Plasma Science and Technology
Room 104D - Session PS+SE-MoM

Atmospheric Pressure Plasma Processing

Moderator: Lorenzo Mangolini, University of California Riverside

9:00am **PS+SE-MoM3 Fundamental Characterization of a Low Frequency, Ambient Air, Plasma Jet Discharge***, **Vladimir Milosavljevic**,* Dublin Institute of Technology, Ireland*; L. Scally, J. Lalor, P.J. Cullen,* Dublin Institute of Technology

Plasma discharge in open air has charged species, energetic photons, active radicals, and also a low degree of ionization gas. Interaction of such plasma with surfaces has been a subject of intense study for many decades. In particular, an atmospheric jet plasma system used to solve surface preparation problems. The biggest advantages of such a system are: high density plasma in contrast to corona discharge, no electrical current or filamentary streamers in the plasma jet, broad material application capability, simple host automation integration, low environmental impact, and low thermal load allows low melting point polymers to be treated. Despite the widespread usage of plasma jet technology, it remains largely unknown whether atmospheric plasma maintains similar characteristics, such as gas temperatures and particle flux, when they breakdown while arcing or whether they possess different operating modes. In this work optical spectroscopy was used as a diagnostic method due to its non-intrusive nature. In additional to this, surface metrology based on a measurement of the water contact angle (WCA) and surface energy was also engaged.

In this study a high pressure (6 bar) atmospheric plasma jet system, which operates with ambient air chemistry, was employed. The plasma jet operated at a frequency of 60 Hz and used a pencil type beam applicator. The low operation frequency makes this system significantly different from a vast majority of other plasma jets. Namely, at low frequencies (<50 kHz) ions and electrons both oscillate and therefore both contributed in interaction with surfaces. At high frequencies (>50 kHz) heavy ions cannot follow switching fields and therefore only electrons oscillate while ions are relatively stationary which has a huge impact on the plasma sheath dynamics.

The polymer used in this work was polyethylene terephthalate (PET) and was widely used in a variety of industries from food packaging to the electrical, electronics, and biomedical industries. PET could be easily thermally damaged at relatively low temperatures and so a delicate balance must be reached where surface activation of the polymer was maximised, while thermal damage was prevented. The level of polymer surface activation was evaluated based on changes to the WCA of PET samples after plasma treatment. A direct correlation was obtained between the polymer WCA changes and the OES measurement. This correlation may indicate that OES peak intensities can be used as an indicator of the treated polymer WCA, without the need for conventional off-line metrology.

This work was a funded by SFI under the PlasmaGrain project.

9:20am **PS+SE-MoM4 CO_2 Splitting by Dielectric Barrier Discharge at Atmospheric Pressure: Understanding the Influence of Electrical Regimes and Electrical Configurations***, **Alp Ozkan**, T. Dufour,* Université Libre de Bruxelles, Belgium*; A. Bogaerts,* University of Antwerp, Research group PLASMANT, Belgium*; F. Reniers,* Université Libre de Bruxelles, Belgium

Dielectric barrier discharges (DBDs) are commonly used to generate cold plasmas at atmospheric pressure. In this experimental work, a flowing tubular DBD is used for the CO_2 splitting into O_2 and CO. The influence of the frequency (from 16 to 28 kHz), the power (from 30 to 100 W), the role of the barrier thickness (2.0, 2.4 and 2.8 mm), the kind of dielectric material (alumina, mullite, pyrex, quartz), and the effect of a pulsed AC discharge (so-called burst mode) are investigated on the filamentary behavior of the plasma and on the CO_2 conversion, by means of mass spectrometry measurements correlated with electrical diagnostics. Their influence on the gas and electrode temperature is also evidenced through optical emission spectroscopy and infrared imaging. A new methodology is developed to investigate the microdischarge properties. For this purpose, electrical measurements, based on a numerical method, are carried out to explain the conversion trends and to characterize the microdischarges through their number (N_{md}), their lifetime (L_{md}), their intensity (i_{pl}) and the induced electrical charge (Q_{pl}) for a given analysis time. These extracted data are usually underestimated or poorly described in literature. It is shown that, when the applied power is modified, the conversion depends mostly on the Q_{pl} and not on the effective plasma voltage ($V_{pl,eff}$). Similarly, a better conversion is observed at low frequencies, where a more diffuse discharge with a higher $V_{pl,eff}$ than at higher frequency is obtained. Moreover, increasing the barrier thickness decreases the capacitance while preserving the electrical charge. As a result, the voltage over the dielectric (V_{diel}) increases and a larger N_{md} is generated, which enhances the CO_2 conversion. Furthermore, changing the dielectric material of the barrier, while keeping the same dimensions, also affects the conversion. The highest CO_2 conversion and energy efficiency are obtained for quartz and alumina. From the electrical characterization, we clearly demonstrate that the most important parameters are the somewhat higher $V_{pl,eff}$ (yielding a higher electric field and electron energy involved in CO_2 dissociation) for quartz, as well as the higher plasma current (thus larger electron density) and the larger N_{md} (mainly for alumina due its higher roughness, but also for quartz due to its higher V_{diel}). Finally, a comparison between DBD ignited in burst mode and pure AC mode is achieved. Decreasing the duty cycle from 100% (pure AC mode) to 40% leads to a rise in the conversion due to a larger N_{md} and a higher voltage.

9:40am **PS+SE-MoM5 Effect of Structural Variations of the Monomer on the Fast Synthesis of Highly Oxygenated Coatings in an Argon DBD***, **Jérémy Mertens**, F. Reniers,* Université Libre de Bruxelles, Belgium

The use of atmospheric plasma DBD for the synthesis of organic coatings has recently become more and more popular. Their unconventional polymerization pathways allow the synthesis of brand new polymers with specific properties which are strongly dependent on the chemical structure of the injected monomer[1,2].

The goal of this research is the development of an intermediate coating presenting a high surface energy with an important deposition rate in order to improve the adhesion of a resin on aluminum by DBD. Because of their initial structure, anhydrides are seen as ideal candidates for the synthesis of such films. We here present how small variations in their chemical structure can affect their behavior in the discharge and the chemical properties of the coatings. Firstly, the influence of the C/O ratio in the injected monomer is investigated by the use of acetic, propionic and butyric anhydride. The addition of double bonds in the initial structure of the precursor is then studied using isobutyric and methacrylate anhydride. Surface analyses such as infrared spectroscopy (IRRAS), X-Ray Photoelectron spectroscopy (XPS) and stylus profilometry showed that highly oxygenated coatings could be synthesized when the C/O ratio of the injected monomer was decreased. Nevertheless, high deposition rates could only be reached with the addition of double bonds in the structure of the monomer. By combining these observations with oscilloscope and mass spectrometry measurements of the discharge, a fragmentation/recombination polymerization is suggested for the non-conventionally polymerizable monomers. On the contrary, a mainly radical propagation through the double bonds is proposed for the methacrylate anhydride. The amount of carboxylic components on the surface can be tuned by the addition of an Ar-O_2 post-treatment but is limited by the degradation of the films that leads to the formation of oxidized volatile compounds.

This work was financially supported by the Walloon Region (FLYCOAT project n°131847) and by the Belgian Federal Government (Interuniversity Attraction Belgian Science Policy IAP research project P7/34 – Physical Chemistry of plasma surface interactions).

[1] J. Hubert & *al.*, *Journal of Materials Research,* **2015**, 30, 21, 3177-3176

[2] A. Batan & *al., Plasma Processes and Polymers,* **2013**, 10, 857-863

10:00am **PS+SE-MoM6 Quantitative Study of Plasma Electrochemical Reduction of Aqueous Metal Salts***, S. Ghosh, A. Aube, R. O'Toole, R. Hawtof, **R.Mohan Sankaran**,* Case Western Reserve University

The possibility of combining ionized gases and ionic solutions to initiate electrochemical reactions in solution with a plasma electrode has been explored for over 100 years. Recently, this idea has been the basis of numerous reports of metal nanoparticle formation when aqueous solutions of metal salts are exposed to a plasma. While this approach has been successfully demonstrated by a range of plasma sources and experimental conditions, the chemistry behind the reactions between plasma and solution species is highly complex and remains poorly understood.

