Grenoble Alpes/ CEA, LETI, France

The precise control of graphene's conductivity and work function is crucial in developing practical applications of graphene based electronics. In order to enhance the conductivity of graphene, we employed a simple doping method where graphene films produced by chemical vapor deposition and transferred onto SiO$_2$, Al$_2$O$_3$, and WO$_3$ substrates are p-doped with iodine vapor through physisorption at temperature of ~ 100 °C [1-3]. The work function values and iodine to carbon ratios of the one-layer (1L) and two-layer (2L) folded regions were analyzed by high spatial- and energy resolution X-ray photoelectron emission microscopy (XPEEM) on a *NanoESCA* instrument. After the iodine doping, the work function values were significantly increased up to ~0.4 eV and ~0.5 eV, respectively, for 1L and 2L graphene on SiO$_2$/Si. This higher degree of doping by iodine was corroborated by I 3$d_{5/2}$ core level imaging of the same area where the 2L graphene exhibited significantly larger concentration of iodine (2 at. % versus 1 at. %) likely due to the intercalation of iodine at the inter-layer space.

The main iodine species identified by high resolution core level X-ray photoemission spectroscopy and Raman spectroscopy were I$_3^-$ and I$_5^-$ poly-iodide anionic complexes with slightly higher concentration of I$_5^-$ in 2L than 1L graphene possibly due to different doping mechanisms. Temperature dependent ultra-high-vacuum, in-situ annealing of the doped films has demonstrated that most of iodine is removed above 300 °C for the both 1L and 2L regions, although a significant removal of iodine is observed for 2L graphene at temperature as low as 100 °C. Surprisingly, after the complete removal of iodine by annealing, the work function value did not return to the original one before the doping treatment and remained at a much higher value. This can be ascribed to the residual hydrocarbon contaminations interacting with the atomic defects within the graphene layer that lead to unintentional n-type doping in our samples[4].

Acknowledgement: The XPEEM and KFM measurements were performed at the Nanocharacterization Platform (PFNC).

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5:40pm 2D+EM+MI+MN+NS+SS+TF-ThA11 Use of XPS for Device Characterization, *P. Aydogan, E.O. Polat, C. Kocabas, **Sefik Suzer**,* Bilkent University, Turkey

A noncontact chemical and electrical measurement technique of XPS is utilized to investigate a number of devices made of graphene. The main objective of the technique is to trace chemical and location specific surface potential variations as shifts of the XPS peak positions under operating conditions. Devices consisting of graphene; (i) acting as a simple resistive element between two gold electrodes, (ii) a semiconducting sheet controlled by a back-gate, and (iii) between the source and the drain metal electrodes in a full transistor geometry, have been analyzed by recording the Au4f of the metal electrodes, the C1s of the graphene layer, and the O1s (or N1s) peaks of the silicon oxide (or nitride) of the substrate. The advantage of this technique is its ability to assess element specific surface electrical potentials of devices under operation based on the deviations of the core level peak positions in surface domains/structures. Detection of the variations in electrical potentials and especially their responses to various stimuli gives unprecedented information about the chemical nature as well as the location of structural and/or other types of defects as a result of doping, oxidation, reduction, etc.

Manufacturing Science and Technology
Room: 302 - Session MS+PS+TF-ThA

Functionalization of Paper and Textiles & Their Applications

Moderator: Jack Rowe, North Carolina State University, Bridget R. Rogers, Vanderbilt University

2:20pm MS+PS+TF-ThA1 Vapor-Phase Infiltration of Cellulose and Cotton, ***Mato Knez**, K. Gregorczyk, M. Garcia, I. Azpitarte,* CIC nanoGUNE, Spain, *D. Pickup, C. Rogero,* Centro de Física de Materiales (CSIC-UPV-EHU), Spain **INVITED**

There is a significant interest in using inexpensive biological materials as substrates and scaffolds for emerging applications due to their natural occurrence. Of particular importance is the use of paper based materials and substrates for potential applications in energy storage, catalysis, solar cells, etc. Atomic layer deposition (ALD) has been proven to be the technique of choice to modify paper and other cellulose based materials due to its low reaction temperatures, extreme thickness control, and conformality. Furthermore, vapor phase infiltration techniques, which are a recent modification to ALD, have allowed infiltration of metal-organic precursors into a variety of organic materials including spider silk, porphyrins, and polytetrafluoroethylene (PTFE), leading to a more detailed understanding of the reaction between these organic substrates and the metal-organic precursors, as-well-as surprising changes in bulk properties. Understanding the chemical interactions between precursors and substrates are crucial in order to approach applications. We modified cellulose and cotton with common ALD precursors and monitored the chemical changes after the reaction a semi-*in-situ* XPS experiments. Our findings show that the precursors induce small, but important changes to the biopolymer upon chemical interaction and that the precursors indeed react different to each other. The experiments also compare well to the final results of standard *ex-situ* XPS. Changes in the bulk mechanical properties of the substrates were studied through use of tensile testing. The ultimate tensile strength (UTS), Young's modulus (YM), and toughness are shown to be a non-linear function of both the precursor used and the number exposure cycles.

3:00pm MS+PS+TF-ThA3 Patterned Photoreduction of Metal Atoms on Polymeric Substrates for Flexible Electronic Applications, ***Halil Akyildiz**, J.C. Halbur,* North Carolina State University, *A.T. Roberts,* Redstone Arsenal, *H.O. Everitt,* Duke University, *J.S. Jur,* North Carolina State University

Flexible electronics are of interest for displays, sensors, and health monitoring systems. Polymeric substrates, being flexible, easy to manufacture and inexpensive, are wanted for such applications. However, polymers, aside from good properties usually require alteration of electronic and optical properties. Sequential vapor infiltration (SVI) is a technique that modifies polymer properties by formation of hybrid materials via infiltration of organometallic precursors into bulk polymers. In this work we

present how SVI tailors the optical properties of polyethylene terephthalate (PET) fibers by infiltration of trimethylaluminum (TMA) precursors to form PET-Alumina hybrid structures. Photoluminescence (PL) spectroscopy showed an order of magnitude increase in photoluminescence as compared to the pristine PET fibers which is attributed to the increased interactions between polymer chains by formation of alumina polymer coordination complexes. Furthermore metal ions out of a metal salt solution were reduced onto the modified substrates by photo catalytic effect. Patterned silver lines on PET fabric were successfully achieved by selective excitation of the fabric using a laser source showing promising results for integration of electronic devices.

3:20pm MS+PS+TF-ThA4 Multifunctional Fabrics via Tungsten ALD on Kevlar, *Sarah Atanasov, B. Kalanyan, G.N. Parsons*, North Carolina State University

Multifunctional materials combine two or more distinct capabilities into a single article unit. Kevlar is a high strength fiber used for personal protection and other mechanically demanding applications. Adding conductivity to Kevlar creates a new multifunctional protective/electronic material for electromagnetic shielding, communications, and erosion resistant, anti-static fabrics and cables for space and automotive technologies. For this study, we coated Kevlar fibers and woven mats with ALD tungsten, using WF_6 and dilute silane (SiH_4, 2% Ar) at 220°C. Kevlar's thermal stability makes it a very amenable polymer for ALD coating at relatively high temperatures. Before W ALD, we deposited a TiO_2/Al_2O_3 bilayer by ALD onto the Kevlar, at various temperatures (50-220°C). The Al_2O_3 layer promotes W nucleation. The TiO_2 layer is important because previous mechanical analysis indicates that the TMA precursor degrades the Kevlar polymer backbone, whereas TiO_2 ALD using $TiCl_4$ and H_2O was less damaging. XPS analysis confirms the presence of TiO_2, Al_2O_3 and W on the fibers after each coating step. After W ALD, the yarns and mats are highly conductive (~3000 S/cm) and remain flexible. Tensile testing shows that upon coating with 20 ALD cycles, the strength of the Kevlar decreases from 3.32 GPa to 3.02 GPa. The ability to create highly conductive Kevlar with mechanical strength within 90% of the original mechanical performance could open new areas of application for large area low temperature ALD processing.

4:00pm MS+PS+TF-ThA6 Direct and Self-Assembly of Nanocellulose Cleaved from Fiber Cell Walls and Integration in Device Manufacture, *Orlando Rojas*, North Carolina State University **INVITED**

We introduce our work related to the application of surface and colloid science in the development of cellulose nanomaterials. These efforts take advantage of the process by which nature assembles fibers in a highly hierarchical structure encompassing a wide range of sizes, from the nano to the meter scales. A number of materials cleaved from the cell wall have been the subject of intensive research, including, nanofibrillar cellulose and cellulose nanocrystals, i.e., defect-free, rod-like crystalline residues after acid hydrolysis of cellulose fibers. Interest in nanocellulose originates from its appealing intrinsic properties: nanoscale dimensions, high surface area, unique morphology, low density, chirality and mechanical strength. Directing their assembly back to different hierarchical structures is a quest that can yield useful results in many revolutionary applications. As such, we will discuss the use of non-specific forces to create ultrathin films of nanocellulose at the air-solid interface for applications in nanocoatings, sensors, etc. Assemblies at other interfaces will be introduced as means to produce Pickering emulsions. Methods common in biophysics and employed to control the packing density of nanocellulose at the air-liquid and air-solid interfaces will be presented. A convective assembly setup assisted by shear and electric fields will be discussed as a suitable method to produce highly ordered structures. Concepts related to piezoelectric cellulose nanocrystal films, organic-inorganic hybrid materials with magnetic and other properties. Overall, the prospects of such novel materials will be explained in light of the unique properties of cellulose and its nanostructured assemblies.

5:20pm MS+PS+TF-ThA10 Van der Waals Materials on Nanostructured Paper -- Aqueous Gating and Sensing Application, *Wenzong Bao, Z. Fang, J. Wan, L.B. Hu*, University of Maryland, College Park

We report the first aqueous transistors on a bilayer-structured paper with a nanoscale smoother surface. Such transistors have a planar structure with source, drain and gate electrodes on the same surface of paper, and the mesoporous paper is used as an electrolyte container. Such transistors are enabled by a bilayer-structured all-cellulose paper with nano-fibrillated cellulose on the top surface that leads to an excellent surface smoothness, while the rest of micro-sized cellulose fibers can absorb electrolyte effectively. Based on 2D Van der Waals materials such as graphene and MoS2, we demonstrate high-performance transistors with large on-off ratio. Our devices also show excellent bending flexibility. Such planar transistors

with absorbed electrolyte gating can be used as sensors integrated with other components towards paper microfluidic systems.

