Monday Morning, November 10, 2014

Nanometer-scale Science and Technology
Room: 304 - Session NS+SE-MoM

Delivering Energy and Mass at the Nanoscale
Moderator: Paul Sheehan, Naval Research Laboratory

8:20am NS+SE-MoM1 Mechanical Properties of Polymer Systems Using Atomic Force Microscopy, *Gregory Meyers*, The Dow Chemical Company **INVITED**
Scanned probe microscopy (SPM) has had a long history at The Dow Chemical Company, beginning in the late 1980s when commercial scanning tunneling microscopes were just hitting the market. Since that time Dow has invested in internal and external collaborative efforts to drive and develop atomic force based technologies for property measurements of polymeric materials at nanometer length scales.

Our most cited early work described a unique phenomenon of surface wear of polystyrene thin films where the interaction of a sliding AFM tip lead to characteristic patterns that depended on the polymer molecular weight. Since that time work such as this has been studied in order to understand elastic, adhesive, and thermal properties of polymer coatings and films near rigid interfaces. Collaborations with NIST in the late 1990s provided our first attempts at quantifying mechanical properties at the nanoscale, combining knowledge gained from classical nanoindentation to the calibration of AFM systems for quantitative AFM based indentation. This work set the stage for a large scale effort in the latter 2000 time frame, funded by the NIST-ATP program in collaboration with Veeco Instruments (now Bruker-Nano). The objective of this program was to develop an AFM based platform for quantitative modulus measurements of polymers at sub 100 nm length scales, to provide better than 10% precision for polymer materials with bulk properties in the 10 MPa to 10 GPa range. As a result of this program, we now have quasistatic AFM based indentation capability that provides the most comprehensive suite of analytical models (elastic, elastic-plastic, and adhesive) to interpret material properties at these scales. Within the last few years the ability to map properties at high spatial resolution via high speed AFM indenting has been realized. A key consideration in all of the mechanical probing is the time scale over which the tip-surface interaction occurs and so we have looked to computational simulations with Purdue University to study the role of dissipative factors – viscoelasticity and surface adhesion hysteresis – to help interpret our measurements.

9:00am NS+SE-MoM3 Extension of Loss-Tangent Mode to Characterization of Materials' Stiffness and Damping, *X. Yu, M. Tao, Nancy Burnham*, Worcester Polytechnic Institute
Viscoelastic materials are engineered and used in a variety of applications; however, it has been a great challenge to characterize their viscoelasticity at the nanoscale, at which the degradation and failure mechanisms often initiate. For linear viscoelastic materials, an atomic force microscopic (AFM) technique, loss-tangent mode, has been recently developed to fulfill this need [1]. The loss tangent of a material is expressed as the ratio of the lost energy (damping) over the stored energy (stiffness) and is claimed to be independent of the tip-sample contact area. Since this new mode was invented, only a few example materials have been studied. In this project, viscoelasticity of several different materials (i.e., asphalt binders [2], epoxy, silica tire, and graphite) were investigated using loss-tangent mode; the damping and stiffness terms were derived with easily measurable terms for a more detailed understanding of materials' viscoelasticity.

Results show that both free amplitude and set-point ratio affect the loss-tangent measurement. For all the examined materials, the loss tangent and damping decreased (power laws of -2.4 ± 1.1 and -2.1 ± 1.0, respectively) with increasing free amplitude at constant set-point ratio, while stiffness increased (power law 0.32 ± 0.18). The loss tangent increased (power law 0.8 ± 0.5) with increasing set-point ratio at constant free amplitude; stiffness decreased more rapidly than damping (power laws of -1.75 ± 0.06 and -1.0 ± 0.4, respectively). These trends might indicate that the loss tangent, as measured by AFM, is not independent of the tip-sample contact area. Computer simulation of loss-tangent mode is ongoing for explanation of these observations, in order to advance understanding of nanoscale viscoelastic measurements.

1. R. Proksch and D.G. Yablon, Appl. Phys. Lett. **100**, 073106 (2012)

2. X. Yu, N.A. Burnham, R.B. Mallick, M. Tao, Fuel **113**, 443 (2013)

9:40am NS+SE-MoM5 Direct Mechanical Measurements of Viscoelasticity in Simple Liquids Using Vibrating Nanostructures, *Matthew Pelton*, University of Maryland, Baltimore County, *D. Chakraborty,* University of Melbourne, Australia, *E. Malachosky, P. Guyot-Sionnest,* University of Chicago, *J.E. Sader*, University of Melbourne, Australia
Studies of acoustic vibrations in nanometer-scale particles can provide fundamental insights into the nanomechanical properties of nanoscale materials, and into the mechanical coupling between the nanoparticles and their environment. Metal nanoparticles allow for all-optical, non-contact measurements, using ultrafast laser pulses to generate and probe high-frequency acoustic vibrations. In early studies, the decay of the signal due to nanoparticle vibrations was dominated due to vibrations in nanoparticle size. By using highly uniform bipryamidal gold nanoparticles, we were able to overcome the effects of inhomogeneous damping and measure the rate at which the acoustic oscillations dissipate energy. Measurements in low-viscosity liquids such as water showed a strong "intrinsic" damping occurring within the nanoparticles themselves, and an environmental damping due to viscous coupling to the surrounding liquid. This fluid damping was described quantitatively using a parameter-free model.

In higher-viscosity liquids, however, the measured oscillation frequencies and damping rates deviate strongly and qualitatively from the predictions of this model. The deviations are explained quantitatively as arising from non-Newtonian effects in the liquid. The nanoparticles vibrate at very high frequencies (20 GHz), so that their vibration periods are comparable to the intrinsic relaxation times of the liquid. The structure-fluid interaction is thus dominated by viscoelastic effects. The observed viscoelasticity is not due to molecular confinement, but is a bulk continuum effect arising from the short time scale of vibration. This represents the first direct mechanical measurement of the intrinsic viscoelastic properties of simple bulk liquids, and opens a new paradigm for understanding extremely high frequency fluid mechanics, nanoscale sensing technologies, and biophysical processes.

10:00am NS+SE-MoM6 Electronic and Optical Properties of Nanometer Sized Structures formed via Local Intercalated of Carbon in Layered Materials, *Andrew Stollenwerk*, University of Northern Iowa
Electron beam radiation is often used to synthesize nanometer scale structures through lithographic techniques, direct altering of chemical bonds, or milling away material. We have recently demonstrated a new method to locally intercalate carbon with nanometer precision using the electron beam of a scanning electron microscope to break apart residual organics. This process was found to work only on layered materials such as topological insulators, novel superconductors, charge density wave materials, and graphite. Structurally, the incorporation of carbon raises the height of the substrate from a few nanometers up to several hundred nanometers depending on the exposure time. While easily observable using atomic force microscopy, these features are effectively invisible to the scanning tunneling microscope at tunneling biases below approximately 0.75 V. Tunneling spectrum of these structures exhibit semiconducting properties with band gaps varying between 0.5 eV – 2.5 eV. This is in agreement with the broad-wavelength photoluminescence observed in the corresponding optical spectrum. Both of these results suggest that the carbon intercalates form nano-clusters with a wide distribution in the size and density.

10:40am NS+SE-MoM8 Effects of Chemical Bonding on Heat Transfer Across Interfaces, *Paul Braun*, M. Losego, M. Grady, N. Sottos, D.G. Cahill, University of Illinois at Urbana-Champaign **INVITED**
Interfaces often dictate heat flow in micro- and nanostructured systems. However, despite the growing importance of thermal management in micro- and nanoscale devices, a unified understanding of the atomic-scale structural features contributing to interfacial heat transport does not exist. Herein, we experimentally demonstrate a link between interfacial bonding character and thermal conductance at the atomic level. Our experimental system consists of a gold film transfer-printed to a self-assembled monolayer (SAM) with systematically varied termination chemistries. Using a combination of ultrafast pump–probe techniques (time-domain thermoreflectance, TDTR, and picosecond acoustics) and laser spallation experiments, we independently measure and correlate changes in bonding strength and heat flow at the gold–SAM interface. For example, we experimentally demonstrate that varying the density of covalent bonds within this single bonding layer modulates both interfacial stiffness and interfacial thermal conductance. We believe that this experimental system will enable future quantification of other interfacial phenomena and will be a critical tool to stimulate and validate new theories describing the mechanisms of interfacial heat transport. Ultimately, these findings will

impact applications, including thermoelectric energy harvesting, microelectronics cooling, and spatial targeting for hyperthermal therapeutics.

11:20am NS+SE-MoM10 Enhanced Thermal Transport at Covalently Functionalized Carbon Nanotube Array Interfaces to Oxide-forming and Noble Metals, *S. Kaur,* Lawrence Berkeley National Laboratory, *N. Raravikar,* Intel Corporation, *B.A. Helms,* Lawrence Berkeley National Laboratory, *R. Prasher,* Sheetak, Inc., *D.Frank Ogletree*, Lawrence Berkeley National Laboratory

It has been more than a decade since the experimental demonstration that the thermal conductivity of carbon nanotubes can exceed that of diamond, which has the highest thermal conductivity among naturally existing materials. In spite of tremendous promise as a thermal material, results have been disappointing for practical thermal systems and applications based on nanotubes. The main culprit for the dramatic shortfall in the performance of nanotubes in practical systems is high thermal interface resistance between them and other components due to weak adhesion at the interface. We demonstrated a six-fold reduction in the thermal interface resistance between both oxide-forming and noble metal surfaces and vertically aligned multi-wall carbon nanotube arrays after bridging the interface with short, covalently-bonded organic molecules. Increased thermal transport was associated with a significant increase in interface mechanical adhesion [1]. Functionalized CNT thermal interfaces were shown to be stable in air for many months and resistant to thermal stress up to 180° C. We were also able to independently determine the intrinsic CNT interface resistance and the fraction of the CNT array contributing to thermal transport by preforming multi-frequency time-domain thermo-reflectance (TDTR) measurements. Since our interface-functionalization method avoids destructive solution-phase processing, this development may lead to the practical integration of CNT arrays for thermal management in microelectronic devices

[1] "Enhanced thermal transport at covalently functionalized carbon nanotube array interfaces", Sumanjeet Kaur, Nachiket Raravikar, Brett A. Helms, Ravi Prasher & D. Frank Ogletree, *Nature Communications* 5 3082 (2014) doi: 10.1038/ncomms4082

11:40am NS+SE-MoM11 Desktop Nanofabrication with Cantilever-Free Scanning Probes, *Keith A. Brown, D.J. Eichelsdoerfer, X. Liao, C.A. Mirkin*, Northwestern University

The availability of reliable nanofabrication methods has dictated the pace of progress in many areas of physics, materials science, electronics, and biotechnology. A major deficiency in these fields is our inability to simultaneously control the architecture of soft materials from macroscopic to nanoscopic length scales. Scanning probe instruments, such as the atomic force microscope, are promising platforms for nanofabrication because they provide direct access to the nanoscale. However, the central barrier to their widespread use as lithographic instruments is throughput, as it is prohibitively slow to pattern large areas with a single nanoscale probe. To address this challenge, we explored a new architecture that utilizes a thin elastomeric film on a glass slide in lieu of cantilevers to enable the use of a massive array of probes in a simple format. Unfortunately, these cantilever-free probe arrays are passive duplication tools where each probe writes a copy of the same pattern. Here, we report on our recent advances in developing techniques for actuating individual probes in cantilever-free arrays and discuss the new scientific directions that these advances enable. Specifically, we present methods for both physically actuating cantilever-free probes using local heating and optically addressing probes that function as light valves for near-field photolithography, and find both to be capable of stitching together high resolution patterns that span multiple probes. These advances in nanofabrication have enabled new types of experiments, and in particular, we present recent progress in the combinatorial study of biochemical interactions and the high throughput fabrication of functional metamaterials using cantilever-free techniques. Taken together, these observations indicate that versatile desktop nanofabrication is possible using scanning probes and that these techniques can address the emerging challenges related to patterning soft materials.