Here, we report quantitative studies of the reduction of aqueous metal salts by a plasma electrode to better understand the reaction kinetics and thermodynamics, analogous to conventional electrochemistry. Kinetic studies were performed by measuring the rate and efficiency of the reduction of a metal salt, silver nitrate. Analogous to weight measurements in electrodeposition of metal thin films, we developed a methodology to measure the mass of the final product, silver (Ag) nanoparticles, by separating the agglomerated particle powder. The reduction efficiency was defined as the actual amount of reduced Ag compared to that predicted by Faraday's law based on the plasma current. We find that in ambient air, the faradaic efficiency for silver nitrate reduction is approximately 80%, and, curiously, the efficiency increases to >100% in a closed reactor cell with an Ar ambient. We interpret these results as follows. Assuming that the chemistry in solution is driven by electrons from the plasma which are directed into solution and can solvate, in ambient air, there is a decrease in the electron flux to the solution because of electron attachment processes involving O_2 gas. Removing air with ambient Ar increases the electron flux and, thus, increases the faradaic efficiency. The surprising efficiency of more than 100% most probably results from an autocatalytic effect whereby reduced Ag (Ag^0) also reduces Ag^+, a mechanism that has been previously reported in radiolytic synthesis of Ag nanoparticles. The thermodynamics of the reduction process was probed by studying a series of metals which have different reduction potentials including copper, iron, and zinc. Successful reduction of the corresponding metal salts for these metals suggests that solvated electrons, which are one of the strongest reducing species, are involved. We will also discuss the respective reduction rates and efficiencies of these metals as compared to Ag.

10:40am **PS+SE-MoM8 LDPE Modified by an Ar/H_2O Dielectric Barrier Discharge: Correlation between Texturization, Wettability and Grafting of Oxygen***, **Stéphanie Collette,*** Université Libre de Bruxelles, Belgium*; P. Viville,* Université de Mons, Belgium*; F. Reniers,* Université Libre de Bruxelles, Belgium

In the literature, some studies focus on the use of H_2O in plasma discharges because of its potential high reactivity. However, is also known to destabilize plasmas. In this study, the reactivity of water at the interface between the plasma and the surface of the low density polyethylene (LDPE) was investigated. LDPE is chosen as polymer because of its high capacity to be functionalized.

In the first part of this project, we study the water reactivity in atmospheric plasma by injecting H_2O vapor in the discharge of a dielectric barrier discharge, supplied with Ar as carrier gas. OES evidenced the production and the consumption of Ar, O, OH, and N_2 species. They can be quantified as a function of the H_2O flow rate and the treatment time in order to have a better understanding of the reactivity. Some chemical reactions occurring within the discharge can be highlighted. To characterize the discharge itself, current measurements are performed and a high speed camera is used to observe the changes of the discharge (number and size of the streamers).

In the second part of this research, LDPE surfaces exposed to water-containing plasma are characterized by XPS. The measurements of the O 1s peak reveal a strong increase of oxygen from 0% to 16%. XPS Depth profiles evidence the diffusion of O in the subsurface. These results have been compared with WCA measurements expressed as a function of time. Between 0 and 30 s, a strong decrease in the WCA is observed (from 100° to 63°) and can be linked to the rise of the O% (from 0% to 13%). After 30 s, the WCA rapidly decreases to 43° which seems inconsistent with the very slow increase of the O% (almost no rise) observed by XPS. In parallel, AFM measurements show a texturization of the treated LDPE, as the surface roughness increases from 27 nm to 75 nm. The effect observed after 30 s of treatment can be explained by the Wenzel equation:

$\text{Cos}\ \Theta_{app} = r \cos \Theta$

Indeed, the "r" factor in the Wenzel corresponds to the roughness ratio defined as the ratio of true area of the solid surface to the apparent area. Cos Θ can be linked to the polar component of the surface energy and therefore to the oxygen concentration at the surface. The roughness and the oxygen content increase simultaneously with time and the combination of these two factors lead to obtain a higher Cos Θ_{app}. Indeed, the texturization and the grafting of oxygen are correlated by the use of the Wenzel equation thereby allow the understanding of the large decrease of WCA.

This work is supported by the Belgian Federal Government (Interuniversity Attraction Belgian Science Policy IAP research project P7/34 – Physical Chemistry of plasma surface interactions).

11:00am **PS+SE-MoM9 Particle-free Fabrication of Stretchable, Electrically Conductive Features by Atmospheric-Pressure Plasma Reduction of Metal-Ion-Containing Polymer Films***, **Souvik Ghosh**[*], P.X.-L. Feng, C.A. Zorman, R.M. Sankaran,* Case Western Reserve University

Stretchable electrically conductive patterns are an importance class of materials for emerging electronic applications. A relatively well-established approach for their fabrication is printing metal nanoparticle inks on elastomeric polymers to combine the high electrical conductivity of metals with the large mechanical deformability of polymers. However, nanoparticle-based inks have organic-based solvents and contain organic capping molecules to stabilize the nanoparticles, limiting the conductivity of as-printed features and requiring high temperature sintering (>200 °C) to remove the organics, which is not compatible with most polymers. Moreover, the printed metal nanoparticle film may not be well-integrated with the polymer, compromising conductivity at large deformation.

Here, we report a plasma-based approach to producing electrically-conductive metallic features at the surface of polymer films that eliminates the need for nanoparticle inks and has the potential to better integrate metals and polymer. In general, metal salts are initially mixed with a polymer and cast as a thin film. The films are then exposed to a plasma which results in reduction of the metal ions to metal nanoparticles. By using an atmospheric-pressure microplasma jet and rastering the metal-ion-containing polymer film, the reduction is localized and two-dimensional patterns of metal nanoparticles are fabricated.

We initially focused our study on films prepared from silver nitrate ($AgNO_3$) and polyacrylic acid (PAA) which is known to cross-link with metal cations. After exposure to the microplasma, films were characterized by X-ray diffraction (XRD) which confirmed crystallinity from the presence of peaks corresponding to face-centered cubic silver (Ag). Further materials analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) revealed that microplasma reduction leads to nanoparticle formation only at the surface of the film. The bulk resistivity of the patterned features was determined by two-point probe measurements and reached values as small as ~1 mΩ-cm.

To obtain stretchable films, two approaches were explored. First, PAA-Ag thin films were cast on top of polydimethylsiloxane (PDMS) - an elastomer, and reduced by the microplasma. Second, we extended our process to a rubber polymer (styrene-isoprene-styrene) (SIS) which could be mixed with silver trifluoroacetate to be reduced and form Ag in a single polymer layer. Results for the resistivity as a function of the strain in the various material systems will be presented, as well as a working model for the role of the plasma in the reduction of the metal in the polymer and its final morphology.

11:20am **PS+SE-MoM10 Plasma Polymerised 4-vinyl Pyridine Films with High Charge Density Synthesised in Atmospheric Roll-to-Roll System***, **Hindrik de Vries,*** FOM institute DIFFER, Netherlands*; W. van Baak, S.A. Starostin,* FUJIFILM Manufacturing Europe B.V., Netherlands*; M.C.M. van de Sanden,* FOM institute DIFFER, Netherlands

Nowadays plasma polymerisation is considered as an attractive tool to synthesise ultra-thin organic functional coatings. In this contribution we report for the first time the synthesis of PP thin 4-vinylpyridine containing films synthesised in a roll-to-roll set-up in an atmospheric pressure plasma enhance chemical vapour deposition (AP-PECVD) reactor using low cost nitrogen gas. The general details of the reactor and plasma parameters were described elsewhere [1]. Specific of the present work is the use of a variable short pulse trains. Nitrogen was used as a carrier gas admixed with a variable flow of argon to control the vaporisation rate of 2 monomers: 4-vinylpyridine (4-VP) and divinylbenzene (DVB) to enable copolymerisation reaction. The film properties were tuned by varying the power per injected precursor molecule and the mixing ratio of the 2 monomers. The films were characterized on thickness (spectroscopic ellipsometry), adhesion (tape test), roughness (interferometric microscopy), and wettability (water contact angle). The microstructure of the 4-VP films was assessed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) and X-ray Photoelectron Spectroscopy (XPS). The fixed charge was characterised by zeta potential measurements. Film analysis showed that the main feature (pyridine group) was preserved although newly formed peaks in the ATR-FTIR spectrum indicate partial dissociation of the 4-VP. Pulse parameters as well as the DVB [2] flow were studied to improve cross-linking of the film. Zeta potential measurements confirmed the presence of positive charge at the surface. Subsequently, the films were quaternized

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[*] **Coburn & Winters Student Award Finalist**

leading to a further enhancement of the fixed charge on the surface. Recent results will be highlighted and recommendations for further improvement of the atmospheric plasma processing will be discussed.