5:40pm MS+PS+TF-ThA11 Mechanistic Understanding of Anomalous Scaling Law of Mechanical Properties of Nano-Cellulose Paper, *S. Zhu, Z. Jia, Y. Li, Z. Fang, S. Parvinian, N.J. Weadock, O. Vaaland, Y.C. Chen, L.B. Hu, Teng Li*, University of Maryland, College Park

The quest of both strength and toughness is perpetual in advanced material design; unfortunately, these two mechanical properties are generally mutually exclusive. A general and feasible mechanism to address the conflict of strength vs. toughness still remains elusive. Here we demonstrate an anomalous but highly desirable scaling law of the mechanical properties of cellulose nanopaper: both its strength and toughness increase simultaneously (40 & 130 times, respectively) as the size of the constituent cellulose fibers decreases (from a diameter of 27 microns to 10 nm). Our theoretical mechanics modeling and molecular dynamics simulations reveal the underlying mechanistic understanding of such an anomalous scaling law. These stimulating results suggest a fundamental bottom-up strategy generally applicable for other material building blocks, and thus hold the promising potential toward a new scaling law: the smaller, the stronger AND the tougher. There are abundant opportunities to utilize the fundamental bottom-up strategy to design a novel class of functional materials that are both strong and tough.

Thin Film
Room: 307 - Session TF-ThA

Thin Film for Permeation Barriers and Membranes
Moderator: Adriana Creatore, Eindhoven University of Technology

2:20pm TF-ThA1 Enhancing Water Desalination Membranes by Initiated Chemical Vapor Deposition (iCVD), *Karen Gleason*, Massachusetts Institute of Technology **INVITED**

The process of iCVD (initiated Chemical Vapor Deposition) is compatible with the fragile polymeric membranes utilized in seawater desalination, since no solvents or high surfaces temperatures are employed. The iCVD method is scaleable over large areas (commercial reactors >1 m across) and to roll-to-roll processing. Over 70 different monomers have been successfully surface polymerized with iCVD.

Two applications of iCVD to water desalination membranes will be discussed. First, iCVD layers have been directly applied to reverse osmosis (RO) membranes for prevention of fouling by molecules and microbes. Second, iCVD enables the deposition of conformal hydrophobic fluoropolymers which are desired for fabricating high performance membranes for desalination by membrane distillation (MD).

The motivation for the antifouling layers is that with the build-up of scale and/or biofilms, system performance declines, resulting in increased operating costs. Fouling also necessitates periodic shutdown for cleaning and replacement of system components and expensive membranes, resulting in higher maintenance costs. Antifouling surface chemistries synthesized by iCVD include amphiphilic and zwitterionic copolymers. Ultrathin (~20 nm) iCVD coatings have been proved to significantly reduce fouling on commercial reverse osmosis (RO) membranes retaining their water permeation and salt rejection performance. The synthesis of iCVD polymer films starts from the membrane surface allowing chemical design strategies for forming grafted interfaces. These grafted interfaces greatly enhance the durability of iCVD surface modification layer which is essential for real-world implementation that would help ensure reliable and economical clean water production.

3:00pm TF-ThA3 Pulsed Plasma Enhanced Chemical Vapor Deposition for Nanoscale Control of the Size, Shape and Surface Properties of Asymmetric Membranes, *Sanket Kelkar, D. Chiavetta, C.A. Wolden*, Colorado School of Mines

The objective of our research is to develop a simple and scalable approach for modification of size and geometry of model membrane supports to fabricate nanopores. In this work, we first employ relatively large template structures (~ 100 nm) produced by track-etching or e-beam lithography. The pore size is then reduced to the desired level by deposition of material using pulsed plasma enhanced chemical vapor deposition (PECVD). Pulsed PECVD has been developed as a high throughput alternative to atomic layer deposition (ALD) to deliver self-limiting growth of thin films. Pulsed PECVD has two growth components that act sequentially: ALD-like component during the plasma off step ($\gamma \sim 0$); and PVD-like growth component during the plasma on step ($\gamma \sim 1$), where γ is the reactive

sticking coefficient. The ALD contribution is constant at ~1 Å /pulse whereas the PVD contribution can be typically varied from 0.5 - 10 Å/pulse by appropriate control of operating conditions. The degree of conformality in pulsed PECVD can thus be engineered by controlling the relative contribution of these 2 growth components. Like ALD, pulsed PECVD provides sub-nm resolution over the pore size. However, pulsed PECVD does not result in perfectly conformal deposition profiles, and as such control of the final nanostructure is more complicated. In this work we develop feature scale modeling tools to predict and design the fabrication of nanostructures, such as asymmetric nanopores, using pulsed PECVD. The model is verified by systematic investigation of deposition profiles on patterned cylinders and trenches through cross-section electron microscopy. Polymeric track etched membrane supports (TEMS) are employed as model template structures to demonstrate the capability of pulsed PECVD for precise pore size reduction. Permeance and solute rejection measurements demonstrate that the pulsed PECVD coated TEMS exhibit higher selectivity without compromising on the flux due to their asymmetric structure. These nanoporous membranes will be utilized to study the effect of pore size and geometry on hindered transport of ions and macromolecules at the nanoscale. Furthermore, the hydrophobicity of polymeric supports will be mitigated by deposition of suitable oxide material.

3:20pm TF-ThA4 A Combined Microstructure Characterization of Moisture Permeation Barrier Layers by Means of Electrochemical Impedance Spectroscopy and Ellipsometric Porosimetry, *Alberto Perrotta*, Eindhoven University of Technology; Dutch Polymer Institute (DPI), Netherlands, *S.J. García,* Delft University of Technology, Netherlands, *J.J. Michels,* Holst Centre / TNO, Netherlands, *W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, Netherlands

In engineering organic electronic devices, encapsulation layers are mandatory due to the sensitivity of active layers and low work function cathodes to moisture. The quality of the moisture permeation barriers is generally validated by means of water vapor transmission rate (WVTR, $gm^{-2}day^{-1}$) measurements as well as visual inspection/identification of the local defects (*e.g.* pinholes) acting as unhindered pathways for water molecules. Furthermore, it has been demonstrated that the water permeation through the nanoporosity - or free volume - of the bulk of the barrier layer can be 15-20 times higher than the one through local defects [1]. While several methods allow the identification of pinholes/defects, novel techniques able to characterize the barrier microstructure in the broad range of nano- and meso-porosity are sought. In a recent work [2], ellipsometric porosimetry has been demonstrated to be a valuable technique for nanopore characterization. Adopting different probing molecules (*i.e* trivinyltrimethyl cyclotrisiloxane, d_{V3D3} = 1 nm, and water, d_{H2O} = 0.3 nm), a correlation has been found between the (residual) nanoporosity in PE-CVD and (PE-)ALD barriers and their *intrinsic* barrier properties. The pore size range of 0.3–1 nm and its relative content have been found to control the transition in WVTR in the regime of 10^{-4} - 10^{-6} gm^{-2} day^{-1}. In order to further investigate this range, electrochemical impedance spectroscopy (EIS) has been adopted for the first time in the study of moisture permeation barriers. EIS allows to follow the diffusion of electrolytes through the barrier and cations having different hydrated shell sizes in the range 0.5-0.7 nm, *i.e.* Na^+, Li^+, K^+ and Cs^+, have been selected. Changes in the barrier layer resistance have been attributed to the formation of conductive pathways due to the ion diffusion and allow to study differences in layer porosity in the above-mentioned pore diameter/cation size range. Moreover, it is possible to investigate the water permeation as a function of the variation of the barrier capacitance value upon immersion in the electrolyte solution. In this way, the water uptake (φ, the volume fraction of water in a coating) and diffusivity coefficient (D) of different moisture barriers are determined. φ and D values in the range of 0.8-4% and 10^{-13}-10^{-15} cm^2s^{-1} have been found, respectively. This demonstrates that EIS is a versatile tool for the characterization of moisture permeation barriers.

[1] J. Affinito *et al.* 47th Annual Technical Conference Proceedings (2004) 563

[2] A. Perrotta *et al.*, *Microporous and Mesoporous Materials* (2014) 163

4:00pm TF-ThA6 Influence of Surface Topography and Defects on the Performance of Nanoscale Thin Film Moisture Permeation Barriers, *Sean King*, D. Jacob, B. Colvin, D. Vanleuven, J. Kelly, Intel Corporation
Nanoscale moisture permeation barriers are needed for a wide range of applications including encapsulation of organic light emitting diodes, passivation of thin film photovoltaic devices, low dielectric constant Cu interconnect capping layers, hermetic food packaging, and protective coatings for biomedical devices. A variety of materials deposited by various methods have been proposed and successfully demonstrated for these diverse applications. However, it is well known (although not rigorously characterized) that surface roughness and surface particulates/defects can dramatically reduce the permeation barrier performance of all coating materials. In this presentation, we specifically investigate the impact that

surface topography and defects can have on the moisture permeation barrier performance of various materials deposited by common methods such as atomic layer deposition (ALD), plasma-enhanced ALD (PEALD), and plasma-enhanced chemical vapor deposition (PECVD). We show that in the absence of significant surface topography a variety of different PECVD, PEALD, and ALD materials can serve as excellent moisture permeation barriers at thicknesses < 10 nm, but the controlled introduction of surface topography dramatically reduces the barrier performance in all cases. To simulate the presence of surface particulates and defects in a controlled manner, various barrier materials of interest were deposited on hanging trenches etched into nano-porous inorganic silicates deposited on a thick moisture absorbing SiO_2 film used for moisture permeation detection. The aspect ratios and dimensions were varied to probe the impact of surface particulates of different size and geometry. It will be shown that increasing surface topography generally increases the minimum thickness for a given material and deposition method to serve as a robust moisture permeation barrier. Over all, the surface topography barrier performance is found to strongly correlate with the step coverage and conformality of the deposition process with ALD and PEALD films out performing PECVD films.

4:20pm TF-ThA7 Atomic Layer Deposition for Encapsulation and Barriers, *F. van den Bruele, F. Grob, Paul Poodt*, Holst Centre / TNO, Netherlands
Developments in the field of flexible electronics, such as organic light emitting diodes (OLEDs), organic photovoltaics (OPV) and other thin-film solar cells, are slowly but surely evolving from lab-scale to industrial production. Proper encapsulation of these moisture sensitive devices is critical, as exposure to moisture from the ambient will degrade these devices, reducing their efficiency, lifetime, or even lead to failure altogether. Especially for OLEDs, the barrier requirements are very challenging, with a Water Vapor Transmission Rate < 10^{-6} $g/m^2/day$. Encapsulation of flexible devices is even more challenging as the encapsulation should not affect the device flexibility too much. Various flexible thin film encapsulation techniques have been recently developed, often combining one ore more thin inorganic diffusion barrier layers (e.g. SiN_x, Al_2O_3) with an organic layer. To achieve these very low WVRTs, very high quality barrier layers are required, being pinhole free over the entire device area.

One approach to make high quality inorganic barrier films is Atomic Layer Deposition (ALD). ALD is a deposition technique capable of producing ultrathin conformal films with control of the thickness and composition of the films at the atomic level. With thin (5-100 nm) Al_2O_3 films deposited by ALD, excellent barrier films (WVTR ~ 10^{-6} $g/m^2/day$) can readily be obtained on lab-scale. The major drawback of ALD, however, is its low deposition rate making compatibility with industrial scale processing of devices challenging. The recent development of roll-to-roll and large-area Spatial ALD technology has however spurred the interest in ALD for encapsulation and barriers and the first commercially available electronic devices with ALD encapsulation are probably not far away.