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^{-2}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.

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$_2$S 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 x 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.

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.

1. Papa F *et al* 2011 *Thin Solid Films* 520.5 1559-1563.

2. He Yu *et al* 2013 *Plasma Sources Sci. Technol.*22 045012.

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 ($\sim10^{19}$-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:

[1] H.Yu, L. Meng, M. Szott, J. McLain, T.S. Cho, D.N. Ruzic, Investigation and optimization of the magnetic field configuration in high-power impulse magnetron sputtering, Plasma Sources Sci. Technol. 22 045012, 2013

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].

[1] A. Kozyrev et al., Plasma Physics Reports 37 (2011) 621

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

[3] A.P. Ehiasarian et al., Appl. Phys. Lett. 100 (2012) 114101

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

[5] A. Anders et al., Appl. Phys. Lett., 103 (2013) 144103

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

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 $\mathbf{E}$ x $\mathbf{B}$ 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 $\mathbf{E}$ x $\mathbf{B}$ 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 – $\mathbf{E}$ x $\mathbf{B}$ 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 LaB₆ 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_2O_5 to a mixture of Ta_3N_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_4C-Si, B_4C-Zr or B_4C-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].

[1] J.Rezek, J.Vlcek, J.Houska, R.Cerstvy, Thin Solid Films (submitted).

[2] J.Vlcek, P.Calta, P.Steidl, P.Zeman, R.Cerstvy, J.Houska, J.Kohout, Surf. Coat. Technol.

226 (2013) 34.

[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_3N_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 $Cu_2O(111)$ 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.

Energy Frontiers Focus Topic
Room: 315 - Session EN+AS+EM+SE-TuM

Fuel Formation and Thermal Transport
Moderator: Michael Filler, Georgia Institute of Technology

8:00am EN+AS+EM+SE-TuM1 Unraveling Thermodynamic and Kinetic Factors in Solar-Thermochemical Fuel Production, *Sossina Haile*, California Institute of Technology **INVITED**
Perhaps the greatest challenge facing our planet is sustainable energy. Given the vast solar energy resource base available to modern society, key to addressing this challenge is the conversion of solar energy into a storable form suitable for on-demand utilization. So emerges the concept of 'Solar Fuels.' Amongst many approaches currently pursued to generate solar fuels, thermochemical dissociation of water splitting is particularly attractive. It provides the benefits of full utilization of the solar spectrum and inherent temporal separation of hydrogen and oxygen gases. In recognition of these advantages, numerous multi-step cycles have been considered over the past several decades. Recently, two-step cycles making use of *non-stoichiometric* oxides have received attention because of the simplicity of their implementation. The approach relies on the large oxygen nonstoichiometry change that the material undergoes in response to variations in oxygen partial pressure (pO_2) and temperature (T). Specifically, upon exposure to high temperatures ceria undergoes reduction without change in crystalline phase to release oxygen. On cooling in the presence of H_2O (or CO_2), the oxide is reoxidized, releasing H_2 (or CO). The success of the method relies not only on favorable thermodynamics but also on facile kinetics, both in terms of surface reaction rates and bulk diffusion coefficient. Accordingly, we have undertaken a comprehensive study of ceria and its doped derivatives to assess both the equilibrium redox behavior by thermogravimetric methods and the kinetic response by conductivity relaxation methods. We find, for example, that introduction of Zr strongly increases the absolute non-stoichiometry of ceria, but at a penalty in terms of the sensitivity of the nonstoichiometry to changes in environmental conditions and in terms of bulk diffusivity. In another example, we find that the relaxation behavior of Sm-doped ceria is substantially more rapid than that of both undoped and Zr-doped ceria, a result that is tentatively assigned to differences in species mobilities. The implications of these fundamental differences in material properties for thermochemical fuel production are discussed.

8:40am EN+AS+EM+SE-TuM3 Controlling Catalysis on Metal Nanoparticles by Direct Photoexcitation of Adsorbate-Metal Bonds, *M.J. Kale, T. Avanesian*, University of California, Riverside, *H. Xin, J. Yan*, SLAC National Accelerator Laboratory, *Phillip Christopher*, University of California, Riverside **INVITED**
Heterogeneous photocatalysis is typically assumed to occur via photon absorption by a solid-state photocatalyst (only the photocatalyst electronic states are involved in photon absorption) followed by charge carrier diffusion through the photocatalyst bulk and subsequent transfer to adsorbates. This process of energetic charge carrier generation and transfer results in wavelength dependent quantum efficiencies that strictly follow the absorption spectrum of the solid-state photocatalysts, regardless of the chemical transformation. The substrate (photocatalyst) mediated photo-absorption process inhibits approaches to control reaction selectivity by matching photon excitation wavelengths to bond specific electronic transitions, as typically done in molecular systems.

Here, we show that strong chemisorption bonds formed between CO and Pt metal surfaces can be activated with visible photons to drive catalysis through direct, resonant photoexcitation of hybridized Pt-CO states. This is enabled as the dominant photoexcitation mechanism (over substrate mediated photoexcitation) driving catalysis by using sub-5-nanometer Pt nanoparticle catalysts, where high surface area to volume ratios force photon absorption onto surface metal atoms. The direct photoexcitation process is observed to be significantly more efficient for driving photocatalysis than the indirect photoexcitation process when the energy of exciting photons is resonant with adsorbate specific electronic transitions involving hybridized metal-adsorbate states. It is also demonstrated that resonant photoexcitation of Pt-CO bonds on sub-5-nanometer Pt nanoparticles by visible light significantly enhances selectivity towards CO_2, over H_2O production, in the selective oxidation of CO by O_2 in an H_2 rich stream (also known as preferential CO oxidation). These results open new avenues to control catalytic reaction selectivity on sub 5-nm catalytic particles by resonant photoexcitation of adsorbate-specific electronic transitions involving hybridized metal and adsorbate states. It is expected that the development of insights into resonant electronic transitions between hybridized metal-adsorbate states should allow rational control of catalytic selectivity that cannot be achieved exclusively with thermal energy input.

9:20am EN+AS+EM+SE-TuM5 Atomistic Insights as the the pH Dependence of Onset Potential of the Oxygen Evolution Reaction on Hematite, *Anders Hellman*, Chalmers University, Sweden
Hematite (α-Fe_2O_3) is an extensively investigated semiconductor for photoelectrochemical water oxidation, and recent research has shed light on many of the atomic processes involved. However, a controversy about the nature and role of surface states in the water oxidation reaction remains. Here first-principles calculations are used to investigate surface states present in hematite under photoelectrochemcial conditions. Most specifically a model describing how the onset potential for oxygen evolution reaction on hematite depend on the pH of the electrolyte is put-forth. The predictions of this model are confirmed to a high extent by measurements of the onset potential on hematite based model photoanodes. In particular, a linear dependence of the onset potential on the pH was observed, with a 49 mV / pH slope. Detailed photoelectrochemical characterization confirmed that the oxygen evolution reaction takes place via the same surface states irrespective of the pH. Moreover, the photovoltage and flat band potential of the hematite were also found to be pH independent. These results provide a framework for a deeper understanding of the OER when taking place on semiconductors (like hematite) via surface states

9:40am EN+AS+EM+SE-TuM6 Rational Design of Pt_3Ni Alloy Surface Structures for Oxygen Reduction, *Liang Cao, T. Mueller*, Johns Hopkins University
A cluster expansion approach based on ab-initio calculations has been used to investigate the relationship between surface structures of $Pt_3Ni(111)$ alloy catalysts and their catalytic activity. With this approach, we build a direct bridge between the atomic structure and catalytic properties of Pt-Ni alloy system at a variety of compositions and chemical environments. The equilibrium near-surface structures are presented as a function of O_2 partial pressure and the chemical potential difference between Ni and Pt. We discuss the relative importance of strain, ligand, and ensemble effects in determining catalytic activity, and demonstrate how ensemble effects can be leveraged to rationally design alloy surfaces with optimal ORR activity by searching for surfaces with targeted oxygen binding energy.

11:00am EN+AS+EM+SE-TuM10 Molecular and Mesoscale Design for Organic and Hybrid Thermoelectrics, *Rachel Segalman*, University of California, Santa Barbara **INVITED**
Thermoelectric materials for energy generation have several advantages over conventional power cycles including lack of moving parts, silent operation, miniaturizability, and CO2 free conversion of heat to electricity. Excellent thermoelectric efficiency requires a combination of high thermopower (S, V/K), high electrical conductivity (σ, S/cm), and low thermal conductivity (κ, W/mK). To date the best materials available have been inorganic compounds with relatively low earth abundance and highly complex, vacuum processing routes (and hence greater expense), such as Bi_2Te_3. Molecular materials and hybrid organic-inorganics bring the promise of solution processible, mechanically durable devices. While highly conductive polymers are now common place, they generally demonstrate low thermopower. Our work on molecular scale junctions that nanostructuring of organics allows them to act as thermionic filters between inorganic junctions which can lead to enhanced thermoelectric properties. We have taken inspiration from this fundamental understanding to design material systems in which we combine a high electrical conductivity, low thermal conductivity polymer with a nanoparticle that contributes high thermopower. Additionally, the work functions of the two materials are well-aligned which introduces the possibility of thermionic filtering at the interface and an additional boost to the power factor. The combination of these effects results in a new hybrid, solution processible material with a thermoelectric figure of merit within an order of magnitude of the Bi_2Te_3. In this talk, I will discuss both the use of thermoelectric measurements to gain insight to molecular junctions and how this insight translates to design principles for polymer and hybrid thermoelectrics.