[1] S.A. Starostin et al. *Plasma Process. and Polym.* 12, no. 6 (2015): 545–54.

[2] R. Yang et al. *Advanced Materials* 26, no. 11 (2014): 1711–18.

11:40am **PS+SE-MoM11 Plasma-Surface Interactions in Atmospheric Pressure Plasmas: *In Situ* Measurements of Local Excitations in Thin Films***,* ***Scott Walton****,* Naval Research Laboratory*; B.M. Foley,* University of Virginia*; D.R. Boris, E.D. Gillman, S.C. Hernández,* Naval Research Laboratory*; A. Giri,* University of Virginia*; Tz.B. Petrova, G.M. Petrov,* Naval Research Laboratory*; P.E. Hopkins,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest as they contribute to the physicochemical changes associated plasma-based materials processing. The unique feature of plasmas compared to other methods of materials synthesis and processing is that the energy flux is delivered and absorbed at or very near the surface over short time scales, and thus requires fast, surface-sensitive techniques to fully appreciate the dynamics of the plasma-surface interface. To achieve this, we employ pump-probe Time-Domain Thermoreflectance (TDTR) to measure the electron and phonon excitation and energy transport dynamics in thin metal films during exposure to an atmospheric pressure plasma jet. The results show the energy delivered by the plasma jet causes a localized thermal spike that is dissipated radially from the point of contact. More specifically, energy delivered via the flux of particles and photons causes the kinetic energy of the electrons within the material to increase over an area commensurate with the plasma jet radius. That energy is then dissipated through electron-electron collisions and electron-phonon interactions as the excited electrons propagate radially from the point of contact. These results, in conjunction with plasma characterization, will be discussed in an effort to develop a first order understanding of energy transfer and relevant kinetics during plasma jet–surface interactions. This work is partially supported by the Naval Research Laboratory base program.

Thin Film
Room 102B - Session TF+PS+SE-MoA
Plasma-based Deposition Techniques and Film Characterization

Moderators: Jim Fitz-Gerald, University of Virginia, Tansel Karabacak, University of Arkansas at Little Rock

1:40pm **TF+PS+SE-MoA1 Microcrystalline Silicon Thin Film Deposited by Tailored Voltage Waveform Plasmas using an $SiF_4/H_2/Ar$ Chemistry and its Application to Photovoltaics***, **Junkang Wang**,* LPICM, CNRS, École Polytechnique, Université Paris Saclay, France*; M. Elyaakoubi,* TFSC-Instrument, Palaiseau, France*; E.V. Johnson,* LPICM, CNRS, École Polytechnique, Université Paris Saclay, France

For the growth of hydrogenated microcrystalline silicon (µc-Si:H) thin film by low temperature plasma-enhanced chemical vapor deposition (PECVD), silicon tetrafluoride (SiF_4) has recently attracted interest as a precursor due to the resilient optoelectronic performance of the resulting material and solar cell device. However, many questions remain concerning the critical factors determining the quality of the PECVD-deposited film.

Tailored voltage waveforms (TVWs), non-sinusoidal voltage waveforms used to excite radio-frequency capacitively coupled plasma (RF-CCP) processes, has recently been shown to be effective to separately control the maximum ion bombardment energy (IBE) and the ion flux on each electrode. Due to this unique feature, TVWs have attracted considerable research interest in a very short time. When applied to the growth of µc-Si:H film by PECVD, it can provide an elegant approach for one to gain more insight into the physical principles governing film growth and the optimization of process parameters.

To advance knowledge on this subject, we present studies looking at the deposition of µc-Si:H film from SiF_4 using TVWs, particularly focusing on the material's optoelectronic properties and its resulting PIN solar cell device. We underline recently obtained results concerning critical experimental findings: (1) the significant impact of the maximum IBE to the crystalline grains sizes of the deposited films, (2) the considerable different in films' properties resulting from two types of "sawtooth" waveforms, i.e. "sawtooth-up" and "sawtooth-down", which give similar films deposition rates and the maximum IBE but opposite plasma sheath dynamics during processing. The films generated in these studies have furthermore been characterized using the steady-state photoconductivity and steady-state photocarrier grating techniques, analyzing the coplanar electronic transport properties of the material. The modulated photoconductivity method is also utilized to reveal more specific details about the materials' sub-gap density of states. These studies - along with residual gas analysis studies and Fourier transform infrared absorption results - allow us to optimize the appropriate process parameters of such film and its resulting PIN solar cell device using SiF_4 as the precursor.

2:00pm **TF+PS+SE-MoA2 Boron Carbide-Aromatic Composite Films by PECVD: A Novel Approach to Electron-hole Separation***, B. Dong, A. Oyelade,* University of North Texas*; E.M. Echeverria,* University of Nebraska-Lincoln*; Y-S. Jun, G.D. Stucky,* University of California at Santa Barbara*; P.A. Dowben,* University of Nebraska-Lincoln*; **Jeffry Kelber**,* University of North Texas

Many photovoltaic and photocatalytic systems employ band-bending at surfaces or interfaces to achieve electron-hole separation and functionality. Boron carbide-aromatic composites, formed by plasma-enhanced co-deposition of carboranes and aromatic precursors, present an alternative approach where such separation is achieved by aromatic coordination to the carborane icosahedra. Photoemission, density functional theory calculations, and variable angle spectroscopic ellipsometry demonstrate that for orthocarborane/pyridine and orthocarborane/aniline films, with controlled aromatic/orthocarborane ratios between 1:1 and 10: 1, states near the valence band maximum are aromatic in character, while states near the conduction band minimum include those of either carborane or aromatic character. Thus, excitation across the band gap results in electrons and holes on carboranes and aromatics, respectively. Further such aromatic-carborane interaction dramatically shrinks the indirect band gap from 3 eV (PECVD orthocarborane) to ~ 1.6 eV (PECVD orthocarborane/pyridine) to ~1.0 eV (PECVD orthocarborane/aniline), with little variation in such properties with aromatic/orthocarborane stoichiometry. Recent photoabsorbance measurements show that in orthocarborane/pyridine films, the indirect band gap energy is significantly less than the exciton formation energy of 2.1 eV, allowing facile exciton elimination by phonon scattering of electrons into the conduction band at room temperature. The opposite is true for the PECVD orthocarborane film, where the exciton formation energy (2.4 eV) is less than the indirect band gap, inhibiting exciton elimination by electron-hole separation. The enhanced electron-hole separation, narrowed band gap, and significantly increased carrier lifetimes (350 µsec for PECVD orthocarborane/pyridine vs 35 µsec for PECVD orthocarborane), indicate the potential for greatly enhanced charge generation, as confirmed by zero-bias neutron voltaic studies. Those results--an 850% increase in charge generation per B atom for the PECVD pyridine/orthocarborane film relative to the PECVD orthocarborane film--indicate that the enhanced electron-hole separation and band gap narrowing observed for aromatic/orthocarborane films relative to PECVD orthocarborane, have significant potential for a range of applications, including neutron detection, photovoltaics, and photocatalysis.

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2:20pm **TF+PS+SE-MoA3 Impact of Pulsing the rf Power and the Precursor Injection on the Structure and Optical Properties of TiO_2 and TiSiO Thin Films Deposited by PECVD***, **Agnes Granier**, S. Elisabeth, R. Michaud, N. Gautier, M. Richard Plouet,* IMN, University of Nantes CNRS, France*; M. Carette,* IEMN CNRS/Université Lille 1, France*; A. Goullet,* IMN, University of Nantes CNRS, France

TiO_2 thin films are good candidates for the development of passive optical components due to high optical refractive index (1.8 < n < 2.7 at 633 nm) combined with high transparency in the visible range. They are compatible with semiconductor technologies and can be synthesized at low temperature by plasma enhanced chemical vapor deposition (PECVD). PECVD is known for its ability to prepare amorphous or partially crystallized films at low temperature and to tune the film composition and optical properties. In the case of TiO_2, columnar polycrystalline anatase films can be prepared by PECVD at substrate temperature less than 150°C. Whereas these TiO2 films are very attractive for photocatalysis, their columnar structure and low optical gap (3.2 eV) appear to be drawbacks for optical applications. Adding a small amount of silicon to TiO_2 allows both obtaining amorphous films and increasing the optical gap, which is highly suitable for optical applications.