The recent developments of ALD for thin-film encapsulation will be reviewed from a point of view of material- and process development, as well as ALD equipment, with a strong focus on spatial ALD. However, producing barriers with ALD is more complex than only the deposition step itself. For this reason, special attention will be given to aspects such as up-scaling, substrate handling and planarization, managing the effects of particles, characterization and costs of the process.

4:40pm TF-ThA8 Lifetime of Atomic Layer Deposited Al_2O_3 and Parylene Bilayer Encapsulation for Passive and Active Neural Interfaces, *Loren Rieth*, R. Caldwell, X. Xie, F. Solzbacher, University of Utah
Encapsulation of penetrating neural interfaces with complex geometries is one of the greatest challenges to achieve long-term functionality and stability need for therapeutic systems. We present results from testing a novel encapsulation scheme that combines atomic layer deposited (ALD) Al_2O_3 and Parylene-C for biomedical implants with integrated electronics. The ALD alumina is utilized for its very low water vapor permeation rate, and the Parylene acts as a kinetic barrier to prevent dissolution of the alumina and as a well-regarded biocompatible coating.

Our devices were first coated with a combination of 52 nm of Al_2O_3 deposited by PA-ALD at 120 °C. The organo-silane adhesion promoter A-174 was applied, followed by a 6-µm film of Parylene-C deposited using a CVD process. Acceleration conditions included temperature and/or voltage bias with interdigitated electrodes (IDEs) and Utah Arrays. IDE testing focused on the effects of additional topography on the encapsulation lifetime at acceleration temperatures up to 80 °C. Topography was added by attachment of 0402 surface mount capacitors and custom 5.5 mm wire-wound Au coils, both used in our fully wireless neural interfaces. A >50% decrease in lifetime from > 280 days to 140 days was measured with the

addition topography. We are investigating the mechanism for the decreased lifetime to determine if it is associated with chemical degradation, contamination, or mechanical forces through a comparison with thermal cycling measurements.

In-vitro measurements of the impedance stability for passive UEAs have been used to test the encapsulation performance of these devices while soaking in phosphate buffered saline (PBS). The impedances of these arrays are widely reported to decrease during soak testing due to water ingress. Contrary to this trend, we saw an increase in the impedance of arrays from median impedances of 60 kΩ to 160 kΩ during soaking for 960 days of equivalent time at 37°C. The mechanism for the increase impedance is likely the loss of tip metal.

The impact of voltage bias was also investigated using IDEs and fully-integrated wireless neural interface systems. These devices were maintained 37 °C or higher temperatures for acceleration, and a continuous 5 V bias. For the fully integrated wireless devices, the bilayer encapsulated devices continued to function for 140 days (37 °C equivalent) compared to > 1860 days of equivalent soaking for unpowered devices, indicating ~10 times shorter lifetimes. The lifetime is also more than 10x longer than devices only encapsulated with Parylene-C, indicating the bilayer encapsulation is a significant improvement for these very challenging conditions.

5:00pm TF-ThA9 Influence of Polymer Microstructure and Process Temperature on the Formation of Tailored ALD Coatings on Polymers, *R.P. Padbury, **Jesse Jur***, North Carolina State University
Atomic layer deposition is a technique that is able to integrate nanoscale inorganic coatings to organic polymers. Through this process a number of different inorganic coating morphologies are able to form during ALD nucleation on a wide variety of polymers. In this work, we provide a systematic analysis of the ALD nucleation characteristics on polymers by investigating the influence of polymer microstructure and ALD process temperature. Specifically, in-situ quartz crystal microgravimetry is employed to understand the nucleation behavior of trimethyl aluminum (TMA) in a series of polyesters and poly-n-methacrylates. The data indicates that the glass transition temperature of the polymer, as influenced by variations in microstructure and process temperatures, has a significant impact on the absorption/desorption characteristics during TMA/water exposures. Finally, we propose potential growth mechanisms and demonstrate adjustments to the ALD process parameters that enable the ability to produce a customized interface for ALD materials growth on polymer substrates.

5:20pm TF-ThA10 Mechanisms of Moisture and Oxygen Transport through Thin Silica-like Barrier Films Deposited in Atmospheric Pressure Dielectric Barrier Discharge, *Sergey Starostin*, FOM Institute DIFFER, Netherlands*, B.C.A.M. van der Velden-Schuermans, S. Quan*, FUJIFILM Manufacturing Europe b.v., Netherlands*, A. Meshkova, M.C.M. van de Sanden, H.W. de Vries*, FOM Institute DIFFER, Netherlands
Atmospheric pressure plasma enhanced chemical vapor deposition (AP PECVD) is attracting steadily growing research interest by having clear benefits in terms of equipment costs, footprint size and possibilities for high throughput in-line processing. However the details of the deposition process and the properties of the synthesized coatings were not studied yet as well as for traditional low pressure PECVD. Recently we have reported that good performing moisture and oxygen silica-like barrier films can be fabricated in atmospheric pressure high current diffuse dielectric barrier discharge [1]. However little is known yet about the dominant gas permeation mechanisms through atmospheric pressure plasma deposited barrier films.

In the present contribution the rates of oxygen and moisture vapor permeation were studied as a function of temperature, film thickness and deposition rate. Activated rate theory was applied to analyze the mechanisms of oxygen and moisture transport through the bilayer system of silica-like film and polymer foil. The experimental value of the apparent activation energy E_a determines the degree of interaction between permeating gas and the barrier film. If the E_a values of the bilayer are close to the activation energy of the polymer (47 kJ/mol for moisture), this indicates that the gas transport is controlled by large pinholes with limited or no interaction with the silica film. A transition from polymer controlled moisture permeation to a transport through the silica-like film was observed by tracing an increase in the apparent activation energy from 47 kJ/mol to 80 kJ/mol with film thickness from 2 nm to 100 nm. The gas permeation measurements for the films with different thicknesses were complemented by a detailed morphological study carried out with atomic force microscopy (AFM). The evolution from a non-self-affine morphology of the polymeric substrate to a characteristic smooth surface of the deposited silica-like layer was observed as the film thickness increased from 2 nm to 20 nm. In addition film composition was analyzed by XPS and ATR-FTIR, showing inorganic silica-like character of the deposited layers.

[1] P. Antony Premkumar, S.A. Starostin, M. Creatore, H.W. de Vries, R.M.J.Paffen, P.M.Koenraad, M.C.M. van de Sanden Plasma Process. Polym.,7, 635-639 (2010)

5:40pm TF-ThA11 Scale Dependent Surface Energies Influence Wetting Behaviour on Ultimately Small Topographies, *Jan Knauf*, Advanced Molecular Films GmbH and RWTH Aachen University, Germany*, L. Reddemann*, Advanced Molecular Films GmbH and Universität zu Köln, Germany*, K. Cheng*, AMF GmbH, Germany*, A. Böker*, DWI-Leibniz-Institute for Interactive Materials, RWTH Aachen University; Lehrstuhl für Makromolekulare Materialien und Oberflächen, RWTH Aachen University, Germany*, K. Reihs*, Advanced Molecular Films GmbH, Germany
For the first time we observe the effect of scale dependent surface energies on a macroscopic wetting phenomenon. We have been able to produce surfaces structured with sub-nm topographies which exhibit liquid wetting deviating considerably from the behaviour expected from thermodynamic models.

It is known from grazing-incidence X-ray scattering experiments on planar liquid surfaces that surface energy is reduced at very small length scales [1,2]. By deliberately transferring this effect to solid-liquid interfaces it would be possible to create surfaces with distinct wetting characteristics. We have achieved this transfer by preparing defined monolayers of mixed compositions deposited from 1H,1H,2H,2H-perfluoroalkyl thiols of differing chain lengths. As an example, an equimolar binary mixed monolayer from 1H,1H,2H,2H-perfluorodecyl and 1H,1H,2H,2H-perfluorododecyl thiols shows an increase in advancing water contact angle of about 2° compared to the single component monolayers. This increase is considerably less than expected from simple thermodynamic models, as Wenzel´s equation of wetting on rough surfaces predicts an advancing angle difference of 7°. We expected that with suitable contacting liquids and tailored topographies the effect of reduced surface energy could be enhanced or even be inverted towards increased surface energies. Thus, it would be possible to manipulate the apparent wetting behaviour of surfaces by creating well-defined ultimately small topographies.

As model system we prepare monolayers from various mixtures of 1H,1H,2H,2H-perfluoroalkyl thiols (FnH2SH, n = 6,8,10,12,14) of different chain lengths on gold, which have been proven to adsorb randomly on the substrate without forming separated domains. Another crucial feature is the stiff helical conformation that is adopted by fluoroalkyl chains. Thus, sub-nm surface topographies with distinct height differences of 1.2 Å per CF_2 group and chain distances of 5.8 Å are created, which have been characterized in detail by static secondary ion mass spectrometry, dynamic contact angle measurements and ellipsometry. Parameters governing the formation of the final monolayers could be obtained and were shown to vary systematically depending on the thiols employed.

[1] S. Mora *et al.*, Phys. Rev. Lett. 90, 216101 (2003)

[2] C. Fradin *et al.,* Nature **403**, 871 (2000)

Thin Film
Room: Hall D - Session TF-ThP

Thin Films Poster Session

TF-ThP1 Synthesis of Multilayered MgO/Ag/MgO Thin Films in the (001) and (111) Orientations by Pulsed Laser Deposition, *Daniel Velazquez*, R. Seibert, Z. Yusof, L. Spentzouris, J. Terry, Illinois Institute of Technology

Crystalline, highly oriented MgO/Ag/MgO ultrathin films were grown in the crystallographic orientations (001) and (111) via pulsed laser deposition at 150 °C and 170 °C, respectively. Buffer Ag films ~40 nm thick on MgO(001) and Si(111) single crystal substrates were used to assist the epitaxial growth of the MgO/Ag/MgO multilayer structures in the corresponding orientation. The formation of multilayers was monitored in-situ via reflection high-energy electron diffraction. The physical and chemical structure of the films is further characterized via X-ray photoelectron spectroscopy and scanning tunneling microscopy.

TF-ThP2 Development of CNT/Ni Composite Plated Films with Excellent Mechanical Properties, *Shoko Yamada*, Aichi Institute of Technology, Japan, *H. Ito,* Aichi Institute of Technology, *A. Matsumuro*, Aichi Institute of Technology, Japan

Surface modification of forming many kinds of films must be one of the most important technologies. For especially many kinds of plating methods are already established and easy processing to the product of complicated forms. Furthermore, the composite plating which contains many kinds of small particles in the film are also fabricated and it contributes to the further improvement in the characteristic.