11:40am EN+AS+EM+SE-TuM12 Advances in Solid-State Energy Harvesting from Asymmetric Thermoelectric Devices, *B. Cook, Jay Lewis*, RTI International
The amount of thermal energy rejected as waste heat from industrial processes in the United States has been estimated at 32 quadrillion BTU per year, with an associated emission of 1,680 million metric tons of carbon

dioxide. The ability to cost-effectively convert a portion of this thermal energy into useful electrical energy could improve energy efficiency, reduce operating costs, and decrease CO_2 emissions. Waste heat is typically categorized by temperature as high-grade (650ºC and above), medium-grade (232ºC to 650ºC, and low-grade (232ºC and below). In order to improve the thermal-to-electrical conversion efficiency of medium-grade waste heat, RTI has combined two different materials to form a high figure-of-merit, hybrid thermoelectric (TE) device. Recently-developed enhanced "TAGS-85", or e-TAGS, was employed as the p-leg, while the n leg was comprised of improved half-Heusler (HH) material. This hybrid material pair provides a high ZT, lead-free TE material solution for waste heat recovery for use in vehicle or industrial platforms. The improved HH material employs two novel techniques to reduce thermal conductivity: (1) high-energy milling, and (2) addition of coherent inclusions. Single n-/p-couples were produced that achieved a 9.2% thermal to electric power conversion efficiency for T_{hot} = 559°C and ΔT = 523K. This is a significant efficiency improvement at a lower hot side temperature with the hybrid e-TAGS/HH single couple over the performance of a conventional, all HH couple. By optimizing the cross sectional areas of the pellets for equal heat flow, the resulting asymmetric couple achieved a conversion efficiency of 10.5% at T_{hot} = 537°C and ΔT = 497°C. A 49-couple hybrid module using HH materials paired with e-TAGS and operated with T_{hot} up to 600°C reached a maximum efficiency of 10%. The improved module efficiency is believed to be due to both improved materials and optimized cross-sectional area ratios between the n- and p- elements. We will also discuss additional advances in thermal to electric power conversion using multi-stage modules.

12:00pm EN+AS+EM+SE-TuM13 The Effect of Particle Size and Surface Termination of n-Si on Thermal and Electrical Conductivity, *Thomas Lopez, L. Mangolini*, University of California - Riverside, *S. Bux, J.P. Fleurial*, California Institute of Technology
A discussion of synthesis and characterization of bulk nanocrystalline silicon with grain sizes of around 20 nm and thermal conductivities as small as 100 mW/cmK at room temperature, will be presented. Nanostructured materials have great potential for thermoelectric applications because of the reduction in thermal conductivity due to phonon scattering at grain boundaries [1] and silicon is a well-understood, cheap, earth-abundant material. Other silicon nanostructures, such as nanowires [2], are being investigated as viable thermoelectric materials. We have used, for the first time, the combination of a non-thermal plasma process for the synthesis of silicon nanocrystals with hot pressing to produce bulk nanostructured silicon samples. The non-thermal plasma synthetic route has been proposed for the production of photo-luminescent silicon quantum dots with narrow size distribution (3 +/- 0.5 nm) [3]. The same reactor has been scaled up to produce silicon nanocrystals at a rate of hundreds of milligrams per hour. Silicon powder with sizes between 5 nm and 15 nm has been produced using either silane (SiH4) or silicon tetrachloride (SiCl4), which are low-cost silicon precursors. Results have shown surface termination of the non-thermal plasma synthesized particle, i.e. H or Cl, play a role in densification kinetics. Hot pressing is a high pressure, high temperature process that allows for the production of samples with bulk like densities while limiting grain growth. In this study we have produced bulk (12 mm diameter, 2-4 mm in thickness) samples of nanocrystalline silicon with relative densities exceeding 95%. Characterization by XRD and TEM confirms that grain sizes are around 30 nm. The effects of surface termination of nano-silicon on grain growth and grain boundary conditions will be extensively discussed.

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Advanced Surface Engineering
Room: 302 - Session SE+NS+TR-TuM

Nanostructured Thin Films and Coatings
Moderator: Robert Franz, Montanuniversität Leoben, Andrey Voevodin, Air Force Research Laboratory

8:00am SE+NS+TR-TuM1 Electrostatic Coating with Ligandless Copper Nanoparticles, *Lance Hubbard, A.J. Muscat*, University of Arizona
Physical vapor deposition is currently used to deposit copper seed layers in through Si vias, but this approach is already close to its limit and may not be an option for future scaling of high performance integrated circuits. An alternative is electroless deposition (ELD) since it produces conformal,

selective coatings at low temperature. ELD occurs by chemical reduction of metal ions without an externally applied potential. In the conventional approach, a metal catalyst such as Pt, Pd, or Ni is used that can be both expensive and increase the resistance of interconnect lines. Previous work was done in an aqueous phase using a complexing agent or polymer to protect the particles. Good film continuity was demonstrated, but the sheet resistance was low.[1,2] In this study, we report on a nonaqueous ELD process that uses a charge compensator, but not a ligand or complexing agent. The weak electrostatic attachment of the charge compensator to the ions and particles in solution and the high pH conditions improve the driving force for metal deposition. Si(100) coupons were hydroxylated using sulfuric acid-hydrogen peroxide mixture. The surface was terminated with an amine adhesion layer by immersion in a 4 mM solution of either (3-aminopropyl)-trimethoxysilane (APTMS) or (3-mercaptopropyl)-trimethoxysilane (MPTMS) in methanol followed by a 150ºC anneal. Metal films were deposited by suspending samples in a bath made by dissolving Cu(II) chloride in ethylene glycol, which also served as the reducing agent, and adding 1-butyl-3-methylimidazolium tetrafluoroborate as a charge compensator. The surface plasmon resonance (SPR) peak of the Cu nanoparticles in the bath and film was at 585 nm. Light scattering measurements and transmission electron microscopy (TEM) images yielded a size distribution of 3.1±1.6 nm. The complex consisting of the Cu particle core and ion shell is attracted to the positively charged amine groups at high pH, and a thin metal film is deposited that is both continuous and cohesive. Annealing the coupons at 200ºC in nitrogen promoted the formation of an electrically conductive film. Electron microscopy images of the coated substrates show a 20-50 nm thick film of 3 nm dia. particles; spectroscopic ellipsometry shows both bulk and nanophase properties. Four-point probe measurements of the films yielded electrical conductivities in the range 10^5-10^6 S/m (bulk Cu conductivity 4-6x10^7 S/m).

References

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8:20am SE+NS+TR-TuM2 Electrically Stable Pt-ZrB₂ Nanocomposite Thin Films for High Temperature Applications, *Julia Sell, D.M. Stewart, G.P. Bernhardt, D.J. Frankel, R.J. Lad*, University of Maine
Considerable cost savings could be achieved by incorporating high temperature sensors into high temperature machinery to optimize processes and monitor materials degradation. However, in order to achieve reliable sensor operation, the thin film electrodes, sensing elements, and packaging materials must remain stable over long times at high temperature. Metallic thin films, such as Pt, agglomerate and lose conductive pathways quickly when exposed to temperatures exceeding 700°C. In this work, we show that Pt-ZrB₂ nanocomposite films retain a continuous morphology and remain electrically conductive up to at least 1100ºC in air. Nanolaminate Pt-ZrB₂ films comprised of ten alternating layers of Pt and ZrB₂ were deposited to a total thickness of 200nm at ambient temperature onto sapphire substrates using e-beam evaporation. Annealing the nanolaminate films above 800ºC in air causes intermixing, resulting in a nanocomposite Pt-ZrB₂ film architecture. Film electrical conductivities were measured using a 4-point probe as a function of time and temperature in air up to 1200°C. These results show that Pt-ZrB₂ nanocomposite films have conductivities in the 10^6-10^7 S/m range and remain stable above 1000°C, but that the overall conductivity and stability depends on the Pt-ZrB₂ layer thickness ratio. Analysis via x-ray photoelectron spectroscopy and x-ray diffraction indicates that both monoclinic and tetragonal ZrO₂ nanocrystallites are formed in the films during the annealing treatment, and they serve to hinder agglomeration of the Pt phase. Scanning electron microscopy shows highly conductive Pt-rich pathways in the films that coexist with the ZrO₂ phase. Some films were coated with an amorphous Al₂O₃ protective capping layer using atomic layer deposition (ALD), and this capping layer helped to limit oxygen diffusion into the films, thereby increasing the long term stability of film conductivity.

8:40am SE+NS+TR-TuM3 A Novel Reactive Plasma-Assisted Coating Technique (RePAC) for Thin BN/Crystalline-Si Structures and their Mechanical and Electrical Properties, *Koji Eriguchi*, Kyoto University, Japan, *M. Noma*, SHINKO SEIKI CO., LTD., Japan, *S. Hasegawa*, Osaka University, Japan, *M. Yamashita*, Hyogo Prefectural Institute of Tech., Japan, *K. Ono*, Kyoto University, Japan
Cubic boron nitride (c-BN) has attracted much attention as a hard coating film on cutting tools, owning to its high oxidation resistance and hardness—the second hardest material to diamond. Although various methods of forming c-BN films on various substrates have been proposed, the interface between c-BN and the substrate material was unstable against delamination and oxidation [1] after long-time machining and air exposure. In this study,

we propose a novel reactive plasma-assisted coating technique (RePAC) for forming sub-μm-thick BN film directly on crystalline Si substrates, where magnetically-confined high-density Ar/N$_2$ plasma was generated with a stable anodic current to promote the reaction between N radicals and B atoms evaporated onto a Si substrate placed on a sample stage [2]. Controlling substrate bias voltage V_{sub} in the RePAC, we fabricated various thin-BN/Si structures and identified a correlation among the properties such as mechanical hardness, friction coefficient, leakage current, and dielectric constants. TEM analyses revealed that nano-structures of the BN films were varied from bulk amorphous (a)-BN, layered hexagonal (h)-BN, to c-BN phase in turbostratic (t)-BN domain, in accordance with V_{sub} ($|V_{sub}|$=10–120 V). We speculate that bombardment of incident ions (Ar$^+$ and/or N$_2^+$) plays a key role in forming these characteristic features, in addition to stoichiometric N and B contents. Moreover, we clarified the high hardness (> 4000HK, by the Knoop indenter) and the dielectric constant higher than previously-reported values (10–20, by the electrical capacitance measurement) for the present thin c-BN/Si structure with anti-delamination feature after long-time air exposure. The obtained results suggest that the present BN film formed by the RePAC has wide applications not only as a hard coating film but also as a high dielectric-constant layer in electronic devices.