In this study, TiO_2 and Ti-Si-O films were deposited in a low pressure rf inductively coupled plasma (ICP) from titanium tetraisopropoxide (TTIP - $Ti(OC_3H_7)_4$) and hexamethyldisiloxane (HMDSO - $SiO_2(CH_3)_6$) vapors mixed with oxygen. The structure and chemical composition of the films were investigated by X-ray diffraction, photoelectron spectroscopy, Fourier transform infrared spectroscopy and Raman spectroscopy. The morphology of the thin films was characterized by scanning and transmission electron microscopies. The optical properties were investigated by UV -Visible spectroscopic ellipsometry and absorption spectroscopy. When deposited at the floating potential, the TiO_2 films deposited in the continuous mode in oxygen rich O_2/TTIP ICP plasmas were previously shown to be columnar and highly crystallized in the anatase form. As silicon is added to titanium, the films become amorphous. Their refractive index decreases and their optical gap increases [1].

Here, we investigate the effects of pulsing both the rf power and the precursor injection on the film structure and optical properties.

On the one hand, in the case of TiO_2 and Ti-O-Si films, the pulse frequency was fixed at 1 kHz and the duty cycle was varied from 100 to 10%. Pulsing the power allows to decrease the deposition temperature (down to about 50°C) while conserving the anatase structure in the case of TiO_2 films, so that anatase and amorphous high refractive index Ti-Si-O films can be deposited on polymer substrates.

On the other hand, TTIP and HMDSO flow rates have been pulsed, either to get benefit from oxygen plasma treatment following oxide deposition or to deposit TiO_2/SiO_2 stacks.

[1] D. Li et al, Plasma Processes and Polymers, 2016

2:40pm **TF+PS+SE-MoA4 Plasma CVD of Boron-Carbon Thin Films from Organoboron Precursors for Next Generation Neutron Detectors*, **Mewlude(Maiwulidan) Imam (Yimamu)**,* Linköping University, Sweden*; C. Höglund,* Linköping University and European Spallation Source ERIC, Sweden*; R. Hall-Wilton,* European Spallation Source ERIC, Sweden*; J. Jensen,* Linköping University, Sweden*; S. Schmidt,* Linköping University and European Spallation Source ERIC, Sweden*; I.G. Ivanov, J. Birch, H. Pedersen,* Linköping University, Sweden

A novel design for neutron detectors based on thin films that are rich in the ^{10}B isotope has been suggested for the European Spallation Source (ESS), in order to overcome the very limited availability of ^{3}He. The detector design uses $^{10}B_4C$ films deposited onto both sides of neutron transparent substrates, e.g., Al blades [1]. The use of aluminum (melting point at 660 °C) limits the deposition temperature for CVD processes and the use of chlorinated precursors due to etching of Al by HCl. Therefore, reactive organoborons are evaluated as precursors for these films using both thermal CVD [2, 3] and plasma CVD.

Plasma CVD of B_xC thin films has been studied by introducing the organoborons trimethylboron $B(CH_3)_3$ (TMB) or triethylboron $B(C_2H_5)_3$ (TEB) into a microwave-induced Ar plasma without using any intentional substrate heating. The effect of plasma power, TMB or TEB to Ar ratio and total pressure on the film composition, morphology, density, chemical structure and internal stress were investigated by means of Tof-ERDA, SEM, XRR, XPS and HRXRD, respectively. Tof-ERDA results showed that the highest B/C ratio of 2 was achieved when using TMB at high plasma power. Densification of the films was accompanied by decreasing the total pressure below 0.4 mbar, resulting in a columnar film with densities of 2.16 ± 0.01 g/cm^3. The H content in the films was high (15±5 at. %) due to the low substrate temperature (~300 °C). XPS revealed that films deposited using TMB mainly contained B-C bonds and small contribution from C-C/CH bonds, that was evidenced by the observed amorphous carbon phases in the films by Raman spectroscopy. The internal compressive stresses in the films were increased with the Ar gas flow causing film delamination, while a low flow of Ar showed good adhesion and stress level is less than 300 MPa. In addition, the plasma composition studied by optical emission spectroscopy (OES) showed that BH, CH, C_2 and H lines were the most intensive lines in the spectrum. Considering the high H content in the films, we propose that BH and CH are the most likely species to contribute to the film formation.

[1] R. Hall-Wilton et al. *IEEE NSS/MIC conference record*, **2012**, 4283

[2] H. Pedersen et al. *Chem. Vap. Deposition***2012**, *18*, 221

[3] M. Imam et al. *J. Mater. Chem. C***2015**, *3*, 10898

3:00pm **TF+PS+SE-MoA5 Plasma Enhanced Atomic Layer Deposition of Superconducting Nb_xTi_yN Films*, **Mark Sowa**,* Ultratech/CNT*; Y. Yemane, J. Provine,* Stanford University*; E.W. Deguns,* Ultratech/CNT*; F. Prinz,* Stanford University

NbN, TiN, and their mixtures have been studied for their use in superconducting applications. These materials are commonly deposited via sputtering techniques, but a lack of thickness control limits this technique from applying thin, uniform films. Atomic Layer Deposition (ALD) has been widely recognized for its ability to coat substrates with uniform film thicknesses ranging from a few Ångstroms to 100's of nanometers. Plasma Enhanced ALD (PEALD) extends the capabilities of the ALD technique, improving the properties of certain films, particularly nitrides deposited at low temperatures. PEALD of NbTiN has previously demonstrated superconducting properties[1] and PEALD NbN has been previously reported with a critical temperature of 10.4K [2].

In this work, Nb_xTi_yN ($0 \le x, y \le 1$) has been deposited using PEALD in an Ultratech/CNT Fiji system at substrate temperatures between 100 and 300°C. Stoichiometry was controlled by adjusting the ratio of NbN:TiN cycles during the film deposition. Precursors utilized for this study were (t-butylimido) tris(diethylamido) niobium (TBTDEN) and tetrakis(dimethylamido) titanium (TDMAT). A mixture of N_2 and H_2 was used as the plasma gas for the NbN cycles while TiN was deposited with an N_2 plasma. Films were analyzed for thickness and optical properties through spectroscopic ellipsometry. Room temperature resistivity was derived from four point probe measurements. Samples were analyzed with X-ray photoelectron spectroscopy to determine stoichiometry and impurity levels. Superconductivity characteristics of the films will also be presented.

A 20nm, 300°C deposition of NbN, which had a room temperature resistivity of 282μΩ-cm, was shown to have a critical temperature of 12.4K and a critical field greater than 12 Tesla.

[1] E. F. C. Driessen, et al., "Strongly Disordered TiN and NbTiN s-Wave Superconductors Probed by Microwave Electrodynamics," Phys. Rev. Lett. 109, 107003, 2012.

[2] M. Ziegler, et al., "Superconducting niobium nitride thin films deposited by metal organic plasma-enhanced atomic layer deposition," Supercond. Sci. Technol. 26 (2013) 025008.