In this study, we focused on development of Ni composite plated films reinforced by dispersed multi-walled CNT with 50 nm in the diameter and several μm in the length using the ultrasonic vibration. An ordinary electroplating method was applied at room temperature. CNT/Ni composite plated film was examined under the conventional plating conditions of pH 4.5-4.7 using a Ni plate as an anode and a Cu plate as a cathode. The mixing weight concentrations of CNT were changed in the range of 0-0.1 wt.%CNT to the weight of the plating bath. It is necessary to prevent from aggregation of CNT in composite plated films because the aggregation parts of CNT must surely cause a loss of strength of the materials. In order to distribute CNT molecules in the plating solution, the ultrasonic vibrations was applied for 1 h before the plating process. The operation conditions was set constant as follows; the bias voltage of 3.7 V, the current density of 3.0 A/dm^2 and the plating time of 10 minutes. Thickness of plated film obtained was about 40 μm. Fabrication of CNT/Ni composite films of all mixing weight ratio plated on a Cu plate was confirmed with flat surfaces. But the remarkable condensation parts were observed at the surface at the weight ratio of 0.1 wt.%CNT. The X-ray diffraction experiments clearly indicated no formation of any compound between Ni metal and CNT, because only Ni crystalline diffraction patterns for all CNT concentrations were identified. Vickers hardness tests showed that the hardness increased with the increase of concentration up to 310 Hv of 0.07 wt.%CNT, and decreased after that. This maximum hardness was about twice of the value of the pure Ni plated film. The decrease of hardness over the concentration of 0.07 wt.%CNT should be due to existence of softer aggregate part CNT in the composite films. The friction and abrasion characteristics were also estimated using by a pin-on-disk tester under the load of 0.5 N with a stainless steel pin. It was clarified that the friction coefficient of the composite film with concentration of 0.07 wt.%CNT decreased to 0.5 in comparison with pure Ni coating of 0.8 and showed an unobservable abrasion mark.

From the above results, industrial validity of this study was surely able to be found out.

TF-ThP3 Fabrication of Dispersed C$_{60}$ Molecules/TiN Composite Film Using by Simultaneous Deposition Method with Both Heating Evaporation and Sputtering, *Yuki Ishiyama*, *A. Matsumuro*, Aichi Institute of Technology, Japan

We fabricated dispersed C$_{60}$ molecules/Al nano-composite thin films using by a conventional vacuum evaporation method. The microstructural characterization of the films obtained clarified the uniform dispersion of C$_{60}$ molecules in Al based film. Nano-indentation hardness of Al-1.0 wt.%C$_{60}$ showed increase up to 3 times larger than that of Al film. These results clearly indicated that dispersion of C$_{60}$ molecules in the conventional films contributes to drastic improvement in mechanical properties.

In this study, we tried to establish the synthesis technology of the composite thin films containing dispersed C$_{60}$ molecules in order to apply practical uses in the industry fields. We focused on conventional high hardness TiN films fabricated using by RF magnetron sputtering method. For the purpose of evaporating C$_{60}$ molecules, the heating evaporator was equipped directly below the substrate of existing RF magnetron sputtering chamber due to prevent from the influence of plasma. It was possible to control the deposition rates of two kinds of evaporation sources to become the predetermined compositions separately.

TiN films with constant thickness of 100 nm were deposited on Si(100) water-cooled substrates using by the RF magnetron sputtering deposition method for 30 minutes. The concentration of C$_{60}$ molecule powder was changed in the range from 0.5 to 50 wt.%, and the evaporation temperature was controlled in the range of 473-673 K. The structure analyses of all nano-composite films prepared by X-ray diffraction method showed TiN crystalline structure, and FT-IR analysis clarified the existence of C$_{60}$ molecules contained in TiN films. Nano-indentation studies showed that the hardness of the composite film of 2.0 wt.%C$_{60}$/TiN showed the maximum hardness of 18 GPa and this value was increased up to 50 % larger than that of TiN film.

The present results clearly indicate that the conventional hard thin films prepared by RF sputtering should be also effective to synthesize remarkable hard composite thin films by dispersing C$_{60}$ molecules. Therefore, this study let us know the bright future view of development of the innovative high-hard composite thin films reinforced using by C$_{60}$ molecules.

TF-ThP4 Improved Reflectance of M/Si Bilayers for Extreme Ultraviolet Lithography Reflective Mirror, *Chao-Te Lee*, D. Chiang, P.-K. Chiu, H.-P. Chen, C.N. Hsiao, National Applied Research Laboratories, Taiwan, Republic of China

The periodic Mo/Si bilayers were deposited on Si substrate by RF magnetron sputtering with Mo and Si targets. The Mo/Si bilayers were designed for reflectivity at the wavelength of 13.5 nm. The effects of substrate temperature range (T=20 to 25 ℃, and 20 to 55℃) on the microstructure, surface roughness and reflectance of Mo/Si bilayers were investigated by atomic force microscopy (AFM), high resolution transmission electron microscopy (HRTEM), and a spectrometer. The AFM measurements showed the Mo/Si bilayers to have a uniform morphology with a very low surface roughness value under 0.2 nm. It was found that the interface between Mo and Si film was clearly discriminated at substrate temperature range 20 to 25 ℃ by HRTEM. The reflectivity of Mo/Si bilayers was 47.9% at substrate temperature range 20 to 55 ℃, and 63.3% at substrate temperature range 20 to 25 ℃, respectively. The incident angle increased from 33.47o to 46.13o with substrate temperature range. The improved reflectance and incident angle shifted were attributed to form the clearly interface and vary the film thickness.

TF-ThP8 Characterization of Fluorine-doped Al$_2$O$_3$ Films Deposited by High-Power Impulse Magnetron Sputtering, *Bohuei Liao*, Instrument Technology Research Center, Taiwan, Republic of China, *C.N. Hsiao,* ITRC, NARL, Taiwan, Republic of China, *C.C. Lee*, National Central University, Taiwan, Republic of China

Fluorine-doped Al$_2$O$_3$ films were deposited by high-power impulse magnetron sputtering with an Al metal target at room temperature. In order to obtain better optical and mechanical properties, films were investigated under different duty cycle and different ratios of O$_2$ to CF$_4$ gas. The optical properties in deep ultraviolet range, microstructure, surface roughness, and crystalline structure, of fluorine-doped Al$_2$O$_3$ films have been studied. The fluorine-doped Al$_2$O$_3$ films deposited with 45/555 duty cycle and 0.6 sccm CF$_4$ has lowest extinction coefficient (5×10^{-4})and highest refractive index (1.70) at 193 nm. Besides, the fluorine-doped Al$_2$O$_3$ films reveal a dense and amorphous structure.

TF-ThP9 Formation of ZnGaON Films Prepared by Two Types of co-Sputtering using ZnO or Zn Target and their Optical Properties, *Junichi Iwata*, Y. Hirano, H. Sase, H. Katsumata, Meiji University, Japan

ZnO is an interesting wurtzitic semiconducting material with a wide band-gap of 3.3 eV. It has been reported that the reduction of the optical band-gap down to 2.4 eV was observed from (ZnO)$_x$(GaN)$_{1-x}$ powders with x = 0.81[1]. Moreover, optical band-gap of nitrogen doped ZnO (ZnON) films decreased from 3.26 to 0.9 eV with increasing the N concentration[2], while that of Zn$_{1-x}$Ga$_x$O films was reported to be engineered from 3.3 to 4.9 eV by varying the Ga content[3]. From these facts, we believe that the band-gap of ZnGaON can be widely controllable from 0.9 to 4.9 eV by changing their chemical composition. In these previous reports, however, there have been few observations on their luminescence properties. The purpose of this

study is to form ZnGaON thin films with various optical band-gaps. The substrates used in this study were c-axis sapphire substrates or glass substrates. ZnGaON thin films were deposited on these substrates by two kinds of radio frequency (RF) magnetron co-sputtering methods. One is co-sputtering (a) of GaN tablets and a ZnO target in N_2/O_2 gas flow, in which the GaN tablets were placed on the ZnO target and the number of GaN tablets (N_{GaN}) was varied from 0 to 3. The other is co-sputtering (b) of Ga_2O_3 tablets and Zn target in Ar/N_2 gas flow, in which the Ga_2O_3 tablets were placed on the Zn target. Samples were subsequently subjected to NH_3 treatment at 500 °C for nitridation in former co-sputtering (a) and N_2 annealing at 500 °C for improvement of crystallinity in latter co-sputtering (b). These samples were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectrometry (EDS), optical transmittance and photoluminescence (PL). First of all, we show the characterization results of films prepared by co-sputtering (a). XRD analysis showed that the crystalline quality of ZnGaON films became worse with increasing N_{GaN}. EDS results revealed that nitrogen doping concentration in ZnGaON films was increased only by NH_3 treatment. Optical band-gap of ZnGaON films became wider from 3.29 to 3.51 eV with increasing N_{GaN} from 0 to 3 due to Burnstein-Moss shift. PL spectra of ZnO films showed band-to-band emission at 380nm, while those of ZnGaON films exhibited a broad and weak peak centered at 530 nm, which results from oxygen interstitial (O_i). On the other hands, optical band-gap of ZnON films prepared by co-sputtering (b) without Ga_2O_3 tablets decreased to 1.18 eV, probably due to formation of Zn_3N_2.

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TF-ThP14 Growth and Characterization of Aluminum Oxide for M/I/S Junctions, *Zachary Barcikowski*, University of Maryland, College Park, *J. Pomeroy*, National Institute of Standards and Technology (NIST)

In progress towards spin polarization measurements, we are using a unique ultra-high vacuum (UHV) deposition chamber equipped with electron gun deposition sources, sputter deposition, and plasma oxidation to fabricate shadow-mask defined tunnel junctions. The formation of the tunnel barrier is one of the most crucial processes in junction fabrication which makes the development of an optimal growth recipe a vital step. While varying plasma oxidation process parameters, we will be growing aluminum oxide thin films as a tunnel barrier for metal/insulator/superconductor junctions. Optical spectra of the oxidation plasma and electrical characterization of the resulting junctions will be used to elucidate optimum growth conditions for our aluminum oxide tunnel barriers. The aforementioned data and experimental details will be discussed in this presentation.