[1] For example, P. B. Mirkarimi *et al.*, Mater. Sci. Engin., **R21**, 47 (1997).

[2] M. Noma *et al.*, Jpn. J. Appl. Phys. **53**, 03DB02 (2014).

9:20am SE+NS+TR-TuM5 Multifunctional Protective Coatings for Aerospace Applications, *Etienne Bousser, L. Martinu, J. Klemberg-Sapieha*, Ecole Polytechnique de Montreal, Canada **INVITED**
Ever increasing technical, economic and environmental requirements give rise to situations where modern equipment and components are often pushed beyond the limits of their design capabilities. This frequently leads to tribological deficiencies, such as lubrication breakdown, excessive wear and tribo-corrosion, resulting in increased operational costs, decreased efficiency and premature failure. Therefore, appropriate material's selection for a given application must be guided by an accurate understanding of the intervening tribological processes while ensuring the maintained functionality of the surface for optimal application performance.

Solid Particle Erosion (SPE) occurs in situations where hard particles, present in the environment, are entrained in a fluid stream, and impact component surfaces such as in aircraft engines. It is well known that ductile materials erode predominantly by plastic cutting or ploughing of the surface, while brittle materials do so by dissipating the particle kinetic energy through crack nucleation and propagation. In the first part of this presentation, we examine the mechanisms by which surfaces dissipate the kinetic energy of impacting particles, and discuss the erosive response of hard protective coating systems. We investigate the means by which surface engineering can enhance erosion resistance, and correlate surface mechanical properties to the erosion behaviour. In addition, we will show that the architectural design of advanced coating systems is also well supported by finite element modelling of single particle impacts of the coated surfaces.

The second part of the talk will focus on the repairability of advanced coating systems. Indeed, because of the high fabrication costs of engine components, it is desirable to develop an effective and efficient industrially-viable technique to remove defective coatings with the aim of recycling the costly engine components. In particular, we will present our recent studies on the removal of TiN-based erosion resistant coatings using a non-line-of-sight reactive ion etching technique and a complementary laser ablation process.

11:00am SE+NS+TR-TuM10 Hard Coatings with Designed Thermal Conductivity, *P.H.M. Boettger,* Empa, ETH Zurich, Switzerland*, V. Shklover,* ETH Zurich, Switzerland*, M. Sobiech,* Oerlikon Balzers Coating AG, Liechtenstein*, Joerg Patscheider*, Empa, Switzerland
Hardness, thermal stability and oxidation resistance are often the main properties to optimize for most tool coatings developments for industrial applications. The thermal conductivity, however, has been regarded to a much lesser extent as property to improve tool life. So far, only little attention has been given to this fact and the explicit role of thermal conductivity in machining Ti and Ni-based alloys. These materials typically have low thermal conductivity, as well as modern tool coatings such as CrAlN and TiAlSiN. This unfavorable combination may lead to the formation of thermal hot spots during machining, which adds to the premature degradation of such coatings. For these reasons the thermal conductivity is an important process parameter.

This talk will discuss the relations between hardness, coatings architecture and thermal conductivity and how advanced coatings can be tuned to achieve significant anisotropy of the thermal conductivity. In arc-evaporated TiO$_x$N$_{1-x}$ and CrO$_x$N$_{1-x}$ thermal conductivity can be adjusted in a wide range between 2 and 35 W/m·K, while keeping hardness and

oxidation resistance intact. The data for single phase oxynitrides as well as of multilayered coatings agree well with a newly developed model based on constant phonon scattering cross section of the introduced oxygen. It will be shown how temperature-mitigating multilayer coatings can be prepared using these materials by introducing highly anisotropic thermal conductivity.

11:20am SE+NS+TR-TuM11 Microstructure and Hardness Gradients in Sputtered CrN Films, *A. Riedl,* Materials Center Leoben, Austria*, R. Daniel,* Montanuniversität Leoben, Austria*, T. Schoeberl, M. Stefenelli,* Austrian Academy of Sciences*, B. Sartory,* Materials Center Leoben, Austria*, J. Keckes, Christian Mitterer*, Montanuniversität Leoben, Austria
Hardness and elastic modulus of a sputtered nanocrystalline CrN thin film, grown under varying ion bombardment conditions, were studied by nanoindentation using a depth-profiling technique and related to cross-sectional X-ray nanodiffraction data on the local microstructure. Changes in texture are shown to have almost no effect on the elastic modulus due to the isotropic response of the polycrystals. However, the locally varying growth conditions, which affect crystal size and number, determine the hardness values across the film thickness. Regions with highly distorted small crystals result in higher hardness in comparison to those with well-developed coarsened grains. This work confirms the notion of the existence of growth-related hardness gradients in single-phase nanocrystalline thin films.

11:40am SE+NS+TR-TuM12 Development of Low Friction Nanocomposite Coatings for Diesel Engine Piston Rings, *Jianliang Lin, R. Wei, K. Coulter, C. Bitsis, P.M. Lee*, Southwest Research Institute
Hard and thick (15-20 μm) TiSiCN nanocomposite coatings have been developed to improve the wear resistance and reduce the overall average friction for diesel engine piston rings. The coatings were deposited by sputtering Ti metal targets in a reactive atmosphere using a plasma enhanced magnetron sputtering (PEMS) process. The reactive mixture contains argon, nitrogen, acetylene gases, and hexamethyldisilazane vapor which were introduced into the chamber using a liquid evaporation/delivery system. The substrates were AISI 304 stainless steel coupons and piston rings. The TiSiCN coatings with different elemental compositions and microstructures were prepared by varying the hexamethyldisilazane and acetylene gas/vapor concentrations and the target power. The microstructure of the coatings was characterized using scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction. The adhesion strength and mechanical and tribological properties of the coatings were measured using HRC tests, nanoindentation and ball-on-disk wear tests. By optimizing the composition and microstructure of the coatings, thick TiSiCN nanocomposite coatings with excellent adhesion and a dry sliding friction less than 0.2 have been obtained. The optimized coating systems were applied on the piston rings, which were evaluated on a Plint TE77 reciprocating bench rig and in the real diesel engine test. The principle for the increased wear resistance and the potential applications will be discussed in the paper.

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 $\mu AH. \mu m^{-1}.cm^{-2}$ 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 ^{o}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 ($2.5x10^{11}$, $9.8x10^{10}$ and $9.32 x 10^{10}$ Ω) for samples annealed at 200, 300 and 400°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.

Advanced Surface Engineering
Room: Hall D - Session SE-TuP

Advanced Surface Engineering Poster Session

SE-TuP1 Oxidation and Nanopatterning of Thin Metal Films on Flexible Substrates via Oxygen Directed Irradiation Synthesis, *Zachariah Koyn, B. Holybee, S.N. Srivastava, J.P. Allain*, University of Illinois at Urbana-Champaign

Ion bombardment of polycrystalline thin metal films is known to induce nanometer-scale surface patterning, including ripples and dots[1,2]. Additionally, the irradiation of metals with oxygen ions has been shown to induce surface oxidation, with a state dependence on fluence[3]. This work seeks to unravel the directed irradiation synthesis of oxide-based thin-films, in particular ZnO thin-films, with low-energy irradiation-driven mechanisms on dissimilar material substrates, such as polymer-based systems. This examines the dual effects of oxygen irradiation as a method of both oxidizing and patterning metal thin-films at ambient temperatures. This represents a scalable process in growing and functionalizing metal-oxide thin-films on polymers, which are sensitive to the high temperatures required in thermal oxidation processes. Ion-beam sputtering (IBS) is known to induce surface nanopatterning in multi-component systems[4] with simultaneous modification of surface chemistry. Irradiation with O^+ is performed at grazing incidence near 70° with particle energies between 25-1000 eV at ambient temperatures. X-ray photoelectron spectroscopy investigates the resulting oxidation states as a function of fluence from early-stage nanopattern formation near 10^{15} cm^{-2} up to fluences nearing a coarsening regime. Atomic force microscopy examines pattern formation under similar conditions. These results are then adapted to nanostructured thin-films on flexible substrates, namely polydimethylsiloxane (PDMS) about 1-mm thick and 1-cm^2. The ability to fabricate heterostructures on transparent, flexible substrates offers exciting applications in areas such as gas sensors, biosensors, and photonics[5]. Additional benefits of an oxygen ion beam are the chemical changes (formation of SiO groups, introduction of water and gaseous byproducts) induced in the PDMS substrate as the active thin-film is nanostructured. Oxidation of this polymer has been shown to induce significant temporary hydrophilicity[6] and thus provide for an effective bioactive nanostructured biointerface for in-situ endovascular protocols.

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Energy Frontiers Focus Topic
Room: 315 - Session EN+AS+EM+SE-WeM

Thin Film Photovoltaics
Moderator: Rachel Morrish, Colorado School of Mines

8:20am EN+AS+EM+SE-WeM2 Epitaxy and Nanochemistry of CdS on Cu(In,Ga)Se$_2$ for Photovoltaic Devices, *X. He,* University of Illinois at Urbana Champaign, *H. Tellez, J. Druce,* Kyushu University, Japan, *K. Demirkan,* Miasole, *P. Ercius,* Lawrence Berkeley National Laboratory, *V. Lordi,* Lawrence Livermore National Laboratory, *J. Kilner,* Imperial College London, UK, *T. Ishihara,* Kyushu University, Japan, **Angus Rockett**, University of Illinois at Urbana Champaign

Cu(In,Ga)Se$_2$ (CIGS) photovoltaics are very promising candidates for high-performance energy generation from sunlight. They typically include a heterojunction between CdS and CIGS. The nature of that heterojunction is critical to the performance of the devices. We present experimental results on the nanochemistry of CIGS and CIGS/CdS heterojunctions and the nanostructure of the junctions. In particular we present low energy ion scattering (LEIS) results on epitaxial single crystal CIGS and CIGS/CdS heterojunctions formed by chemical bath deposition of CdS. Also shown are results of high-resolution transmission electron microscopy (TEM) studies of the CIGS/CdS heterojunction where the junction is formed by physical vapor deposition. LEIS has single-atomic-layer chemical sensitivity that provides a unique ability to distinguish the nanochemical nature of CIGS surfaces and heterojunctions. TEM provides both nanostructural information and the possibility to determine the chemistry of the junction on the nanoscale by energy dispersive spectroscopy and energy filtered imaging. Complete epitaxy of the CdS throughout its ~50 nm thickness is observed in the physical-vapor-deposited CdS. Domains of cubic zincblende and hexagonal wurtzite structure CdS have been observed. Twins in the CIGS grains were found to propagate into and often through the CdS layer, resulting in a twin or grain boundary in the CdS. The CdS epitaxial relationship and the effect of surface steps on the CIGS surface are shown. The nanochemical analysis results show significant penetration of Cu into the CdS layer, although no alteration in the CdS nanostructure is observed. The other elements show an abrupt nanochemical junction. LEIS results show the presence of segregated layers on the CIGS surface and further refine the nature of the nanochemical intermixing across the interface.