3:20pm **TF+PS+SE-MoA6 Mechanical Reliability of PECVD Barrier Films for Flexible Electronics*, **Kyungjin Kim**, A. Singh, H. Luo, T. Zhu, O. Pierron, S. Graham,* Georgia Institute of Technology

The development of PECVD and ALD barrier films have proven to be viable approaches to create barrier films for flexible electronic applications. While much research has focused on the water vapor transport properties of these films, the mechanical reliability during flexural deformation is critical to the performance and durability of these coatings. Overall, the use of the critical onset strain is limiting in trying to define the limits of performance since it ignores time-dependent processes that can occur during mechanical deformation. In this work, we investigate the time-dependent channel crack growth behavior of silicon nitride and ALD barrier films on polyethylene substrates in humid and dry air. The evaluation of the cracking process versus applied strain and load was measuring in-situ using optical and laser scanning confocal microscopy. The results show that crack growth can occur at strains that are much lower than the standard measured onset critical strains. The results of the work show that both polymer relaxation of the PET substrate as well as environmentally assisted crack growth occurs in the films, both in a time dependent manner. Tests in dry air versus tests in humid air show crack growth rates increasing from 100 nm/s to 10 um/s for an applied stress intensity factor of 1.6 MPa.m^0.5. In addition to the dramatic changes in crack growth rates with environmental conditions, larger crack densities were observed in humid environments. This suggests an easier initiation and growth of crack in humidity versus dry air. Overall, the results presented will show the strong link between environment, temperature, and the rate at which cracks grow in barrier films. Finally, the energetics of the crack growth process will be presented as a better metric than onset crack strain to evaluate the mechanical reliability of the barriers for a given application.

4:00pm **TF+PS+SE-MoA8 Origin of Stress in Sputtered CdTe and ZnS Films: Influence of Sputter Ion Mass on Mechanical and Chemical Layer Properties*, **Ségolène Liénard**,* Univ. Grenoble Alpes, LTM CNRS, 38000 Grenoble, France*; D. Sam-Giao, A. Kerlain,* Sofradir, BP 21-38113, Veurey-Voroize, France*; F. Boulard, C. Vallée,* Univ. Grenoble Alpes, France

Physical vapor depostion is a mature, well understood and established technology in integrated circuit fabrication. CdTe and ZnS binary II-VI compounds materials are commonly used in photovoltaic solar cells or infrared optics. However, sputtering deposition of these materials still suffer from a lack of comprehensive study to optimize process integration.

Our study is focused on the influence of projectile ions mass on properties of sputtered deposition CdTe and ZnS films. We compare physico-chemical, mechanical and electrical properties of CdTe and ZnS films deposited with Ar and Xe ions as sputter gas. Ar and Xe concentration in these films are characterized by Time of Flight Secondary Ions Mass Spectrometry (TOF-SIMS). Dedicated implanted reference samples are used to quantify the absolute concentration. Layers microstructures are characterized by Scanning Tunneling Electron Microscopy (STEM) and dielectric constant by capacitance-voltage measurements. We use the curvature method based on the well known Stoney concept [1] to calculate film stress while density is estimated by differential weighing.

With Ar ion deposition process (low sputter on target mass ratio), we observe Ar and cavities inside the CdTe layer. The density as well as the dielectric constant are below bulk values. A good agreement is found between the cavity density and the effective dielectric constant determined by the Bruggeman model [2-3]. on the contrary, Xe ion target sputtering (high sputter on target mass ratio) leads to denser films, without Xe inside the layers, and close to theory density and dielectric constant values. We discuss these observations in terms of backscattered ions incorporation. Moreover, the effect of thermal annealing time on stress evolution is discussed in regards of Ar or Xe incorporation and outgasing.

[1] G.G. Stoney, Proc. Soc. London, A82, 1909, 172

[2] Aspnes D. E., Thin Solid Films 89 (1982) 249.

[3] Othman M.T., PhD "Spectroscopic Ellipsometry Analysis of Nanoporous Low Dielectric Constant films Processed via Supercritical CO2 for Next-generation Microelectronic Devices"., University of Missouri-Columbia, 2007

4:20pm **TF+PS+SE-MoA9 Synthesis and Characterisation of MoB_{2-x} and Mo-B-C Thin Films by Non-Reactive DC Magnetron Sputtering***, **Paulius Malinovskis**,* Uppsala University, Sweden*; J.P. Palisaitis,* Linkoping University, Sweden*; P.O.A. Persson,* Linköping University, Sweden*; E.L. Lewin, U.J. Jansson,* Uppsala University, Sweden

Transition metal diborides (MeB_2) with the AlB_2-type structure have many unique properties such as high hardness, high conductivity and oxidation resistance One of the most studied diboride compounds is TiB_2 but also other transition metals like Cr, Nb and Mo can form the simple AlB_2 type structure.

Non-reactive magnetron sputtering is an excellent technique to deposit thin films of different MeB_2 phases. It is well-known that phases with rather simple crystal structures are preferably formed in magnetron sputtering where the quenching rates of the incoming atoms are high. Such metastable MeB_2 films may be chemically more reactive in a tribocontact and form a lubricating tribofilm of metal oxides and layered BO_x. Some metal oxides such as MoO_3 and boric acid (forming in humid atmosphere from BO_x) have been predicted to exhibit low friction coefficients. Consequently, it is possible that metastable MeB_2 films with the AlB_2-structure may exhibit excellent low friction properties. Another way to tailor metal diboride properties is to alloy it with third element, e.g. carbon.

In this study we have investigated the microstructure, mechanical and tribological properties of DC magnetron sputtered MoB_{2-x} and Mo-B-C thin films from Mo/B and graphite carbon target. The films were characterized with XRD, XPS, TEM, nanoindentation and tribological ball-on-disk method. All films exhibited the AlB_2-type structure with substoichiometric MeB_{2-x} grains surrounded by a tissue phase of a-B and a-BC_x. The MoB_{2-x} films were substoichiometric with respect to boron and exhibited a much higher hardness compared to bulk samples, which could be attributed to a hardening effect of the tissue phase. Friction measurements confirmed the hypothesis that a significant tribofilm formation is present on the metastable MoB_{2-x} films. However, a reduced friction coefficient could not be observed. Addition of carbon resulted in a change in the composition of the tissue phase. This caused a reduction in hardness and a reduction of the friction coefficient. General trends in the phase formation and properties of Mo-B-C films will be explained in detail and compared with other Me-B-C systems (Me= Ti, Cr, Nb).

4:40pm **TF+PS+SE-MoA10 Molybdenum Back Contacts Deposited by High Power Impulse Magnetron Sputtering***, D.A. Loch, **Arutiun Ehiasarian**,* Sheffield Hallam University, UK

Molybdenum thin films used in chalcopyrite solar cells can influence the Na diffusion rates and the texture of the $Cu(InGa)Se_2$ absorber according to the microstructure and morphology. The lowest resistivity films are achieved at low working pressure and are accompanied by high residual stress and poor adhesion due to the resulting high energy of the deposited flux. High Power Impulse Magnetron Sputtering was employed to ionise the sputtered flux, achieve high adatom mobility at low energy and influence the growth of Mo back contacts. Pulse durations in the range 60 to 1000 µs, sputtering voltages between 800 and 1500 V and deposition pressures of 2×10^{-3} mbar and 4×10^{-3} mbar resulted in ten-fold variations in the flux ratios of Mo^{1+}/Mo^{0} Mo^{2+}/Mo^{1+}, Ar^{2+}/Ar^{1+} and Mo^{1+}/Ar^{1+} as determined by optical emission spectroscopy and time-resolved plasma-sampling energy-resolved mass spectroscopy. The energy of metal and gas double and single-charged ions reduced with pulse duration and increased with voltage. The microstructure of the films varied from open columnar with faceted tops to fully dense as observed by secondary electron microscopy. The reflectivity of the films improved by 20% compared to industry-standard materials. The lowest resistivity was in the range of 12 µΩ-cm as observed by four-point probe measurements of 570 nm thick films. The correlation between resistivity, microstructure, crystallographic texture, stress and deposition flux characteristics is discussed.

5:00pm **TF+PS+SE-MoA11 Plasma Characterization of Al and Cu with HIPIMS***, **Jason Hrebik**,* Kurt J. Lesker Company*; R. Bandorf, H. Gerdes, D. Spreemann,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

High power impulse magnetron sputtering (HIPIMS) is a well-known technique for tailoring the coating properties in comparison to DC. In many cases the thin films were developed in smaller scale R&D facilities and afterwards transferred to industrial scaled machines. But the source configuration, magnetic field, and overall mechanical layout differs for the larger sputtering plant, and therefore a direct upscaling of the process is quite difficult. Since often the thin film properties are correlating with the plasma properties, plasma characterization is very useful tool for determining the main important parameters for a process transfer.