TF-ThP15   Low–Temperature Thin Dielectric Films Obtained by ECR–CVD for Application in Non–Volatile Memories, *David Mateos, J.A. Diniz,* University of Campinas, Brazil, *S.N. Mestanza Muñoz,* Federal University of ABC, Brazil, *N. Nedev, M.A. Curiel Alvarez,* Autonomous University of Baja California, Mexico, *M. Mederos Vidal,* Federal University of ABC, Brazil, *B. Valdez, G. Montero*, Autonomous University of Baja California, Mexico

In this work we present results for two types of thin films deposited by ECR–CVD: silicon oxide (SiO_2) and hydrogenated amorphous silicon (a–Si:H) with thicknesses of about 6–8nm and 3–4nm respectively. SiO_2/a–Si:H and SiO_2/a–Si:H/SiO_2 structures for potential application in Non–Volatile Memories, were deposited on p–type (100) c–Si wafers under the following conditions: a gas pressure of 2.0mTorr, an applied ECR microwave (frequency of 2.45GHz) with power of 250Watts and a substrate temperature of 20°C. The precursor gases used for SiO_2 deposition were 2% of SiH_4 diluted in Ar, Ar and O_2 with flows of 125, 5 and 2.5sccm, respectively. The a–Si:H layers were deposited without oxygen using the same SiH_4 and Ar flows. The films were subjected to furnace annealing in N_2 at temperatures in the 800–1100°C range for 60min. Different oxygen and silicon incorporation into the films were extracted using Energy Dispersive X–ray (EDX) analysis (Fig1). Information for the layer thicknesses and optical properties was carried out by Single Wavelength Ellipsometry (SWE) λ~638nm. The thickness measured was 7–11nm and 9–20nm for two and three layers, respectively. Refractive index (n) values between 1.46–1.53 that were obtained are greater than stoichiometric silicon oxide (n=1.457) reported in the literature, indicating formation of thin films rich in silicon. MOS capacitors were fabricated by r.f. sputtering of Al as top (d~0.5 μm) and back contacts. These capacitors were sintered at 450°C in forming gas (92%N_2 and 8%H_2) for 5, 10 and 20min. Electrical characterization was carried out by Capacitance–Voltage (C-V) measurements. The increase of the low temperature annealing time, leads to an improvement of the SiO_2/Si interface seen as an increase of the slope of the high frequency C–V dependence. The capacitance variation in accumulation (C_{acc}) is in the range of 160–180pF for two layer capacitors

which correspond to a thickness of 6–7nm (Fig2). In the same way for three layers the variation of C_{acc} is larger and the thickness calculated is 11–17nm (Fig3). The obtained values are in agreement with the expected thickness determined by SWE. Three–layer MOS capacitors annealing in forming gas for 20min showed hysteresis in their C–V measurements with ramps varying from negative to positive voltages and back. The flat–band Voltage shift (ΔV_{FB}) obtained for capacitors annealed at 800°C and 1000°C were: -2.7V to -2.13V and -4.3V to -2.48V showing an hysteresis window of 0.57V and 1.82V, respectively (Fig4). By the other hand for two–region structures do not present hysteresis (Fig5) which means that three-layer structures could be a possible application as memory devices.

TF-ThP16 MOCVD Growth of 2-D MgZnO Wurtzite Thin Films for Solar-blind Detector Applications, *Judith Reynolds, J.E. Rowe, L. Reynolds, D.E. Aspnes*, North Carolina State University

We report the MOCVD growth of doped thin 2-D MgZnO films on c-plane sapphire substrates for solar-blind detector applications. Spectroscopic ellipsometry (SE), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) are used to determine the composition. The carrier gas is N_2. For pure ZnO, the precursors are diethylzinc (DEZ) and nitrous oxide (N_2O). When growing *p*-type material, 3% nitric oxide (NO) in N_2 provides N ions in the +2 oxidation state needed for doping, and growth occurs as a two-step process monitored in real time by the SE. In the first step, we use a low Zn partial pressure to induce V_{Zn} formation. Because V_{Zn} energies are low for Fermi levels from mid-gap to the conduction band edge, and because the absorption energy for N_{Zn} is 0.08 eV for the hexagonal close packed site of the Zn-polar surface, this allows the N to incorporate at Zn sites as N_{Zn}. In the second step, we use a high Zn partial pressure to drive the formation of oxygen vacancies (V_O). Growth is then followed by an appropriate annealing sequence. While substitutional N on the O sublattice is a deep acceptor, we find that acceptor complexes involving N, H and V_{Zn} can provide p-type ZnO films with a hole concentration of ~10^{18} cm^{-3} at room temperature. For MgZnO growth, we use bis-cyclopentadienyl magnesium (BcMg) in addition to DEZ, N_2O, and NO. Although we deposit MgZnO, films of a quality that we consider acceptable have not yet been produced owing to the large parameter space of temperature, precursor flows, and gas pressure.

TF-ThP17 Investigation of RF-sputtered Tin Sulfide Thin Films with *In Situ* **and Post-Deposition Heating for Photovoltaic Applications**, *R.E. Banai, Jacob Cordell, J.R. Nasr, R.E. Urena, N.J. Tanen, J.R.S. Brownson, M.W. Horn*, Penn State University

Tin (II) Monosulfide (SnS) has become an interesting new material for thin film photovoltaics (PV). The optoelectronic properties indicate that SnS is a suitable material for PV. Its high absorption coefficient, greater than 10^4 cm^{-1}, and band gap near 1.3 eV are well matched with the solar spectrum. SnS also has a carrier concentration greater than 10^{15} cm^{-3} and potential to be both n-type and p-type. With recent success in achieving 4% efficiency, SnS-based devices demonstrated their potential. However, the success comes with extensive optimization of each layer in the device, suggesting that further understanding of SnS is crucial to improving performance.

Sulfur is more volatile than tin and despite strong Sn-S bonds in tin sulfide compounds, sulfur loss to the gas phase while annealing in a vacuum environment. Therefore, it is important to start with a sulfur-rich thin film prior to annealing. Annealing of sulfur-rich sputtered tin sulfide thin films has not been done before. This work will investigate the optoelectronic properties, composition and morphology of annealed, sputtered tin sulfide thin films. Specifically, we will investigate the change in phase and improvement in material quality as a result of post-deposition heat treatments.

Tin sulfide thin films are sputtered on glass and silicon substrates from a distance of 11.5 cm at 115 W with a Ar chamber pressure of 10 mTorr. The sputter target was a 3" SnS_2 with 99.999% purity (LTS Research Laboratories, Inc.). SnS_x samples are deposited at room temperature and 150°C. These samples are then annealed some under medium vacuum (<$2x10^{-6}$ Torr) in the deposition chamber without breaking vacuum at 200, 300, and 400°C.

Preliminary results show promise for high-quality SnS thin films. Significantly improved crystallinity was seen in sulfur-rich thin films annealed at 400°C for 30 minutes. Morphology is not the same for film deposited with and without substrate heating, although both film exhibit a uniform SnS phase as determined by X-ray diffraction. Longer anneal times are expected to further improve crystal quality. Reasonable resistivities are seen in these annealed thin films. The presentation will include details on producing high-quality SnS thin films as well as detailed results of optoelectronic properties, composition and morphology.

TF-ThP19 Sputter-Deposited Carbon Fuses in Long-Term Digital Data Storage, *Jacob Bagley*, H. Wang, A. Diwan, R.C. Davis, B. Lunt, M.R. Linford, Brigham Young University

Solid-state digital data storage devices with the capacity of storing data for 1000 years are being developed. One implementation of this effort is a device that employs a series of carbon fuses. This study explores whether sputtering can yield sufficiently conductive carbon for this application. We hypothesize that reducing the amount of oxygen in the sputtered carbon may sufficiently improve its conductivity. Accordingly, carbon is deposited by DC magnetron sputtering. Sputtering conditions studied include argon pressures of 5 mTorr and 7 mTorr and powers of 250 W and 400 W. Titanium is also co-sputtered at 150 W with a closed shutter to act as an oxygen getter. The oxygen contents of the films were measured by X-ray photoelectron spectroscopy (XPS), and their conductivity was measured with a 500 V megaohmmeter. The oxygen content of the films slightly decreases with decreasing argon pressure and decreasing power on the carbon target. Use of the titanium getter significantly decreases the oxygen contents of the films. However, no significant increase in conductivity is observed, i.e., the deposited carbon is not conductive enough for our purposes. We conclude that sputtered carbon, as deposited with our current system, is not suitable for our devices.

TF-ThP20 Low Hydrogen Silicon Nitride Films Deposited by Plasma Enhanced Chemical Vapor Deposition, *Erica Douglas*, A. Starbuck, C. DeRose, Sandia National Laboratories

Due to exceptional material properties, such as refractive index and others, the use of silicon nitride (SiN) as an optical waveguide has become common. SiN films are used in many applications, from gate dielectrics to encapsulation layers. However, the use of SiN as a waveguide is greatly affected by hydrogen incorporation, particularly at telecommunication wavelengths of ~1550 nm.

Hydrogen incorporation for plasma enhanced chemical vapor deposition (PECVD) of SiN_x is a due to the Si-H species from the use of SiH_4 as well as the standard precursor NH_3 for the N component for SiN_x. The resulting hydrogen bonds, both Si-H species and N-H species, result in absorption and thus loss in the telecommunication spectrum. In particular, the N-H bond has high absorption around 1550 nm.

Previous studies have investigated the use of N_2 as a replacement precursor for NH_3 for low-hydrogen PECVD SiN_x.[1,2] However, these studies have only investigated a few process parameters and their effect on the optical characteristics of the film. In our investigation, a detailed study was performed on a production PECVD system to look at the effect of SiH_4 flow, NH_3 flow, N_2 flow, ratios of all precursors, chamber pressure, and RF bias. The relative hydrogen content was measured for all process parameters through Fourier transform infrared spectroscopy (FTIR). Additionally, we measured the refractive index (from 375 nm to 1675 nm), deposition rate, uniformity, and stress of the SiN_x films. We are able to not only tune the relative hydrogen content of the film, but the uniformity, stress and refractive index independently, in order to fabricate SiN_x optical waveguides for photonic applications.

It was observed that although substituting N_2 in place of NH_3 for the source of N in SiN_x resulted in lower relative hydrogen content, it greatly affected the refractive index and stress of the film resulting in a film that is not ideal for photonic integrated circuits. In order to balance these film properties, we were able to exploit other process parameters, such as chamber pressure and RF bias, in order to tune the film. We also measured the insertion loss of SiN_x optical waveguides with select SiN_x films in order to further understand the role of different film properties.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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TF-ThP21 Enhancing the Water Vapour Barrier Properties of Polymer Substrates with ALD Metal Oxide Films, *Karyn Jarvis*, G. Griffiths, Australian Nuclear Science and Technology Organisation (ANSTO), Australia, L. Hyde, Melbourne Centre for Nanofabrication (MCN), Australia, P. Evans, G. Triani, Australian Nuclear Science and Technology Organisation (ANSTO), Australia

Polymer substrates are used for flexible organic electronics due to being lightweight, cheap, transparent and printable in continuous roll to roll manufacturing technology. However, a significant disadvantage of these materials is their high gas/vapour permeability. A permeation barrier is therefore essential when using polymer substrates in organic electronics to reduce both oxygen and moisture ingress to an acceptable level. Films deposited by atomic layer deposition (ALD) have shown to improve the barrier properties of polymeric films [1-2]. In the present study, single alumina (Al_2O_3) films were deposited onto one surface of PET substrates (Multapex, biaxially oriented, 75 μm thick) using thermal and plasma enhanced ALD. Films with thicknesses in the range of 7 - 25 nm were deposited at 100 or 120°C. The water vapour transmission rate (WVTR) of the ALD films was determined predominately by tritium permeation, but was also measured using the MOCON and Ca-tests for comparison. Thermally grown 20 nm thick alumina films were also deposited onto PET and PEN substrates with thicknesses of 75 and 125 μm to evaluate the effect of substrate type and thickness on WVTR. In addition, several mixed oxide structures such as alumina/hafnia and alumina/titania were also investigated to examine their potential for further decreasing the WVTR. Characterisation of the ALD grown films was carried out using X-ray photoelectron spectroscopy, atomic force microscopy and optical microscopy. For single Al_2O_3 layers, film thickness and deposition temperature influenced the WVTR. The WVTR decreased with increasing film thickness and deposition temperature. The deposition of ALD metal oxide films was successful in reducing water permeation through polymer substrates, demonstrating the potential of these coatings as a barrier technology for organic electronics over wide range of polymer based products.