8:40am EN+AS+EM+SE-WeM3 Microstructure Development in Cu$_2$ZnSn(S$_x$Se$_{1-x}$)4 Thin Films During Annealing of Colloidal Nanocrystal Coatings, *B.D. Chernomordik, M. Ketkar, K. Hunter, A.E. Béland,* **Eray Aydil**, University of Minnesota

A potentially high-throughput and inexpensive method for making Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ (CZTSSe) thin film absorber layers for solar cells is annealing of coatings cast from colloidal dispersions of CZTS nanocrystals (NCs). The nanocrystal coatings can be annealed in sulfur or selenium atmosphere to make CZTS or CZTSSe, respectively. During annealing, the nanocrystal films can transform into polycrystalline thin films with micrometer size grains. Understanding the roles of key annealing parameters in the development of microstructure in CZTSSe thin films is critical for achieving inexpensive and high-efficiency CZTSSe solar cells. In this presentation, we will discuss the effects of parameters such as selenium vapor pressure, annealing temperature, substrate, and h eating ramp-rate on the microstructure development in CZTSSe films and contrast the results with films annealed in sulfur. By using a closed system, rather than a flow furnace, we can quantify and systematically control selenium pressure. Annealing films at high selenium pressure (450 Torr) leads to the formation of a layer of 2-5 μm size CZTSSe grains on top of a nanocrystalline layer that is rich in carbon. This segregation of carbon at the CZTSSe-substrate interface is commonly ascribed to the immediate formation of a capping/blocking layer of CZTSSe grains, which trap the carbon, originating from the ligands on NC surfaces, beneath these grains. However, we found that a continuous layer of CZTSSe grains is not necessary to observe carbon segregation to the film-substrate interface. In contrast, films annealed with sulfur do not show such distinct carbon-rich layers and most of the carbon volatilizes from the film during annealing. Increasing the heating ramp-rate to the annealing temperature eliminates the formation the carbon-rich layer and results in grains that are approximately 500 nm. We will discuss the results of a series of experiments which led us conclude that Se condensation during annealing may play a key role in grain growth and carbon segregation.

9:00am EN+AS+EM+SE-WeM4 Effect of Chemical Wet Cleaning on Surface Composition and Work Function of Thin Film CZTS,Se, *Kasra Sardashti,* University of California at San Diego, *E.A. Chagarov, T. Kaufman-Osborn,* University of California, San Diego, *S.W. Park,* University of California San Diego, *R. Haight, W. Wang, D.B. Mitzi,* IBM T.J. Watson Research Center, *A.C. Kummel,* University of California at San Diego

Polycrystalline Copper-tin-zinc-sulfide/selenide (CZTS,Se) compounds have received wide research interest due to their potential as inexpensive absorber materials composed earth-abundant elements. Photovoltaic devices fabricated on CZTS,Se has reached the highest (or record) conversion efficiency of the 12.6 %. One of the key parameters to further boost the conversion efficiency is to control the concentration of recombination sites at the surface, in the grain boundaries, and in the bulk. Surface states formed on the sample surface as a result of carbon and oxygen contamination can act as non-radiative recombination sites which limit the ultimate cell efficiency. Therefore, a surface-cleaning method which can effectively reduce the amount of surface oxygen and carbon is necessary for CZTS,Se processing. In this work, 2 μm thick CZTS,Se films were prepared by spin coating hydrazine-based precursor solutions onto Mo-coated soda lime glass substrates in a nitrogen-filled glove box. To clean the CZTS,Se surfaces, three different wet cleaning recipes were used: a) NH4OH only; b) HCl followed by NH4OH; 3) H2O2 followed by NH4OH. The effect of the wet cleaning on the surface composition including carbon and oxygen content has been studied via X-ray photoelectron spectroscopy (XPS) and femtosecond ultraviolet photoelectron spectroscopy (fs-UPS). Spatial variation of work function over the surface upon surface cleaning was measured via Kelvin Probe Force Microscopy (KPFM). The stability of the clean surface against reoxidation in ambient was modeled by density functional theory (DFT). The H2O2/NH4OH recipe showed the best result reducing the amount of surface O and C down to 5% and 20%, respectively. This is due to the oxidizing effect of H2O2 which converted the carbonaceous surfaces contaminants into oxides which were later removed by NH4OH. DFT calculations are consistent with a group VI surface being stable against oxidation by ambient moisture. KPFM measurements showed strongly non-homogeneous surfaces after both NH4OH-only and H2O2/NH4OH clean. Areas with work function different from CZTS could be the binary chalcogenides formed during the growth and were covered by the native oxide. NH4OH etch successfully removed the covering oxide and made those phases visible to KPFM.

9:20am EN+AS+EM+SE-WeM5 Phase Transformation, Surface States, and Electronic Structures of Pyrite Thin Films Under *In Situ* Heating and Oxygen Gas Exposure, *Yu Liu, N. Berry, Y.N. Zhang,* University of California Irvine, *C.-C. Chen,* Argonne National Laboratory, *H. Bluhm, Z. Liu,* Lawrence Berkeley National Laboratory, *R.Q. Wu, M. Law, J.C. Hemminger,* University of California Irvine

Iron pyrite (cubic FeS$_2$) with its exceptional optical absorption and suitable band gap is a promising earth-abundant semiconductor for thin film solar cells. Using ambient pressure synchrotron x-ray spectroscopies, we report the nanoscale depth profiles of surface and electronic structures for phase-pure pyrite thin films under *in situ* heating and oxygen gas exposure. Polarized x-ray absorption spectra show that the absorption edge of Fe L_2-edge shifts closer to the Fermi surface with increasing temperature. The XAS line shapes of Fe and S L-edge provide the information of ligand crystal field environment and the phases of the FeS$_2$ particles. We also report the non-destructive photoemission depth distributions of sulfur defects, vacancies, impurities and oxide as a function of temperature and oxygen dose. Valence band spectra indicate a band gap narrowing related to the creation of surface states at elevated temperature. An irreversible phase transition from pyrite (FeS$_2$) to pyrrhotites (Fe$_{1-x}$S) occurs above 430 °C. In addition, our results under *in situ* oxygen gas exposure suggest that the surface monosulfide species is oxidized first, and the reduction in the total density of states near the Fermi surface is caused by oxide layers of sulfate like and iron oxide products on the top ~2 nm.

9:40am EN+AS+EM+SE-WeM6 Improvement of SnS-based Photovoltaic Devices via Reverse Engineering of the V$_{oc}$ and Study of Optimal n-Type Material, *Rona Banai, N.J. Tanen, J.J. Cordell, J.R. Nasr, R.E. Urena, H. Lee, J.R.S. Brownson, M.W. Horn,* Penn State University

Tin (II) Monosulfide (SnS) has theoretical promise as a new material for thin film photovoltaics (PV). Despite a full decade of rigorous research to develop SnS-based devices, improvement beyond single-digit percent efficiencies seems unattainable. Engineering this material into a usable device is crucial for future development. Our group has been investigating

the optical and structural properties of magnetron sputtered SnS_x thin films [1,2,3] . This work will investigate the properties that govern open-circuit voltage, including band gap, series resistance, carrier concentration and built-in potential. Some of these parameters are directly related to the junction material paired with SnS. Several partner materials will be presented with p-SnS including, but not limited to highly doped n-ZnO and n-SnS. Current work is underway to produce n-type SnS as well which would have potential to produce a homojunction.

The optoelectronic properties of SnS make it 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. Our group is able to produce dense SnS thin films with optimal electronic properties. Sputtering the material gives great control over the material properties and recent work optimizing post-deposition heat treatment has shown great promise for improving the material.

Tin sulfide thin films were sputtered on glass and oxidized silicon substrates at varying substrate-to-target distances, substrate temperature, target power, and chamber pressure. The sputter target was a 3" SnS_2 with 99.999% purity (LTS Research Laboratories, Inc.). These sulfur-rich samples were then annealed under medium vacuum ($<2x10^{-6}$ Torr) in the deposition chamber at 400°C to produce a uniform α -SnS, which is most likely to be p-type. Producing n-type SnS is possible via annealing of the films in a methanol/$SnCl_4$ solution. Production of homojunction SnS-based thin film devices is not found in the literature. Our work aims to produce these devices for the first time and compare them to a well-known partner material such as ZnO.

[1] R. E. Banai, et al., in *Proceedings of 2012 38th IEEE Photovoltaics Specialists Conference*, Austin, 2012, pp. 164-169.

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11:00am EN+AS+EM+SE-WeM10 Advanced Contacts for High Efficiency CdTe Solar Cells, *D. Meysing, J.J. Li, J. Beach, T.R. Ohno,* Colorado School of Mines, *M.O. Reese, T.M. Barnes,* National Renewable Energy Laboratory, *Colin Wolden*, Colorado School of Mines

Record CdTe device efficiency has recently surpassed 20%, and it is the leading thin film photovoltaic technology in terms of commercial installation with current manufacturing capacity exceeding 1 GW/year. However, with a Shockley-Queisser limit of ~33% there remains substantial room for additional improvements in efficiency. The quality of both the front and back contacts has substantial influence on CdTe solar cells device efficiency, impacting the current and voltage respectively. This talk will focus on recent work directed at understanding the materials science of both the front and back contact interfaces and optimizing their performance.

Cadmium sulfide is the most commonly employed window layer in the front contact, and its properties can greatly affect cell performance through optical absorption and the quality of the CdS-CdTe junction. In this work, we develop reactive sputtering as an alternative to chemical bath deposition (CBD) for the production of oxygenated cadmium sulfide (CdS:O) to enable high efficiency CdTe solar cells. The intrinsic properties of CdS:O as well as their impact on device performance were studied by varying the oxygen content in the Ar sputtering ambient over the range of 0–10%. XRD, RBS, XPS, and spectrophotometry were used to measure the crystal structure, composition, bonding, and optical properties, respectively. The variation in properties is unsurprisingly non-linear, and optimal performance is attributed to a compromise between optical transmission, which improve monotonically with oxygen content, and band alignment which sharply attenuates device performance beyond a critical threshold.