This investigation is focused on the plasma characterization of Al and Cu on a small circular target (3 inch) and will give a short comparison to a rectangular target (10 inch by 15 inch). As plasma properties the ion density and the optical emission was measured. The measurements were carried out in a time resoled mode and can be correlated to target voltage and current.

Advanced Surface Engineering
Room 101C - Session SE+NS+TF+TR-TuM

Nanostructured Thin Films and Coatings

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Robert Franz, Montanuniversität Leoben, Austria

8:00am **SE+NS+TF+TR-TuM1 Design and Predictive Synthesis of Thin Films and Coatings***, P.A. Salvador, **Gregory Rohrer**,* Carnegie Mellon University **INVITED**

A fundamental challenges in materials synthesis is to obtain a specific targeted composition in a functional crystal structure. For example, the synthesis of hexagonal BN is relatively easy, but synthesizing thick films of cubic BN is more difficult. In other words, we cannot currently predict exact synthesis conditions of many targeted polymorphs, and so their formation is often left to lengthy "design-of-experiments" (DOE) methodologies or, more commonly, basic trial-and-error practices. It is essential to improve the output of computational and physical experimental practices to move closer to predictive synthesis and design of coatings.

This talk will describe some recent results of a methodology called combinatorial substrate epitaxy (CSE), which we have used to understand the preferred epitaxial orientations (PEOs) of a wide range of heteroepitaxial structures and to fabricate various novel metastable materials. In this approach, the target compound is deposited on polished polycrystalline substrates, rather than commercial single crystals or buffer layers. The primary hypotheses underpinning CSE is that the each grain surface in the polycrystalline substrate can be treated as the equivalent of a single-crystal surface in a traditional DOE experiment, therefore providing every combination of substrate orientation in a single experiment. The local structure is probed in a scanning electron microscope using electron backscatter diffraction and automated orientation assignments. The method not only allows for hundreds of experiments to be carried out in a single growth run, it has the unique advantage of not being restricted to the use of commercially available single crystals.

This talk will focus on three important observations. First, when a film is grown on a polycrystal, the growth occurs by grain-over-grain epitaxy. In other words, films can grow on microcrystalline substrates in the same way they grow on millimeter scale substrates, or every grain is in an independent observation of growth. Second, there are PEOs, regardless of the substrate surface plane, and these can be easily predicted. For many of the cases we have observed, the PEO is the one that aligns the closest packed planes and directions in the eutactic (nearly close packed) arrangement of oxide ions in different structures. Third, we have already fabricated new and novel metastable coatings using this methodology, where novel substrates provide the epitaxial template to control phase formation. Observations relative to functional ceramics, including examples from the BO_2, B_2O_3, ABO_3, A_2BO_4, and $A_2B_2O_7$ families, will be described.

8:40am **SE+NS+TF+TR-TuM3 Nanoscale Atomic Arrangement in Multicomponent Thin Films Synthesized Far-from-Equilibrium***, V. Elofsson, G.A. Almyras, B. Lü, R.D. Boyd, **Kostas Sarakinos**,* Linköping University, Sweden

Synthesis of multicomponent thin films using vapor fluxes with a modulated deposition pattern is a potential route for accessing a wide gamut of atomic arrangements and morphologies for property tuning. In the current study, we present a research concept that allows for understanding the combined effect of flux modulation, kinetics and thermodynamics on the growth of multinary thin films. This concept entails the combined use of thin film synthesis by means of multiatomic vapor fluxes modulated with sub-monolayer resolution [1], deterministic growth simulations and nanoscale microstructure probes. Using this research concept we study structure formation within the archetype immiscible Ag-Cu binary system showing that atomic arrangement and morphology at different length scales is governed by diffusion of near-surface Ag atoms to encapsulate 3D Cu islands growing on 2D Ag layers [2]. Moreover, we explore the relevance of the mechanism outlined above for morphology evolution and structure formation within the miscible Ag-Au binary system. The knowledge generated and the methodology presented herein provides the scientific foundation for tailoring atomic arrangement and physical properties in a wide range of miscible and immiscible multinary systems.

[1] "*A METHOD OF CONTROLLING IN-PLANE COMPOSITIONAL MODULATION*", Patent Pending Application, PCT/EP2014/052831.

[2] V. Elofsson, G.A. Almyras, B. Lü, R.D. Boyd, and K. Sarakinos, "*Atomic arrangement in immiscible Ag-Cu alloys synthesized far-from-equilibrium*", Acta Mater. 110, 114 (2016).

9:00am **SE+NS+TF+TR-TuM4 Is *Intrinsic* Nanocrystalline Stability Practically Achievable? Insights from Investigations with Pt-Au Alloys***, **Nicolas Argibay**, T.A. Furnish, D.P. Adams, P. Lu, M. Chandross, M.A. Rodriguez, B.L. Boyce, B.L. Clark, M.T. Dugger,* Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been proposed recently, supported by some notable demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of stress on this stability. In this presentation we present results of an investigation on the stress and temperature dependent nanocrystalline stability of a noble-metal alloy (Pt-Au) in the form of sputter co-deposited thin films. In situ XRD and TEM annealing revealed an extraordinary degree of thermal stability, confirming literature predictions. Tribological experiments and molecular dynamics simulations were used to further explore the impact of stress as a destabilizing factor.

9:20am **SE+NS+TF+TR-TuM5 Improved Mechanical Properties In Tungsten-Molybdenum Nanostructured Thin Films***, **Gustavo Martinez**, C.V. Ramana,* University of Texas at El Paso

Preventing materials failure and improving the performance of materials in nuclear reactors demand novel materials to serve under extreme environment conditions. For nuclear applications, tungsten (W) has been alloyed in the past with La and Re to improve its performance and properties including low fracture and high ductile to brittle transition. In this work, molybdenum (Mo) solute atoms were added to W matrix with the intention of creating interstitial point defects in the crystals that impede dislocation motion, increasing the hardness and young modulus of the material. Nanostructured W-Mo thin films with variable Mo content were deposited by the sputter-deposition. W-Mo films were stabilized in bcc structure of W. Studies showed that as grain size formation increases the residual stress distribution will reach the maximum and stabilize after a deposition temperature of 350 °C. The residual stress still continues to follow a parabolic pattern, indicating that the stresses mainly depend on grain organization rather than atomic packing. From Nano-scratch testing, it is found that depth penetration decreases with increasing sputtering temperature. The effect of Mo on the overall mechanical properties improvement in W-Mo nanostructured thin films will be presented and discussed.

Keywords: Tungsten-Molybdenum Thin Films, Mechanical Properties, Nano-Indentation

9:40am **SE+NS+TF+TR-TuM6 Hierarchical Monolith Scaffolds for Silicon Lithium Ion Battery Electrodes***, **Kevin Laughlin**,* Brigham Young University

Research has shown stable high gravimetric capacity lithium ion battery anodes can be made from silicon deposited on carbon nanotubes (CNTs). High stability operation however requires nanostructuring of the silicon to alleviate stresses caused by the large expansion of the silicon upon Li alloying. At high silicon loadings even nanoscale layers of silicon result in stresses large enough to cause mechanical damage to the electrode. Here we present work on a hierarchical approach to structuring carbon nanotube based carbon monoliths that provide for electrode stress management on multiple scales.

11:00am **SE+NS+TF+TR-TuM10 Technological Developments in Coatings for Components and Cutting Tools***, **Roel Tietema**,* IHI Hauzer Techno Coating B.V., Netherlands*; D. Doerwald,* Hauzer, Netherlands*; R. Jacobs, G. Negrea, I. Kolev, J. Zhu, J. Landsbergen,* Hauzer **INVITED**

Nanostructured and amorphous coatings play an important role in today's industrial applications. This is the case both in applications for cutting tools, as well as in applications for components.

In cutting tools nanostructured coatings with high hardness, including hot hardness, and ductility have been extremely helpful to increase the productivity of the machining process. On one hand superlattice multilayers have shown here great benefits and on the other hand nanocrystallites in the material have been created to give the coating materials an inherent high hardness and ductility.