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TF-ThP22 Sol-Gel Deposited TiO_2 Thin Films for Propane Gas Sensors, *Ismael Garduño-Wilches*, A. Maldonado Álvarez, CINVESTAV-IPN, México, D.R. Acosta-Najarro, Universidad Nacional Autonoma de México

Titanium-dioxide films are produced by the dip coating method, using a solution of 2-propanol and titanium isopropoxide in a concentration of 0.17M and an immersion speed of 0.122 cm/s. Films with different thickness are obtained by changing the number of immersion cycles. Analysis results indicate that the obtained films present the TiO_2 anatase structure when treated at 400 °C for 3 hrs, the film thickness ranged from 20nm to 150 nm and the rate deposition is of 18 nm/cycle.

Gas sensing studies indicate that at a work temperatures of 300 °C sensors present a significant change in electrical resistance. When analyzing sensors sensitivity as a function of propane concentration and film thickness a two-regime behavior is observed, being the sensitivity independent of the film thickness when partial pressures are above 400 ppm, and thickness dependant at lower partial pressures. The maximum sensitivity is obtained in the range from 5 ppm to 300 ppm for the film grown with 5 immersion cycles.

TF-ThP23 Investigation of Optical Property and Crystalline of the Sliver Mirror in the 35 Krad Co-60 Radiation Environment, *Po-Kai Chiu*, D. Chiang, C.T. Lee, Y.W. Lin, C.N. Hsiao, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China

This study investigated the optical design of silver mirror and effected of optical properties in the radiation environment. In different optical designed by Macleod software was studied in the same radiation environment. The optical properties were measured by the integrating sphere spectrophotometer and material properties by X-ray diffraction instrument. After the 35 Krad Co-60 radiation testing, the titanium dioxide film, silicon dioxide film, pure chromium and silver film could efficient reduce the damage of the B270 substrate by radiation. In the visible light, the titanium dioxide film had smaller spectral absorption about 0.5% at 450 nm and about 25 nm spectral drift. In the metal film,ΔT% in visible light of the sliver film was about 0.5% and chrome film about 1.5%. So, the radiation resistance of silver film was better than chrome film. By X-Ray diffraction analysis showed that the crystalline of silver film would be slightly improved by exposure to radiation.

TF-ThP25 Effect of Mg Doping Concentration on Resistance Switching Behavior of Oxygen Deficient Mg-doped Al_2O_3 Films, *Kyumin Lee*, Y. Kim, T. Kim, H. Na, H. Sohn, Yonsei University, Korea

In this study, the effect of Mg doping concentration on the resistance switching behavior of Al_2O_3 films was investigated in conjunction with an analysis of the chemical bonding states. Mg doping concentration is increased from 0 to 8.6% with increasing Mg gun power. In micro-structure, the Al_2O_3 and Mg-doped Al_2O_3 films have amorphous structure in all conditions. In non-lattice oxygen, the concentration of non-lattice oxygen is increased with increasing Mg doping concentration in Al_2O_3 films. In order to identify the effect of only non-lattice oxygen

concentration without crystal structure change, the resistance switching characteristics such as operating current, forming electric field, endurance, and retention was compared. The operating current and uniformity of endurance is increased with increasing Mg doping concentration. And also the conduction mechanism and activation energy from Poole-Frenkel equation of resistance switching characteristics of Mg-doped Al_2O_3 films was investigated. The activation energy is decreased with increasing non-lattice oxygen concentration because non-lattice oxygen is defect in Al_2O_3 films. From these findings, the resistance switching characteristics are influenced by non-lattice oxygen concentration.

TF-ThP26 Failure of Semiclassical Models to Describe Resistivity Size Effect in sub 15nm Films., *Daniel Yates*, University of Central Florida*, X. Liu,* Carnegie Mellon University*, D. Choi,* Korea Railroad Research Institute, Republic of Korea*, P. Schelling,* University of Central Florida*, K. Barmak,* Columbia University*, K.R. Coffey*, University of Central Florida

Previous work in copper thin films with thickness > 30nm demonstrated excellent agreement with the semiclassical models of the resistivity size effect. Using the same methodology developed for Cu, electron scattering at surfaces and grain boundaries in polycrystalline Ni, Ru, and W films was examined. 2-200 nm thick films were prepared via DC magnetron sputtering onto thermally oxidized silicon wafers. Films with thicknesses below 10nm were encapsulated in 0.5nm thick layers of Ta to improve film stability.

Films were annealed in the range of 200°C to 900°C in Ar+3% H_2. They were characterized using X-ray reflectivity, Rutherford backscatter spectrometry, and transmission electron microscopy with precession electron diffraction techniques to measure thickness, grain size, and film continuity. Resistivity was measured using the Van Der Pauw method.

The contributions of surface and grain boundary scattering were assessed using the semiclassical models of Fuchs-Sondheimer and Mayadas-Shatzkes. Systematic deviations from model predictions were observed for films less than approximately 15nm thick in all three metals. The complex Fermi surfaces of these metals result in a variety of Fermi velocities, as several bands cross the Fermi level. This complexity may be a likely cause for the failure of the semiclassical models, which consider only an average mean free path value. The deviations are most pronounced in the thinnest films.

Electronic Materials and Processing
Room: 314 - Session EM+NS+TF-FrM

Transparent Electronics
Moderator: Lisa M. Porter, Carnegie Mellon University

9:00am **EM+NS+TF-FrM3** **Transparent Amorphous Oxide Semiconductors: Interfacial Chemistries and New Applications**, *Gregory Herman*, Oregon State University **INVITED**
During the past decade research in the area of transparent amorphous oxide semiconductors (TAOS) has increased substantially due to the ability to fabricate thin film transistors (TFT) at relatively low processing temperatures while still maintaining large electron mobilities. The primary applications for these materials include active matrix displays with the possibility for integration onto flexible polymeric substrates. More recently potential applications have expanded to include non-volatile memory, sensing, and memristive neurological networks. We have studied amorphous zinc tin oxide (ZTO) and indium gallium zinc oxide (IGZO) that have been deposited by both vacuum and solution based approaches. The electrical characteristics of the films have been evaluated in both TFT and metal-insulator-metal memristive devices. Excellent device characteristics have been obtained, however we have found that surface impurities can strongly affect device stabilities. We have found that the chemistry of absorbed species on the back-channel strongly influences the bias stress stabilities of ZTO and IGZO TFTs, while reactions at the Al/ZTO interface leads to the resistive switching characteristics of memristors, and post annealing leads to interfacial reactions and modifies the Schottky barrier for Pt/IGZO diode structures. To better understand the role of interfacial reactions on TFT and memristive devices we have developed methods to prepare clean well defined surfaces for ZTO and IGZO, and further characterized there surface and interface properties with X-ray photoelectron spectroscopy and secondary ion mass spectrometry.

9:40am **EM+NS+TF-FrM5** **HMDSO/O$_2$-Plasma-Deposited Organic-Inorganic-Hybrid Materials as Gate Dielectrics for MgZnO Thin Film Transistors and Encapsulation Layers for Solar Cells**, *Y.S. Li, C.H. Tsai, I.C. Cheng, Jian-Zhang Chen*, National Taiwan University, Taiwan, Republic of China
Organic-inorganic hybrid materials can be deposited from hexamethyldisiloxane (HMDSO) diluted with oxidants using plasmas technology. The properties of the deposited material can be controlled by varying the dilution ratio of the oxidants. The chemical compositions can vary from polymer-like (organic-like) to SiO$_2$-like (inorganic-like) depending on the oxidant dilution ratio and the process power. In this paper, we report two applications of HMDSO/O$_2$-plasma-deposited organic-inorganic-hybrid materials developed in our group: (1) as gate dielectrics of MgZnO TFTs, and (2) as the encapsulation layers for organic-inorganic hybrid solar cells.

The inorganic/organic component ratios in hybrid films were tailored by varying the process power and the O$_2$/HMDSO flow rate ratio. The FTIR analysis and contact angle measurement show that higher deposition power and/or larger O$_2$/HMDSO flow rate ratio result in more SiO$_2$-like films. For rf-sputtered MgZnO TFTs, a more organic-like film affords a better interface to the MgZnO active layer and higher dielectric constant, leading to a smaller threshold voltage and a steeper subthreshold slope; while an inorganic-like film has lower leakage currents, resulting in a larger on/off current ratio in the transistors. The TFT with an organic-inorganic-hybrid gate dielectric deposited at an O$_2$/HMDSO ratio of 40 and process power of 30 W exhibits a threshold voltage of 6.8 V, a subthresold slope of 0.48 V/dec, an on/off current ratio of >10^7 and a linear mobility of ~60 cm^{2}V^{-1}s^{-1}, respectively. We also have demonstrated that this O$_2$/HMDSO-plasma-deposited organic-inorganic material can be used as an efficient single-layer encapsulation technique for organic photovoltaic cells. Calcium test was used to evaluate the water vapor transmission rate (WVTR) of the barrier film deposited on a polyimide foil. A water vapor transmission rate of 3.6×10^{-6} g/m^2-day was obtained for a 1.5 um-thick single permeation layer. Inverted type organic photovoltaic passivated by the hybrid material was used to evaluate the effectiveness of this encapsulation. Efficiency decay was not observed in the cell coated with this encapsulation layer after 3000-hour exposure to the air; on the contrary, the un-encapsulated counterpart cell degraded rapidly and completely failed after 120-hour exposure to the air. The result shows that this single-layer hybrid material encapsulation can enhance the stability of organic photovoltaic cell. The cell life time is greatly improved.

10:00am **EM+NS+TF-FrM6** **Solution Processed Oxide Semiconductor and Dielectric Thin Films: Towards High Performance, Low Temperature ZnO Field-effect Transistors with Low Operation Voltage**, *Yu Liu, H. Katz*, Johns Hopkins University
Solution processing is a preferred method for manufacturing large-area low-cost electronic devices. High performance metal oxide semiconductor-based field-effect transistors can be fabricated in this manner. For applications of flexible electronics, a low processing temperature is required to avoid overheating of the substrate material. It is a challenge to fabricate a dense impurity-free oxide semiconductor film at low temperature. A water-based ZnO precursor with ammine-hydroxo complex was introduced to decrease the processing temperature. However, repeated time-consuming centrifugation and decantation steps are required in this process.

To simplify the processing steps we discovered a new strategy to prepare aqueous ZnO precursor. Based on this precursor, ZnO FETs with a benchmark dielectric SiO$_2$ have been fabricated at 200 °C. The transistors exhibited promising performance with a saturation field-effect mobility of 0.7 cm^2·V^{-1}·s^{-1} and a typical on/off current ratio on the order of 10^4. To prepare the precursor, zinc nitrate hexahydrate and acetylacetone were dissolved in ammonium hydroxide with a concentration of 0.6 M. As prepared precursor was then filtered and dilute it with DI water. A similar strategy was applied in the preparation of aqueous zinc tin oxide precursor with tin fluoride as tin source.