It is notoriously difficult to make a good ohmic contact to CdTe using conventional metals, because this requires a work function of greater than 5.7 eV. Copper-doped zinc telluride (ZnTe:Cu) is one of the most commonly employed buffer layers to mitigate this issue. ZnTe was identified due to its valence band alignment and compatibility with CdTe. Copper has both positive and deleterious effects and it is critical to precisely control both its amount and spatial distribution in order to obtain high efficiency. We have developed a back contacting procedure that employs rapid thermal processing (RTP) to deliver precise control over the activation and distribution of Cu. The RTP process is coupled with atom probe tomography and advanced optoelectronic characterization to improve our understanding of the structure-property-performance relationships in this system. The advances achieved here using commercially scalable processes are combined to produce devices with V_{oc} > 850 mV and efficiencies exceeding 16%.

11:20am EN+AS+EM+SE-WeM11 Structural Variations and their Effects on the Fundamental Bandgap of $ZnSnN_2$, *Nathaniel Feldberg*, University at Buffalo-SUNY, *Y. Yang,* University of Michigan, *W.M. Linhart, T.D. Veal,* University of Liverpool, UK, *P.A. Stampe, R.J. Kennedy,* Florida A&M University, *D.O. Scanlon,* University College London, UK, *L.F.J. Piper,* Binghamton University, *N. Senabulya, R. Clarke,* University of Michigan, *R.J. Reeves,* University of Canterbury, New Zealand, *S. Durbin,* Western Michigan University

In recent years Zn-IV-N_2 compounds have seen increased interest as potential earth abundant element semiconductors for photovoltaic and solid state lighting applications. Several reports of successful growth for the Ge and Si containing compounds are extant as well as more recent publications on the Sn containing member of the family. This material offers a possible alternative to indium containing materials which have experienced large price fluctuations due to limited domestic supply, lack of recycling and heightened demand. Our films were grown by plasma assisted molecular beam epitaxy on (111)-yittria stabilized zirconia. In the case of an ordered lattice, density functional theory (DFT) predicts an orthorhombic structure; however, the disordered lattice is predicted to be pseudo-hexagonal. Reflection high energy electron diffraction patterns for these films indicate single crystal structure with hexagonal symmetry, consistent with X-ray diffraction measurements. Hall effect indicates carrier concentrations in the $3-10x10^{21}$ cm^{-3} range for which we would expect a significant Burstein-Moss shift. Contrary to expectations, optical measurements of absorption onset occur at higher energy in films with lower carrier concentrations. As in $ZnSnP_2$, the bandgap is expected to narrow with the introduction of disorder for this material; this narrowing behavior is consistent with observed variations in absorption spectra. Of practical interest is the possibility of a material with a tunable bandgap without the need for traditional alloying. Zn-Sn-N_2 is expected to have a bandgap varying from 1.1 to 2 eV controlled by the continuous degree of order in the cation sub-lattice. Although hard X-ray diffraction measurements of these films do not show any variation from a hexagonal structure, Hall measurements of carrier concentrations compared with absorption data indicates that our samples vary their absorption onset, not as would be expected from Burstein-Moss Shift, but in a manner consistent with a variation in the lattice order. DFT calculations indicate that there is a variation in the Density of States between the ordered and disordered films. Films which were consistent with increased order absorption are also consistent with an increased order density of states measured by HAXPES.

11:40am EN+AS+EM+SE-WeM12 Inhomogeneity of *p-n* Junction and Grain Structure of Thin Film CdTe Solar Cells Studied by Electron Beams, *Heayoung Yoon*, *P. Haney,* NIST, *P. Koirala,* University of Toledo, *J.I. Basham, Y. Yoon,* NIST, *R.W. Collins,* University of Toledo, *N.B. Zhitenev,* NIST

Thin film CdTe solar cells are a promising photovoltaic (PV) technology in today's market due t o their high optical absorption and inexpensive fabrication processes . However, the current module efficiency is well below the theoretically estimated maximum efficiency (13 % vs. 30 %) . Recent studies have suggested that inhomogeneity of the PV materials is mainly responsible for the low power conversion efficiency. In this work, we investigate the variation of local PV properties of CdTe solar cells, focusing on grain bulk, grain boundaries, and *n*-CdS / *p*-CdTe junctions. The window (≈ 120 nm thick CdS) and absorber (≈ 2.2 μm thick CdTe) layers were sputtered on a TCO (transparent conductive oxide) coated glass substrate followed by $CdCl_2$ treatment. The back contact metals (3 nm Cu / 30 nm Au) were deposited and annealed, creating 256 devices in a 15 cm by 15 cm solar panel. Following light and dark current-voltage measurements, we performed local characterizations using electron beams for high (> 13 %) and low efficiency (< 6 %) devices within the panel. Electron beam induced current (EBIC) was used to measure the local carrier collection efficiency with a spatial resolution of ≈20 nm exciting carriers either from the top surface or the cross-sections of the devices. Cross-sectional EBIC data reveals that the peak of efficiency is in the middle of CdTe layer in the low efficiency devices, while the carrier collection is maximal near the *p-n* junction in the high efficiency devices. The EBIC contrasts at grains/grain boundaries in these devices are also compared. The measured local electronic properties are correlated to microstructural morphology (Transmission Electron Microscopy), orientation (Electron Back Scattered Diffraction), and chemical composition (Energy Dispersive X-ray spectroscopy). We perform 2D model drift-diffusion simulations to determine the magnitude of downward band-bending near grain boundaries (with typical magnitude of 0.2 eV). We will discuss the impact of carrier generation rate (high level injection *vs*. low level injection) in EBIC analysis.

12:00pm **EN+AS+EM+SE-WeM13** **Micro-Structural Activation Mechanisms in Thin Film CdTe Photovoltaic Devices**, *John Walls*, *A. Abbas*, *J.W. Bowers*, *P.M. Kaminski*, Loughborough University, UK, *K. Barth*, *W. Sampath*, Colorado State University

Thin Film CdTe photovoltaics is a commercially successful second generation technology now used extensively in solar energy generation at the utility scale. Although the cadmium chloride treatment is a process that is essential to produce high efficiency devices, the precise mechanisms involved in the re-crystallization and associated improvement in electronic properties have not been fully understood. In this paper we report on the application of advanced micro-structural characterization techniques to study the effect of the cadmium chloride treatment on the physical properties of the cadmium telluride solar cell deposited by both close space sublimation (CSS) and magnetron sputtering and relate these observations to device performance. In particular, High Resolution Transmission Electron Microcopy (HRTEM) reveals that the untreated material contains high densities of planar defects which are predominantly stacking faults and that the optimized cadmium chloride treatment removes these completely with only twins remaining. Parallel theoretical studies using Density Functional Theory (DFT) shows that certain types of stacking fault are responsible for the poor performance of the untreated material. Extending the treatment time or increasing the annealing temperature above ~400^{0}C improves the microstructure but results in lower efficiency devices. Composition –depth profiling using XPS and SIMS reveals that this deterioration in performance is linked with chlorine build up at the CdS/CdTe junction. These experiments and parallel theoretical studies have improved our understanding of the mechanisms at work in the cadmium chloride assisted re-crystallization of CdTe and could lead to further increases in device efficiency

Plasma Science and Technology
Room: 308 - Session PS+SE-ThA

Atmospheric Pressure Plasma Processing; Fundamental and Applications
Moderator: Richard van de Sanden, DIFFER, Stefan Welzel, FOM Institute DIFFER

2:20pm **PS+SE-ThA1 Insights into the Chemistry of Atmospheric Pressure Plasma Deposition Processes**, *Fiorenza Fanelli*, Institute of Inorganic Methodologies and Plasmas - National Research Council, Italy, *P. Bosso, A.M. Mastrangelo, F. Fracassi*, University of Bari 'Aldo Moro', Italy **INVITED**
Over the last decade there have been considerable advances in the utilization of atmospheric pressure cold plasmas for thin film deposition. Intense research efforts have been made to develop a large variety of processes which exploit different types of atmospheric pressure discharges for the direct and remote deposition of thin films from monomers in gas, vapor and aerosol form [1]. However diagnostic studies of the plasma chemistry and mechanistic investigations of thin film growth are still scarce, while being crucial prerequisite for further process optimization. The research should be addressed to detect the film precursors, to identify the main reaction pathways (both homogeneous and heterogeneous processes) and to clarify the plasma-surface interaction.

In this contribution, our studies on thin film deposition by dielectric barrier discharges (DBDs) will be presented to provide insights into the chemistry of atmospheric pressure plasma processes. Examples discussed will include the investigation of the role of the monomer chemical structure in the plasma-enhanced chemical vapor deposition of organosilicon coatings from different methyldisiloxanes [2], and the study of the influence of air and water vapor feed gas impurities in the deposition of fluorocarbon coatings from argon-hexafluoropropene fed DBDs [3]. Our recent work on the deposition and characterization of organic-inorganic hydrocarbon polymer/ZnO nanoparticles nanocomposite coatings by a DBD fed with helium and the aerosol of a dispersion of oleate-capped ZnO nanoparticles in hydrocarbon solvents will be presented [4]. Results from the plasma jet co-deposition of acrylic acid and ethylene towards water-stable coatings containing carboxylic functionalities will be also shown.

The overall deposition mechanisms will be outlined on the basis of the results from the chemical and morphological characterization of the coatings, the optical emission spectroscopy investigation of the plasma phase, the analysis of the exhaust gas by means of gaschromatography-mass spectrometry. The latter is a powerful *indirect* diagnostic technique of the gas phase which allows the assessment of the monomer depletion and the quali-quantitative determination of stable byproducts formed by plasma activation.

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[3] F. Fanelli, R. d'Agostino, F. Fracassi, *Plasma Process. Polym.*, 8, 557 (2011).

[4] F. Fanelli, A. M. Mastrangelo, F. Fracassi, *Langmuir*, 30, 857 (2014).

3:00pm **PS+SE-ThA3 Understanding Charge Transfer Reactions at a Plasma-Liquid Interface**, *Paul Rumbach**, University of Notre Dame, *R.M. Sankaran*, Case Western Reserve University, *D.M. Bartels, D.B. Go*, University of Notre Dame
The interaction of atmospheric-pressure plasma jets with liquids is becoming increasingly important for medical and materials applications. Despite empirical evidence of reactions occurring both in the bulk plasma and liquid phases, a basic understanding of the chemistry, particularly at the interface of the plasma and liquid, remains poorly understood. Previous studies have shown that species produced in the plasma phase such as nitric oxide (NO) and hydroxyl radicals (OH) can solvate in the liquid, yielding products such as nitrous acid (HNO_2) and hydrogen peroxide (H_2O_2) in the bulk solution [1]. In addition, we have recently shown that charge can be transferred from a DC microplasma jet into an aqueous solution to promote electrolytic reduction reactions [2]. However, it remains unclear how these charge transfer reactions occur and, in particular, if plasma electrons solvate in the liquid before subsequently reducing solution species.