In automotive coatings these material properties were leading to technological breakthroughs as well. First coatings on the market were nanostructured WC-C:H sputtered coatings, developed by Prof. Dimiggen of Fraunhofer IST. These developments were soon followed by hybrid a-C:H coatings, combining the WC-C:H developments with a multilayered structure to achieve a gradual adaptation of the Young's modulus of the relatively soft steel as base material to the very hard a-C:H-DLC top layer. In this way it has been possible to produce coatings with a very high ductility, despite the high hardness. Hardness values as applied today on components are ranging from 2000-2500 HV for a-C:H coatings up to 4000-7000 HV for ta-C coatings.

The importance of petreatment and post treatment steps for cutting tools and components, being as important as the actual coating step, will be addressed in this talk.

The main focus in this talk will be on the equipment aspects. Several technologies for cutting tools and for components will be presented. The equipment design and even the selection of most suitable process technology is however also strongly determined by the productivity. Besides technological properties of the coating there is a focus on the cost reduction of the coating per coated part. Cost reduction is main driver in many fields, especially in the field of components. Reduction of the cost of ownership leads to a tendency to use fast processes in large systems, respectively application of in-line systems.

11:40am **SE+NS+TF+TR-TuM12 Influence of Transition Metal Dopants on Target Poisoning and Oxidation Mechanisms of Reactively Sputtered γ-Al_2O_3 Thin Films***, **Helmut Riedl,** B. Kohlhauser,* TU Wien, Institute of Materials Science and Technology, Austria*; V. Paneta,* Uppsala University, Sweden*; C.M. Koller,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The outstanding oxidation resistance, thermo-mechanical stability and chemical inertness of Al_2O_3 attracts particular attention in various industrial applications. Especially, in the field of protective barrier coatings there are many research activities focusing on the synthesis of the different polymorphs α- and γ-Al_2O_3 (corundum and cubic), respectively. Apart from the fact that the deposition of the thermodynamically stable α-Al_2O_3 is strongly limited by the depositing temperature, the formation of electrically isolating Al_2O_3 at the target surface leads to massive arcing processes and destabilizes the deposition process. These problems could be overcome by varying the powering method to pulsed DC and especially RF sputtering, but at the cost of decreased deposition rates and plasma densities.

Therefore, we study in detail the influence of small amounts of transition metals such as M = Cr, Nb, Mo, and W on the process stability and coating properties of reactive DC sputter deposited $(Al_{1-x}M_x)_2O_3$ thin films. To keep the influence of the alloying elements on the outstanding properties of alumina as low as possible only targets with alloying contents of x = 2 and 5 at.% are investigated. All micro-alloyed targets allow for significantly improved process stability and massively reduced arcing processes at the target as compared to the non-alloyed Al target. The morphology of all coatings deposited is highly dense, smooth and partly columnar with cubic γ-Al_2O_3 crystalline structure. The mechanical properties of the Cr, Mo, and W containing coatings are slightly enhanced by solid solution hardening in comparison to pure Al_2O_3 obtaining e.g. hardness values of about 25 GPa. In contrast, alloying contents of about 1 at.% Nb are already degrading the mechanical properties of alumina thin films. The significantly enhanced process stability when using Cr, Mo, and W alloyed Al targets, leads to coatings with improved thin film quality. Therefore, the oxidation resistance of these films even outperform the Al_2O_3 DC sputtered film.

Advanced Surface Engineering
Room 101C - Session SE+MS+TF-TuA

Innovations in PVD, CVD, Atmospheric Pressure Plasma and Other Surface Technologies

Moderators: Michael Stueber, Karlsruhe Institute of Technology, Germany, Robert Franz, Montanuniversität Leoben, Austria

2:20pm **SE+MS+TF-TuA1 Investigation of Critical Processing Parameters on Laser Surface Processing of Mg-Al-Zn Alloys: Impact on Corrosion Kinetics***, **Michael Melia**, D.C. Florian, J.R. Scully, J.M. Fitz-Gerald,* University of Virginia

Magnesium (Mg) and its alloys have been the topic of intense research over the past 15 years as the automotive and aeronautic industries strive to increase fuel efficiency by reducing the weight of vehicles. However their wide spread implementation is currently limited by poor intrinsic corrosion resistance. Preferential dissolution of the Mg matrix occurs due to the electrochemically noble secondary phases formed during traditional processing routes of Mg alloys. To mitigate the impact secondary phases (e.g. γ-Al_8Mn_5) have on corrosion, pulsed laser surface processing was employed in the ns time regime. Lasers operating in this time regime are capable of melting and solidification rates on the order of 10^9 K/s with the ability to extend the solid solubility limit of the alloying elements. The research herein shows the impact laser processing parameters have on the dissolution of the secondary phases and corrosion resistance in the Mg-Al-Zn alloy, AZ31B.

A KrF excimer laser (λ = 248 nm, pulse duration = 25 ns FWHM) was utilized with a cylindrical focusing lens, a laser spot size of 27 mm x 1.2 mm, and a pulse overlap of 95%. The processing parameters investigated include the laser fluence (0.7, 0.8 and 1.5 J/cm^2), irradiation dosage (pulse per area (PPA) = 20 to 400), and processing pressure (1 to 1280 Torr Ar). The dissolution of the γ-Al_8Mn_5 particles was observed by scanning electron microscopy equipped with a backscatter electron detector. Fiduciary image recognition was utilized to observe the change in γ-Al_8Mn_5 particle size before and after processing. Analysis of the H_2 evolution reaction rate, related to the quantity and density of electrochemically noble secondary phases, was performed by potentiodynamic polarization measurements in 0.6 M NaCl solution.

Results from the fluence study revealed significant dissolution of the γ-Al_8Mn_5 particles when processing was performed above the ablation threshold suggesting that material transport was afforded by a laser induced plasma pressure acting on the irradiated layer, increasing the extent of dissolution. This was also observed by an order of magnitude reduction in H_2 evolution reaction rate. The lowest pressure of Ar investigated, 1 Torr, consistently exhibited the smallest reduction in H_2 evolution reaction rate from the bulk material. All other processing pressures showed an order of magnitude reduction in H_2 evolution reaction rate when a fluence above the ablation threshold was used. The PPA study revealed a plateau in the reduction of the H_2 evolution reaction rate, observed dissolution of γ-Al_8Mn_5 particles, and time to breakdown of the corroding surface after 100 PPA.

2:40pm **SE+MS+TF-TuA2 Engineering a WC/Co Carbide Surface for PVD and CVD coatings***, **Aharon Inspektor**, P.A. Salvador,* Carnegie Mellon University*; D. Banerjee, C. McNerny, M. Rowe, P. Mehrotra,* Kennametal Inc.

The emergence of new coating technologies is driving the development of new cutting tools and improved metal cutting techniques. However, to reach these goals, the coating has to work in concert with the tool substrate material. Hence, building a functional surface that consists of coating and substrate working together, is a key step in the development of new cutting tool. In this paper we will look at the substrate side of the coating - surface interface and discuss how it affects the properties of the subsequent coating. The focus will be on surface engineering of WC/Co carbide surface for Physical Vapor Deposition, PVD, for Chemical Vapor Deposition, CVD, and for CVD diamond coatings. Specifically, Co mobility in the subsurface zone for CVD coatings and surface treatment for PVD coatings. Structure and properties of the resultant surface - coating combination will be presented and discussed.

3:00pm **SE+MS+TF-TuA3 Room-Temperature Ductility in Refractory Transition-Metal Carbides: Potential to Create Ultra-Tough, Flexible Thin Films***, **Suneel Kodambaka**,* University of California at Los Angeles **INVITED**

Transition-metal carbides are high-melting (> 3000 K), extremely hard (10s of GPa), mechanically robust, and chemically resilient compounds capable of operating in extreme environments and are attractive for aerospace and other industries. These hard materials are generally considered to be brittle at low temperatures. Improving their ductility, and hence toughness, is highly desirable but progress thus far has been limited by the lack of a basic understanding of the intrinsic deformation mechanisms in this class of materials. Here, using *in situ* transmission electron microscopy (TEM) coupled with uniaxial compression tests conducted on sub-µm-size pillars, in combination with density functional theory (DFT) calculations, we show that dislocations are mobile at room-temperature and lead to plastic deformation in NaCl-structured group IV and group V transition-metal carbide single crystals, zirconium carbide (ZrC) and tantalum carbide (TaC). We find that the yield strengths of ZrC crystals increase with decreasing size and ZrC(111) is softer than ZrC(100) crystals, an unexpected finding for NaCl-structured compounds. We attribute this anomalous behavior to surprisingly easy dislocation motion and low shear stresses along {001}<1-10> rather than along the commonly assumed {110}<1-10> slip systems. For TaC, in contrast to ZrC, the yield strengths are found to be independent of crystal size and orientation. Our observations suggest that multiple slip systems can be active and operate at room temperature in these hard, refractory ceramics and we expect similar behavior in other transition-metal carbides and nitrides. The insights gained from these studies may help in the development of new material architectures, such as tough and flexible membranes, for new small-scale structural applications.