Based on a redox chemical reaction between fuel and highly exothermic oxidizer, a combustion processing method has been found to be promising for decreasing the annealing temperature of oxide semiconductor thin films. In this study, combustion processing strategy was used in preparing high capacitance ion-incorporated alumina dielectrics at 200 °C by using urea as the fuel and aluminum nitrate nonahydrate as oxidizer.

Both zinc tin oxide and sodium-incorporated alumina low temperature precursors showed strong exthothermic reaction peaks at temperatures lower than 200 °C. This suggests a conversion from ammine-hydroxo/combustion precursor to solid zinc tin oxide/sodium incorporated alumina thin films at a temperature lower than 200 °C. A sharp (002) peak is shown in the XRD pattern of 200 °C processed ZnO thin film, which demonstrates a wurtzite crystal structure.

The high-k dielectrics exhibited a good compatibility with our low temperature ZnO precursor and excellent transistor performance has been achieved in these devices. With this, we are able to fabricate low temperature low voltage transistors on plastic substrates such as polyimide. This low temperature ZnO precursor could also be applied to fabricate flexible inverters in combination with p-type solution processed polymer semiconductors, such as PBTTT and TIPS-pentacene.

10:40am **EM+NS+TF-FrM8** **Metal Oxide Conductors and Semiconductors: From Materials to Device Applications**, *Elvira Fortunato, R. Martins*, FCT-UNL and CEMOP-UNINOVA, Portugal **INVITED**
Transparent electronics has arrived and is contributing for generating a free real state electronics that is able to add new electronic functionalities onto surfaces, which currently are not used in this manner and where silicon cannot contribute [1,2]. The already high performance developed n- and p-type TFTs have been processed by physical vapour deposition (PVD) techniques like rf magnetron sputtering at room temperature which is already compatible with the use of low cost and flexible substrates (polymers, cellulose paper, among others). Besides that a tremendous development is coming through solution-based technologies very exciting for ink-jet printing, where the theoretical limitations are becoming practical evidences. In this presentation we will review some of the most promising new technologies for n- and p-type thin film transistors based on oxide semiconductors and its currently and future applications.

[1] E. Fortunato, P. Barquinha, and R. Martins, "Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances," Advanced Materials, vol. 24, pp. 2945-2986, Jun 2012.

[2] P. Barquinha, R. Martins, L. Pereira and E. Fortunato, Transparent Oxide Electronics: From Materials to Devices. West Sussex: Wiley & Sons (March 2012). ISBN 9780470683736.

11:20am EM+NS+TF-FrM10 Influence of Oxygen Diffusion in Transparent In$_{0.9}$Sn$_{0.1}$O$_x$ Film on Effective Work Function Change, *Toshihide Nabatame*, NIMS, Japan, *H. Yamada,* Shibaura Institute of Technology, Japan, *A. Ohi,* NIMS, Japan, *T. Oishi,* Shibaura Institute of Technology, Japan, *T. Chikyo*, NIMS, Japan

The In$_{0.9}$Sn$_{0.1}$O$_x$ (ITO) films is widely used as transparent electrodes in optical and optoelectronic devices. The work function (WF) of the ITO film was generally evaluated by optical measurements such as ultraviolet photoemission spectroscope and Kelvin probe. However, the optically measured WF differs from the effective work function (EWF) estimated by electrical measurement. The influence of oxygen diffusion in ITO film on EWF change has not been also understood. In this paper, we systematically investigate EWF change of ITO film by oxidation and reduction annealing. We also examine oxygen diffusion coefficient (D) of ITO film, using isotope ^{18}O tracer, to discuss influence of oxygen diffusion of ITO film on EWF change.

The ITO films were prepared under an Ar/O$_2$ by sputtering using an In$_{0.9}$Sn$_{0.1}$O$_x$ target. The ITO-gated metal-oxide-semiconductor (MOS) capacitors with HfO$_2$ and SiO$_2$ gate insulators were fabricated to estimate EWF value of ITO film. The ITO (150 nm)/SiO$_2$/Si films were annealed at 300 – 500 °C for 30 min under 10^4 Pa of ^{18}O isotope (99%) gas to obtain D value.

The resistivity of ITO film, which consists of cubic structure, shows an almost same value regardless of oxidation and reduction annealing temperatures. The EWF of ITO-gated MOS capacitors significantly changes from 4.4 to 5.2 eV as the oxidation annealing temperature increases from 250 to 350 °C. The EWF change is saturated at 350 °C. On the other hand, the EWF value decreases in reduction annealing temperature ranging from 200 to 350 °C. This must be due to oxygen introduction and removal in ITO film during oxidation and reduction annealing, respectively. To understand the mechanism of oxygen transfer in the ITO film, we examine D behavior of ITO film. The ITO film has a large D value of about a 1.1X10-20cm2/s at 300 °C and a small activation energy (Ea) of about 1.4 eV. We found that the D and Ea values are similar to those of grain boundary in monoclinic ZrO$_2$. This results indicate that oxygen diffusion of ITO film occurs even at low temperature of 300 °C and affects to the EWF change during oxidation and reduction annealing at around 300 °C.

11:40am EM+NS+TF-FrM11 Transparent Conducting Films from Ultraporous Aerogels of Single-Walled Carbon Nanotubes / PEDOT:PSS Composites, *Xi Liu*, *L.M. Porter, M.F. Islam*, Carnegie Mellon University

In this study we report on the fabrication and characterization of ultralight (>99% porosity) aerogels based on single-walled carbon nanotubes (SWCNTs) and poly(ethylene dioxythiophene) : poly(styrene sulfonate) (PEDOT:PSS), that are electrically conducting and highly stretchable. The aerogels were created by critical-point drying of aqueous elastic co-gels of individually dispersed SWCNTs mixed with PEDOT:PSS to yield either free-standing films or thin films supported on flexible (PET) or glass substrates; the nanotubes substantially reduce the percolation threshold of PEDOT:PSS. These transparent conductors with sheet resistance of 35 ohm/sq and 60% transparency (at 550 nm) also proved to be highly flexible – they can be repeatedly stretched to 20% with < 1% change in resistivity. The electrical, optical, mechanical, and microstructural properties of these materials will be presented, along with their application in devices.

Thin Film
Room: 307 - Session TF+AS-FrM

Thin Film Characterization
Moderator: Mark Davidson, University of Florida

8:20am TF+AS-FrM1 Stability of Platinum Silicide Thin Films above 1000°C, *Robert Fryer*, *R.W. Meulenberg, G.P. Bernhardt, R.J. Lad*, University of Maine

Stable, electrically conductive thin films are needed as components for sensors and actuators operating in harsh environments at temperatures above 1000°C, such as those found in turbine engines, power plants, and high temperature materials manufacturing. The Pt-Si thin film system has been extensively studied in the microelectronics industry but the focus has been on film characteristics below 800°C. In this work, Pt-Si films were grown at varying compositions and deposition temperatures on sapphire and fused silica substrates by electron-beam evaporation of Pt and Si sources in ultra-high vacuum (<10^{-9} Torr); the chemical and thermal stability of the Pt-Si films, both in air and in vacuum, at temperatures between 1000–1200°C were studied. X-ray diffraction (XRD) of as-deposited films indicates the formation of a polycrystalline tetragonal-Pt$_2$Si phase for Pt-rich film

compositions, an orthorhombic-PtSi phase near the Pt$_{50}$Si$_{50}$ composition, and an amorphous film for Si-rich film compositions. The electrical conductivities of these films, measured by a 4-point probe, are in the range of 1x10^6 to 5x10^4 S/m, with the conductivity decreasing at higher Si content. Annealing in vacuum at 1000°C causes grain growth and a marked increase in film conductivities. During annealing in air at 1000°C, film oxidation occurs leading to the formation of Pt-oxide phases coinciding with the Pt-Si phases, but only a ~3-fold decrease in film conductivities. After four hours at 1200°C in air, the Pt-Si films become insulating due to morphological roughening and formation of highly faceted Pt (111) and (200) nanocrystallites coexisting in a SiO$_2$ matrix. Scanning electron microscopy (SEM) revealed that the use of a 50 nm capping layer of amorphous Al$_2$O$_3$, grown by atomic layer deposition (ALD) on top of the Pt-Si films, helps retard oxidation thereby preserving film conductivities in the 10^6-10^4 S/m range and leading to greater film stability as a function of annealing time at 1000°C in air.

8:40am TF+AS-FrM2 Bulge Testing for Mechanical Characterization of sp^2/sp^3 Carbon Thin Films, *Joseph Rowley*, *R.C. Davis, R.R. Vanfleet, N. Boyer*, Brigham Young University, *S. Liddiard, M. Harker*, Moxtek, Inc, *L. Pei*, Brigham Young University

Bulge testing is a technique employed to measure material properties of thin films. Pressurized gas is applied to one side of a film and it's subsequent deformation measured. In many cases, thin films are fragile and therefore difficult to handle. Bulge testing has the advantage of requiring much less handling than other methods, resulting in fewer samples lost to error or accident. Carbon membranes have a wide range of characteristics, depending on their bonding and nano-structure. They can have very desirable properties such as: being chemically inert, high wear resistance and low friction, and high hardness and/or strength. In this work, reactively sputtered sp^2 carbon, diamondlike carbon from a pulsed laser deposition process, and a carbon nanotube reinforced polymer were characterized. PEELS and Raman Spectroscopy were used to determine sp^3/sp^2 ratios and density, CHN testing was used to determine hydrogen content, measuring the resonant frequency was a measure to check stiffness, and bulge testing was used to obtain the Young's Modulus and tensile strength.

9:00am TF+AS-FrM3 Time Dependent Dielectric Breakdown Measurements of Porous Organosilicate Glass using Mercury and Solid Metal Probes, *Dongfei Pei*, University of Wisconsin-Madison, *M.T. Nichols,* Applied Materials, *S.W. King, J.M. Clarke,* Intel Corporation, *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Time-dependent dielectric breakdown (TDDB) is a major concern for low-k organosilicate (SiCOH) dielectrics. To examine the effect of plasma exposure on TDDB degradation, both the time-to-failure (TTF) and charge-to-failure (CTF) measurements [1] were made on porous SiCOH before and after exposure to Ar plasma. Significant discrepancies between mercury and solid-metal probes are observed. With XPS measurement data, a significant amount of mercury was found to have drifted into the porous SiCOH film. This implies that the electrical measurement of porous low-k material under mercury probe may be inaccurate due to this mercury drift effect.