To clarify the role of electrons solvating at a plasma-liquid interface, we have designed and built an experiment to detect solvated electrons using optical absorption spectroscopy. Electrons solvated in aqueous solutions are well known to absorb strongly in the red. Initial models suggest that because of the short lifetime of solvated electrons in aqueous solutions (~1 μ s) and anticipated solvation depths on the order $10 - 100$ nm, optical absorption will be on the order of one part in 10^6, making this an inherently challenging measurement. In this presentation, we will give an overview of our experimental method and present preliminary findings on direct measurements of electron solvation.

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[2] M. Witzke, P. Rumbach, D. B. Go, and R. M. Sankaran, *J. Phys. D: Appl. Phys.* **45** 442001 (2012).

3:20pm **PS+SE-ThA4 A Novel Atmospheric Pressure Plasma Application for Fuel Tank Inerting**, *Matthew Price*, *A. Srivastava*, Interspace, Inc.
Aircraft fuel tanks have traditionally been protected from ballistic threats caused from explosive vapors by filling the area above the fuel with suppressant foam or inert gas. More recently fuel tank inerting systems have been developed for commercial transport aircraft. Inert gas is the preferred method since foam is heavy, reduces fuel tank capacity and is expensive to maintain. Current solutions consist of Onboard Inert Gas Generation Systems (OBIGGS) to reduce oxygen content in fuel tanks through the use of nitrogen-air separators. These membrane-based separators require high-powered pumps to flow air through small pores in the membranes. OBIGGS systems are bulky and too power hungry to be practical for smaller aircraft with multiple fuel tanks and limited electrical power. INTERSPACE has developed an innovative and efficient inerting system that does not rely on a pre-stored inerting agent or bleed air and is scalable to support multiple independent tanks. The system requires minimal electrical power and is capable of inerting to trace oxygen concentration levels without contaminating the fuel.

Our solution uses a getter material to readily sequester oxygen as surface oxides. A non-thermal, atmospheric pressure plasma then combines hydrocarbons in the tank with the getter to reduce the oxide and reverse the process to form water vapor. No consumable inerting product is used. Experimental data shows the getter absorbs 20 times its volume in oxygen before saturation. Scaling up this reaction would inert a 500 gallon fuel tank in 11.4 minutes with one liter getter at standard temperature and pressure conditions. Time-to-inert decreases at higher altitudes due to lower pressure. Time-to-inert curves were calculated for the typical aircraft flight envelope based on this model. We have successfully demonstrated the feasibility of our inerting system in a laboratory environment. Our inerting system is highly selective to oxygen, and eliminates the membranes and high power pumps used in existing systems. The next step will be to evaluate a prototype system through demonstration testing on the replica of a military aircraft fuel tank system. A customized plasma source will be developed optimized in size and weight competitive with aircraft applications.

4:00pm **PS+SE-ThA6 *In Situ* Diagnostic Studies of CO_2 containing Dielectric Barrier Discharges**, *Stefan Welzel*, FOM Institute DIFFER; Eindhoven University of Technology, Netherlands, *F. Brehmer*, Eindhoven University of Technology; AFS GmbH, Germany, *B.L.M. Klarenaar*, Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, FOM Institute DIFFER; Eindhoven University of Technology, Netherlands, *R. Engeln*, Eindhoven University of Technology, Netherlands
Carbon dioxide will be a key enabler for the integration of renewable energy into a future CO_2 neutral energy system as well as into chemical industry. The application of non-equilibrium plasmas offers a promising route to overcome the initial energy-demanding CO_2 dissociation step. Through subsequent hydrogenation of the CO produced, gaseous or liquid hydrocarbon(ate)s are synthesised. Dielectric barrier discharges (DBDs) are known as useful tools in plasma-assisted gas conversion. The main objective was to unravel main reaction mechanisms in CO_2 containing DBDs through combination of several *in-situ* diagnostic techniques.

Optical emission spectroscopy, (infrared) absorption spectroscopy along with rotational Raman scattering were employed to study the CO_2 conversion and deduce gas temperatures in mid-frequency (kHz) driven DBDs at elevated pressures. To study the kinetics of CO formation the DBD was additionally operated in pulsed mode. Absolute densities of CO, O_2 and O_3 were established downstream the plasma reactor. The CO yield

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* Coburn & Winters Student Award Finalist

was typically below 5% for gas flow rates that would allow reasonable throughput. The generally weak emission of electronically excited species (CO_2^+, CO) was monitored during individual AC cycles. Additionally, phase- and time-resolved signals of ro-vibrational absorption lines of CO and CO_2 in their (electronic) ground state were detected by quantum cascade laser absorption spectroscopy. In contrast to emission, the CO absorption remained constant throughout individual AC cycles. The modulation of CO absorption signals during pulsed operation can be successfully modelled by considering the power density of the DBD, the reactor wall and gas temperatures (up to 550 K), and the residence time of the gas along with the reactor geometry.

The results suggest electron-impact CO_2 excitation and ionisation followed by potentially surface enhanced recombination. The stoichiometric $CO:O_2$ ratio is described by a uniform trend as function of the number of charges transferred during the residence time of CO_2 in the active plasma zone.

4:20pm PS+SE-ThA7 Effect of the Nature of the Plasma Gas on the Resulting Chemistry of Atmospheric Plasma Deposited Coatings and of Plasma Treated Gases, *D. Merche, N. Vandencasteele, A. Ozkan, J. Hubert, François Reniers*, Université Libre de Bruxelles, Belgium
In atmospheric plasma processes, the use of a main gas, usually considered as inert, to sustain the plasma is common. Nitrogen, argon and helium are the most regularly used gases. If the nature of the gas has a strong influence in the breakdown discharge voltage (due to Paschen Law), it also leads to plasmas which are optically and electrically different. This has drastic consequences on the chemistry and structure of plasma deposited coatings and on the chemistry of plasma treated gases. In this study, we compare, and try to explain, the results obtained on different topics using either argon or helium as main plasma gas.

All experiments have been conducted in dielectric barrier discharge reactors, powered with sinusoidal AFS generators, operating at frequencies lower than 40 kHz. For all the studies the reactors have been pumped down to evacuate contaminations and then backfilled with the plasma gas (Ar or He). The precursor is then injected in the DBD through the appropriate flow of the carrier gas.

Internal chemistry of coatings :

Through a combined XPS, FTIR and SIMS study, it is shown that the degree of cross-linking, the branching and the number of insaturations of plasma-polymerized polystyrene or sulfonated polystyrene (for fuel cell applications) is higher with argon than with helium, whereas the density of aromatics exhibits the opposite behavior.

Surface roughness of coatings

Similarly, for all the organic coatings synthesized by a dielectric barrier discharge (PS, CFx from C_6F_{12}, PA), the roughness, determined by AFM is always higher with argon than with helium.

Conversion of CO_2 by DBD

Finally, the conversion rate of CO_2 into CO in atmospheric plasma conditions (DBD), is higher when argon is the main plasma gas than with helium.

It is suggested that all these effects are strongly related to the plasma operating mode and to the energy distribution inside the plasma.

This work is supported by PSI-IAP 7 (plasma surface interactions) from the Belgian Federal Government BELSPO agency

4:40pm PS+SE-ThA8 Diagnostics of an Atmospheric-Pressure dc Glow Plasma in Contact with Solution: Insight into Plasma-Liquid Interaction, *Koichi Sasaki*, Hokkaido University, Japan **INVITED**
The interaction between an atmospheric-pressure plasma and a liquid attracts much attention in conjunction with plasma-aided medical treatments and plasma-assisted agriculture. Major interests are the production and the transport of OH radicals in plasmas in contact with liquids. In this work, we examined the spatial distribution of the OH radical density in the gas phase of a dc glow plasma produced between a stainless-steel nozzle as the anode and electrolyte of NaCl solution as the cathode by laser-induced fluorescence (LIF) imaging spectroscopy. We were careful about the influence of collisional quenching and the rotational temperature in deducing the spatial distribution of the OH radical density from the LIF images.

The maximum rotational temperature was approximately 3000 K, which was observed in the plasma column in contact with the electrolyte surface. The frequency of collisional quenching was also high in the contacting region to the electrolyte surface, suggesting that the dominant quencher of the excited state of OH was water vapor. The absolute density of water vapor was evaluated from the quenching frequency and the rate coefficient of collisional quenching. It was found that the partial pressure of water vapor was more than five times higher than the saturated vapor pressure of water at room temperature.

The OH radical density was high in the neighboring region to the electrolyte surface, suggesting that water vapor produced from the electrolyte is the parent of OH radical. However, the peak of the OH radical density was separated from the electrolyte surface, and also the OH radical density on the electrolyte surface was not zero. It is noted that, if OH radicals are not reactive on the electrolyte surface, the decrease in the OH density toward the electrolyte surface would not be observed. On the other hand, if OH radicals are too reactive in the gas phase, the OH radical density on the electrolyte surface would become zero (Note that the production of OH in the cathode sheath is negligible), and in this case we cannot expect the interaction of OH radicals with the electrolyte. The axial distribution of the OH density observed in this work indicates that the electrolyte surface interacts with OH radicals as their sink. In other words, OH radicals are lost on the electrolyte surface. A possibility of the loss process is recombination to form hydrogen peroxide and water. In addition, we can also expect the transport of OH radicals into the inside of the electrolyte.

5:20pm PS+SE-ThA10 Absolute Measurements of Short Lived Reactive Species in Cold Atmospheric Pressure Plasmas, *Deborah O'Connell, K. Niemi, J. Dedrick, S. Schroeter, J. Bredin, A. West, E. Wagenaars, T. Gans*, University of York, UK
Low temperature plasmas are emerging as an exciting development for therapeutics. The unique properties of cold non-equilibrium plasmas have enormous potential in disease therapeutics and plasma pharmacology as drug alternatives. Applications of these plasmas include surface sterilization and bacterial decontamination, biofilm inactivation, antimicrobial treatment in food preservation, wound healing, to cancer treatment.

Non-equilibrium plasmas, operated at ambient atmospheric pressure and temperature, are very efficient sources for highly reactive neutral particles e.g. reactive oxygen and nitrogen species (RONS) (such as atomic oxygen, atomic nitrogen, hydroxyl radical, superoxide, singlet delta oxygen, nitrogen oxides), charged particles, UV-radiation, and electro-magnetic fields. Individually many of these components have been implicated in therapeutics. RONS are known to play a crucial role in biological systems, such as signalling, and generating oxidative damage to a variety of cellular components, which can ultimately lead to cell death. Plasmas have the advantage of delivering these simultaneously providing potentially superior processes.