[1] M. T. Nichols, H. Sinha, C. A. Wiltbank, G. A. Antonelli, Y. Nishi, and J. L. Shohet, Appl. Phys. Lett **100**, 112905 (2012)

9:20am TF+AS-FrM4 The Equivalent Width as a Figure of Merit for XPS Narrow Scans, *Matthew Linford, B. Singh,* Brigham Young University, *J. Terry*, Illinois Institute of Technology

X-ray Photoelectron Spectroscopy (XPS) is a widely used surface analytical tool that provides information about the near surface regions of materials. In particular, chemical state information is often obtained from peak fitting XPS narrow scans. And while indispensable for XPS data analysis, peak fitting can be a fairly subjective exercise. Herein we introduce the use of the equivalent width (EW) as an additional and less subjective figure of merit for XPS narrow scans. The EW$_{XPS}$ is simply defined as the area of a narrow scan divided by the height of the maximum of its peak envelope. To limit any ambiguity in EW$_{XPS}$ for a series of spectra, we may also list the peak position of the maximum of the envelope (PE$_{max}$). We provide and discuss four examples that demonstrate the use of these parameters including (i) four C 1s narrow scans of ozone-treated carbon nanotubes (EW$_{XPS}$ ~ 2.11 – 2.16 eV for a Shirley background, and up to 2.88 eV for no background, PE$_{max}$ ~ 284.4 – 284.5 eV), (ii) a series of silicon wafers with different oxide thicknesses (EW$_{XPS}$ ~ 1.5 – 2.8 eV, PE$_{max}$ ~ 99 – 103 eV), (iii) hydrogen-terminated silicon before and after derivatization with pentyl groups, and after annealing of the pentyl-modified material (EW$_{XPS}$ ~ 0.7 – 1.0 eV, PE$_{max}$ ~ 25.9 – 26.1 eV), and (iv) five C 1s narrow scans of nanodiamond

samples, where three of the spectra showed charging ($EW_{XPS} \sim 2.6 - 4.9$ eV, $PE_{max} \sim 272.7 - 293.9$ eV). In this final example, EW_{XPS} was plotted against PE_{max} to identify the region corresponding to the materials that showed the least charging. EW_{XPS} and PE_{max} appear to correlate with the expected chemistries of all the systems studied. We calculate EW_{XPS} using a Shirley baseline and with no baseline at all. In setting the baseline limits for EW_{XPS}, we consider the derivative of C 1s narrow scans. We also show the application of EW_{XPS} to single, fitted components within a narrow scan. Other width functions are also discussed.

9:40am **TF+AS-FrM5 Characterization of Epitaxial Oxides for Electronics, Magnetics, and Photoactivity**, *Tiffany Kaspar*, Pacific Northwest National Laboratory **INVITED**
Transition metal oxides offer an incredibly rich variety of properties which can be harnessed for countless applications. Unfortunately, this variety can be a curse as well as a blessing: the myriad oxidation states, crystal structures, and defects which may occur in the bulk and/or on the surface of any given oxide system makes it challenging to draw meaningful structure-property relationships without employing a full suite of materials characterization techniques. To keep the system as simple and well-defined as possible, and to explore materials and compositions not easily attainable by equilibrium techniques, epitaxial deposition of oxide thin films is widely utilized. However, even in these "simple" systems, thorough characterization of the crystallinity and structural defects, oxidation state, stoichiometry and dopants is critical. Unwelcome surprises are often found in nominally "good" material when one takes the time to investigate. Our laboratory has explored the electronic, magnetic, and photoactive properties of binary and complex oxides as epitaxial thin films, and several examples illustrating the importance of thorough thin film characterization will be presented. In our work on Cr-doped anatase TiO_2, a candidate dilute magnetic semiconductor (DMS), room temperature ferromagnetism was observed that appeared to depend sensitively on "preparation conditions." We applied several characterization techniques, particularly x-ray diffraction (XRD) and transmission electron microscopy (TEM), and were able to correlate the presence of structural defects with room temperature ferromagnetic ordering. One of the most widely investigated materials as a potential DMS has been Co-doped ZnO, but the presence of intrinsic ferromagnetism in this system has been widely debated in the literature. We investigated very high quality epitaxial thin films with several x-ray absorption-based characterization techniques (XANES, EXAFS, XLD) to disprove the presence of intrinsic ferromagnetism in nominally defect-free material. In more recent work, we have explored the visible-light photoactivity of hematite Fe_2O_3 doped with Cr or V. XRD, x-ray photoelectron spectroscopy (XPS), scanning TEM (STEM), and XANES/EXAFS have been applied, as well as less widely utilized techniques such as non-Rutherford resonant elastic scattering (RES) to quantitatively measure oxygen stoichiometry non-destructively, and lab-based x-ray photoelectron diffraction (XPD) to elucidate unique surface oxidation features observed by XPS. The structural properties of doped hematite could then be correlated with the bandgap and spectroscopic photoconductivity measurements.

10:40am **TF+AS-FrM8 Low Energy Ion Scattering Data Analysis for Ultra Thin Films using TRBS**, *Thomas Grehl*, *P. Brüner,* ION-TOF GmbH, Germany, *B. Detlefs, E. Nolot, H. Grampeix,* CEA-LETI, France, *E. Steinbauer, P. Bauer,* Johannes Kepler University, Austria, *H.H. Brongersma*, ION-TOF GmbH, Germany
Low Energy Ion Scattering (LEIS) is well known for its extreme surface sensitivity, allowing elemental characterization and quantification of the outermost atomic layer. This makes it a valuable tool for thin film analysis, e.g. to gain insights to the early stages of film growth or determine film closure. Also contamination analysis can be performed, again making use of the high surface sensitivity to assess the surface composition as the basis for subsequent deposition steps.

In addition, distinct information about sub-surface layers is obtained in a non-destructive way, giving information about the depth distribution of elements up to 10 nm. Although the mechanism for this in-depth signal is well understood, a model for the quantification of the data needs to be established.

One way of modeling the data is demonstrated using TRBS [1], a specialized version of TRIM [2] which was optimized for simulating ion scattering. Combining the TRBS data for backscattering of primary ions and an empirical model for the energy dependent reionization probability gives promising results. By fitting the simulation to the measured data conclusions about film composition, thickness and interface quality can be drawn.

This approach will be demonstrated using different thin film examples. One of the sample sets consisting of HfO_2/Al_2O_3 stacks also characterized by AR-XPS, XRR and GIXRF will be discussed in detail. We will show the

possibility to determine film thickness variations in the Å range. These measurements can be performed in a few minutes without destroying the sample by sputtering. At the same time, the composition of the outer atomic layer is detected, making the approach well suited for routine analysis of films during or after deposition.

[1] A particularly fast TRIM version for ion backscattering and high energy implantation, Biersack, J.P.; Steinbauer, E.; Bauer, P.; Nucl. Instr. and Meth. in Phys. Res., B61, 1991, 77-82

[2] The Stopping and Range of Ions in Solids; Pergamon, New York, 1985

11:00am **TF+AS-FrM9 Polarization-dependent X-ray Absorption Fine Structure Analysis of TES Pentacene Thin Films**, *Beatrix Pollakowski*, Physikalisch-Technische Bundesanstalt (PTB), Germany, *J. Wade, JS. Kim,* Imperial College London, UK, *F.A. Castro,* National Physical Laboratory (NPL), UK, *J. Lubeck, R. Unterumsberger,* Physikalisch-Technische Bundesanstalt (PTB), Germany, *A. Zoladek-Lemanczyk,* National Physical Laboratory, UK, *B. Beckhoff,* Physikalisch-Technische Bundesanstalt (PTB), Germany
Research in organic electronics shall open up alleys for many of its promising applications, including promising applications, including: light emitting diodes, photovoltaics, transistors, biosensors and photonic devices. Despite of the diversity of device functionalities, all these applications are based on thin films of organic materials and in each case their performance is critically dependent upon the precise arrangement and packing structure of the organic molecules in thin films. Our research focuses on this fundamental issue, seeking to better understand the relationships between device performance and thin film morphology of organic semiconductors on the molecular scale [1,2].

A set of 6,13-Bis((triethylsilyl)ethynyl)pentacene (TES-PEN) samples has been prepared on a silicon substrate by using a well controlled printing technique.[2] Different substrate shift speeds were used to modify the layer thickness and the crystallinity.

All X-ray based measurements were carried out at the plane grating monochromator PGM beamline for undulator radiation in the laboratory of the Physikalisch-Technische Bundesanstalt PTB at BESSY II, providing tunable radiation of both high photon flux and high spectral purity in the soft x-ray range [3]. Different kinds of X-ray spectrometry (XRS) analyses were employed to determine the chemical binding state, elemental distribution depending on the depth, and lateral mass deposition.

To analyze the chemical binding state of the molecules, the method Near-Edge X-ray

Absorption Fine Structure spectroscopy (NEXAFS) in fluorescence mode has been employed. Varying the angle of incidence in the fluorescence mode the information depth can be tuned to a pre-selectable depth of interest. In addition, the mean penetration depth at large angles of incidence is high enough to analyze even thicker layers of up to a few hundreds of nanometers as is often the case for complex organic materials. For an analysis of the molecular orientation, the angle between the electric field vector and predominant direction of the molecules has to be varied.

Initial measurement sequences exhibit the potential of this X-ray spectrometry method to significantly contribute to the quantitative analysis of organic materials in thin films. In particular, polarization dependent NEXAFS offers a clear discrimination capability for the orientation of the molecules.

[1] S. Wood, J.S. Kim, D.T. James, W.C. Tsoi, C.E. Murphy, and J. S. Kim, J. Chem. Phys. 139, 2013, 064901

[2] D.T. James, J. M. Frost, J. Wade, J. Nelson, J. S. Kim, ACS Nano 7(9), 2013, 7983.

[3] J. Lubeck, B. Beckhoff, R. Fliegauf, I. Holfelder, P. Hönicke, M. Müller, B. Pollakowski, F. Reinhardt, J.

11:20am **TF+AS-FrM10 Surface Induced Phases in Organic Thin Films: Methods of Crystal Structure Solutions**, *Roland Resel, C. Röthel, A. Pichler,* Graz University of Technology, Austria, *I. Salzmann,* Humboldt University, Germany, *R.G. DellaValle, O. Rosconi,* University Bologna, Italy, *T. Dingeman,* Delft University of Technology, Netherlands, *C. Simbrunner*, University Linz, Austria
A large number of organic molecules exhibit polymorphism and a well-known phenomenon are specific crystallographic phases which are present exclusively in thin films. Such crystallographic phases are often denoted as surface induced phases, since the presence of a surface during the crystallisation is of primary importance for their formation. In general, such thin-film polymorphs do not exist as macroscopic free standing single crystals, so that existing methods of crystal structure solution e.g. from single crystal diffraction or powder diffraction does not work. A number of surface induced crystal structures of conjugated molecules are solved during

the last years, examples are in relevant molecules for organic electronic applications like pentacene or sexithophene.

Two different methods of structure solution from a thin films will be introduced. Both methods are based on grazing incidence x-ray diffraction. In a first step the crystallographic unit cells and the lattice constants are determined by indexing the diffraction pattern. The evaluation of the molecular packing is based on either rigid body refinement or molecular dynamics simulations. While rigid body refinement is based on test structures and a comparison of the calculated diffraction intensities with the experimental intensities, molecular dynamics work on energy minimisation of the molecular packing. It is found that the approach works best for fully rigid molecules like pentacene or parylene. Good results are also obtained for semi-rigid molecules like ternaphtalene or molecules with flexible side-chains like dioctyl-terthiophene. In both cases the crystallographic unit cell is filled by two molecules. However an increasing number of molecules per unit cell (e.g. four) makes the solution of the surface induced phases difficult. Similarities and differences in the molecular packing between known crystal structures (from single crystal solutions) and surface induced phases will be discussed.

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