Transport of the plasma components to the target is complex. In the core plasma production region a large, but defined, number of species can be created (including for example O, N, NO, O_2^-). As the plasma interacts with ambient air new reactions and components are formed. Upon interaction with either humidity or liquid layers on biological samples new species of varying lifetimes can be created (e.g. OH, H, H_2O_2, $ONOO^-$). Energy dissipation at these interfaces is important and to date unclear.

In order to understand the chemical kinetics and plasma-liquid-biological interaction mechanisms measurements of the relevant RONS are key. Measurements and simulations under this atmospheric pressure environment are challenging, primarily due to the multi-phase (solid, liquid, gas and plasma), strongly non-equilibrium with large gradients (e.g. in electric field), high collisionality, thus requiring extremely high temporal (picosecond to nanosecond) and spatial (microns) resolution.

Two advanced optical diagnostic techniques are applied, and will be presented, to measure absolute radical densities: Pico-second two-photon absorption laser induced fluorescence (ps-TALIF) and high-resolution synchrotron VUV absorption spectroscopy will be presented. Radicals measured in an atmospheric pressure plasma operated in helium with varying admixtures of oxygen, nitrogen and water vapour will be presented.

5:40pm PS+SE-ThA11 Recent Progress in the Diagnostics of Microwave Discharges for Optimization of CO_2 Dissociation, *Tiago Silva, N. Britun, T. Godfroid, R. Snyders*, University of Mons, Belgium
The increase in global emissions of carbon dioxide (CO_2) due to fossil-fuel combustion and other energy-related human activities is strongly related with the global warming issue. Due to this effect, the study of CO_2 dissociation process is a highly demanding topic, which requires attention and efficient solutions. Among the proposed strategies, one possible way to limit CO_2 emission is to use plasma technology to break the CO_2 molecule into oxygen (O) and carbon monoxide (CO), which can be later used for production of valuable chemicals, e.g. for the fuel synthesis (syngas).

Recently, energy-efficient powerful plasma-chemical systems have been developed based on microwave plasmas. These discharges are often generated using electromagnetic waves in the range of 300 MHz to 10 GHz, and can operate over a wide range of conditions of pressure and power. In particular, microwave surfaguide discharges (MSGD) where the gas flow in the discharge tube is perpendicular to the waves propagation, are proven to be good solution for an efficient molecular dissociation of di- or multi-atomic species [1].

In this work, the recent results on CO_2-containing MSGD operating at 0.9 GHz and 2.45 GHz in pulsed and continuous regimes are presented. The plasma is sustained in CO_2 and CO_2+N_2 flowing gas mixtures in a quartz tube crossing a copper waveguide. The microwave discharges are characterized in terms of various plasma parameters using various optical emission spectroscopy (OES) methods. In particular, the characteristic plasma temperatures, such as the gas temperature (via CO rotational spectra), and vibrational temperature (via N_2 vibrational bands) are determined as a function of time at different axial positions along the gas flow in the discharge tube. The CO_2 conversion rate in the discharge volume, along with the measurements of plasma energetic efficiency of such conversion is performed by means of optical emission actinometry. The results of the time- and space- resolved OES measurements demonstrate a non-uniform dissociation rate of CO_2 along the gas propagation direction in the discharge. As a result, the dissociation degree can be substantially modified by varying the power balance and the composition of the gas mixture [2]. In addition, in order to get a complete picture of the process, gas chromatography measurements were performed in the post discharge region. The obtained integrated results allow better understanding the μwave plasma-based dissociation of CO_2.

[1] T. Godfroid, J. P. Dauchot and M. Hecq, *Surf. Coating Technol* **174-175** 1276-1281 (2003)

[2] T. Silva, N. Britun, T. Godfroid, R. Snyders *Plasma Sources Sci. Technol* **23** 025009 (2014)

Friday Morning, November 14, 2014

Scanning Probe Microscopy Focus Topic
Room: 312 - Session SP+AS+BI+EM+NS+SE+SS-FrM

Probe-Sample Interactions and Emerging Instrument Formats
Moderator: Carl Ventrice, Jr., University at Albany-SUNY

8:40am **SP+AS+BI+EM+NS+SE+SS-FrM2 2013 ASSD Student Award Talk: New Insights into Nanoscale Adhesion from *In Situ* TEM Studies**, *Tevis Jacobs, J.A. Lefever,* University of Pennsylvania*, J. Liu,* University of Wisconsin-Madison*, D.S. Grierson,* SysteMECH LLC*, K.E. Ryan, P.L. Keating, J.A. Harrison,* United States Naval Academy*, K.T. Turner, R.W. Carpick*, University of Pennsylvania
A fundamental understanding of adhesion is important for applications at all length scales, but is particularly critical in nanoscale devices and applications due to their high surface-to-volume ratio. Advancements in studying such tribological phenomena are typically hindered by the inaccessibility of the sliding interface. We will present nanoscale adhesion measurements conducted inside of a transmission electron microscope (TEM), using a modified in situ nanoindentation apparatus that makes contact with atomic force microscope (AFM) cantilever tips. This tool provides new opportunities to observe, identify, and quantify tribological processes with unprecedented access and resolution. First, using ultra-strong carbon-based tip materials, we find that roughness of tips can greatly reduce the pull off force and lead to severe underestimation of the work of adhesion [1]. Furthermore, we have quantified adhesion by making and breaking contact between nanoscale silicon asperities and a flat diamond substrate. The snap-in distance and the pull-off force are measured with sub-nanometer and sub-nanonewton resolution, respectively. The shape of the Si asperity is determined with sub-nanometer resolution immediately before and after contact to verify that elastic conditions were maintained. From this, we independently determine the work of adhesion and range of adhesion. The results show that accounting for roughness has a strong effect on both parameters. These two results demonstrate the importance of applying in situ approaches to studies of adhesion. --- 1. Jacobs, T.D.B., Ryan, K.E., Keating, P.L., Grierson, D.S., Lefever, J.A., Turner, K.T., Harrison, J.A. and Carpick, R.W. The Effect of Atomic-Scale Roughness on the Adhesion of Nanoscale Asperities: A Combined Simulation and Experimental Investigation. Tribol. Lett. 50, 81-93 (2013).

9:40am **SP+AS+BI+EM+NS+SE+SS-FrM5 Nanoscale Mapping of the W/Si(001) Schottky Barrier using Ballistic Electron Emission Microscopy**, *Christopher Durcan*, University of Albany-SUNY*, V.P. LaBella*, University at Albany-SUNY
The W/Si(001) Schottky barrier was spatially mapped using ballistic electron emission microscopy (BEEM) and ballistic hole emission microscopy (BHEM) using high resistivity n-type and p-type silicon substrates. A thin tungsten silicide is observed upon deposition utilizing transmission electron microscopy (TEM) and Rutherford backscattering spectrometry (RBS). The sum of the Schottky barrier heights from n-type and p-type silicon substrates agree with the silicon band gap. The BEEM and BHEM spectra are fit utilizing a linearization method to the power law of the BEEM model. Spatially resolved Schottky barrier maps are generated over a 1μm x 1μm area and provide insight into the spatial homogeneity of the barrier height. Histograms of the barrier heights show a Gaussian distribution, consistent with an interface dipole model.

10:00am **SP+AS+BI+EM+NS+SE+SS-FrM6 Local Probing of Superconductivity in Half Heusler Compounds**, *Hongwoo Baek*, NIST & Seoul National University, Republic of Korea*, J. Ha, D. Zhang*, NIST/Maryland Nano Center, University of Maryland*, Y. Nakajima, P.S. Syers, X. Wang, K. Wang, J. Paglione*, University of Maryland*, Y. Kuk*, Seoul National University, Republic of Korea*, J.A. Stroscio*, NIST
Heusler alloys have attracted interest as multifunctional experimental platforms for topological quantum phenomena ranging from magnetism to superconductivity and heavy fermion behavior. The rare-earth chalcogenide ternary half Heusler compounds were theoretically predicted to have topologically nontrivial surface states due to band inversion [1]. The lack of inversion symmetry of the crystal lattice makes unconventional pairing symmetry feasible. The superconductivity in the non-centrosymmetric half Heusler compound YPtBi was recently reported as a promising system for the investigation of topological superconductivity [2]. In this work, we use ultra low temperature scanning tunneling micro scopy to investigate the superconducting properties of the ternary half Heusler compounds YPdBi and YPtBi. Both were theoretically proposed to have topological states with different band inversion strength [1], and experimentally reported as a topological insulator [3]. Strong spin-orbit coupling and the lack of inversion symmetry present the possibility of spin-triplet superconductivity in these materials. T he tunneling spectra of YPdBi show two different superconducting gaps of 0.36 meV and 0.16 meV depending on the measurement location. The variation in gaps might originate from inhomogeneity in the crystal. The superconducting gap of 0.36 meV is completely suppressed above a critical magnetic field of B=2.5 T, in agreement with bulk transport measurements. A superconducting gap of 0.21 meV and an upper critical field of 1.25 T were measured in a circular superconducting domain of diameter ≈180 nm in YPtBi. Sequential addition of single vortices to the superconducting YPtBi domain could be observed with increasing magnetic field, with vortices occupying the perimeter of the island. These observations will be discussed in terms of island confinement and pairing symmetry of YPtBi.

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[3] W. Wang, Y. Du, G. Xu, X. Zhang, E. Liu, Z. Liu, Y. Shi, J. Chen, G. Wu, and X. Zhang, Scientific Reports **3** (2013).

10:40am **SP+AS+BI+EM+NS+SE+SS-FrM8 Multimodal Intermittent Contact Atomic Force Microscopy: Topographical Imaging, Compositional Mapping, Subsurface Visualization and Beyond**, *Santiago Solares*, George Washington University
Multifrequency atomic force microscopy (AFM) refers to a family of techniques that involve excitation of the microcantilever probe at more than one frequency [R. Garcia and E.T. Herruzo, Nature Nanotechnology 7, 217 (2012)]. This can be carried out in a sequential manner, varying the excitation frequency over time, as in chirp band excitation methods, or simultaneously supplying drive signals containing more than one frequency to the cantilever shaker. The latter mode of operation commonly involves the simultaneous excitation of more than one cantilever eigenmode, such that each eigenmode is used to carry out different functions. For example, in a recently developed trimodal imaging scheme for soft sample characterization [D. Ebeling, B. Eslami and S.D. Solares, ACS Nano, 7, 10387 (2013)], the fundamental eigenmode is used for topographical acquisition, as in standard tapping-mode AFM, while two higher eigenmodes are used for compositional mapping and subsurface visualization, respectively. This talk presents experimental and computational results for validated multimodal imaging schemes involving one to three eigenmodes, and discusses the expected benefits and complexities of including more than three eigenmodes.

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