4:20pm **SE+MS+TF-TuA7 Spray-Coated Carbon-Nanotubes for Crack-Tolerant Metal Matrix Composites as Photovoltaic Gridlines***, **Omar K. Abudayyeh**,* University of New Mexico*; N.D. Gapp, G.K. Bradshaw, D.M. Wilt,* Air Force Research Laboratories*; S.M. Han,* University of New Mexico

Microcracks developing in photovoltaic cells, due to growth defects or due to external mechanical factors, can lead to substantial power loss in solar cells. Microcracks can be critical as they propagate from the semiconductor bulk to the metal gridlines isolating portions of the cell and leading to decreased cell performance. In this work, multiwalled carbon nanotubes are being investigated for reinforcement of metal contacts on photovoltaic solar cells that serve as a secondary conductive network in the presence of cracks. In this effort we have focused on a silver-carbon-nanotube layer-by-layer microstructure. We present the use of a simple, cost-effective, and manufacturable method of depositing carbon nanotubes onto electroplated metal films to create metal matrix composite gridlines for photovoltaic cells. Carbon nanotubes are deposited using a spray coating method to create layer-by-layer microstructure composites. To increase adhesion strength to metal and achieve efficient metal-nanotube stress transfer, carbon nanotubes are chemically functionalized with carboxylic group prior to deposition. Initial strain failure tests show the ability of composite lines to remain electrically connected with fractures up to 28-µm-wide on average, where carbon nanotubes electrically bridge the gap. The metal-carbon-nanotube composites are electrically characterized though current-voltage (*I-V*) sweeps. Our composite lines can carry current densities ranging from 500 to 2500 A/cm^2 in the presence of cracks (5, 10, and 15-µ m-wide). MMC gridlines are successfully integrated on commercial triple-junction solar cells with measured fill factor and efficiency 86% and 26.8% respectively, closely comparing to current triple-junction cells with standard metallization. Dark *I-V* measurements indicate further improvement in the series and shunt resistances of the cells with the optimization of MMC integration process.

4:40pm **SE+MS+TF-TuA8 Atmospheric Pressure Plasma Enhanced CVD of High Quality Silica-Like Bilayer Encapsulation Films***, **Fiona Elam**,* FUJIFILM Manufacturing Europe B.V., Netherlands*; A.S. Meshkova,* DIFFER, Netherlands*; S.A. Starostin, J.B. Bouwstra,* FUJIFILM Manufacturing Europe B.V.*; M.C.M. van de Sanden,* Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands*; H.W. de Vries,* DIFFER, Netherlands

Atmospheric pressure-plasma enhanced chemical vapour deposition (AP-PECVD) is an innovative technology that can be integrated into many existing manufacturing systems to facilitate the mass production of functional films; specifically encapsulation foils. These barrier films are essential to the flexible electronics industry, envisioned to protect devices such as flexible solar cells and organic light emitting diodes against degradation from oxygen and water.

Roll-to-roll AP-PECVD was recently used to produce smooth, 90 nm silica bilayer thin films comprising a 'dense layer' and 'porous layer' that demonstrated exceptionally good encapsulation performance with effective water vapour transmission rates in the region of 6.9×10^{-4} g m^2 day^{-1} (at 40^{o}C, 90% relative humidity). By using the same material in the multilayer film architecture, and by having AP-PECVD as the deposition method, rendered this investigation highly industrially and commercially relevant to the eventual large scale production of flexible encapsulation foils. It was discovered that increasing the input energy per precursor gas molecule during the deposition of the dense layer, resulted in an improved encapsulation performance. However, the individual role performed by each layer in the overall success of the bilayer films is not yet fully understood, nor is the potential for energy conservation by varying process throughput.

A glow-like AP dielectric barrier discharge in a roll-to-roll set-up was used to deposit silica bilayer thin films onto a polyethylene 2,6 naphthalate substrate by means of PECVD. Tetraethyl orthosilicate (TEOS) was used as the precursor gas, together with a mixture of nitrogen, oxygen and argon. In each case, the deposition conditions for the synthesis of the dense layers were varied in order to study the effect of input energy per TEOS molecule and process throughput on the chemical composition and porosity of the layer. Deposition conditions for the porous layers were kept constant, with process throughput the only exception. Each film was characterised in terms of its water vapour transmission rate, its chemical composition and its morphology as a function of the input energy per TEOS molecule during the dense layer deposition and overall process throughput.

For the first time in AP-PECVD, it was found that the porous layer plays a critical role regarding encapsulation performance and surface smoothening of silica bilayer films. Due to increased throughput, the bilayer architecture also enables a 50% reduction in deposition energy consumption per barrier area, with respect to single layer silica films of equivalent encapsulation performance and thickness.

5:00pm **SE+MS+TF-TuA9 Plasma Polymerization of Organic Coatings at Atmospheric Pressure: Relationship between the Precursor Chemistry, the Plasma Chemistry and the Final Coating Chemistry***, B. Nisol, N. Vandencasteele, J. Hubert, C. De Vos, J. Ghesquière, D. Merche,* ***François Reniers,*** Université Libre de Bruxelles, Belgium

The synthesis of organic coatings using plasma technologies has been developed since many decades. This paper investigates a full series of organic coatings, synthesized in the same dielectric barrier discharge system, in the same operational conditions. The >10 precursors vary from fully saturated molecules, with or without heteroatoms (hexamethylnonane, CxCly, CxFy), to anhydrides, acrylates, with or without double or triple bonds. It is shown that the presence of double bonds not only significantly increase the polymerization rate, but also protect the ester function in acrylates. A combined effect of the plasma power and the presence of double bonds on the C/O ratio is observed for all the relevant precursors used. Correlation between the plasma chemistry and the fragment pattern in the gas phase, as recorded by atmospheric mass spectrometry, with the final chemical composition of the coatings, determined by XPS and FTIR is established. Coatings properties can be easily tuned either by combining precursors, by varying the plasma power or by changing the main plasma gas. By an appropriate combination of the plasma parameters and the precursor, very high deposition rates can be achieved, highly hydrophobic or hydrophilic coatings can be synthesized. These macroscopic results are interpreted in terms of plasma properties, and chemical reactivity.

This work was supported by the Belgian Federal Government (IAP research project P7/34 – Physical Chemistry of Plasma Surface Interactions).

5:20pm **SE+MS+TF-TuA10 Innovations in Atmospheric Pressure Plasma Technologies for Surface Engineering***,* ***David Ruzic,*** *Y.L. Wu, L. Na, S. Hammouti, I.A. Shchelkanov,* University of Illinois at Urbana-Champaign **INVITED**

The growing need for high efficiency-low cost coating tools for large area surfaces drives research efforts for development of innovative techniques. One of the options is an Evaporative Coating at Atmospheric Pressure process (ECAP). The principal of this deposition method is an evaporation of a material, with-in a plasma environment. The appealing advantage of this deposition technique is its atomic nature, and its environmentally safe process as no harmful chemicals compounds are used. With ECAP the evaporated material atoms end up deposited molecule-by-molecule or atom-by-atom as in a Physical Vapor Deposition but without the need for a vacuum chamber. This effect is achieved by using a thermal energy from the microwave plasma, when solid 99.99%+ purity metallic and ceramic target such as Al, Sn, Cr, Au, Ag and $AlCl_3$ could be evaporated and then produce a PVD-like coating on a work piece. The tool is designed to have the evaporated material being submerged into the center of the atmosphere microwave discharge. As the result evaporation occur in a controlled environment where a pure metals can be deposited or their compounds. For example in the aluminum case, a pure alpha phase of Al_2O_3 can be deposited using oxygen from the environment, or if a metallic coating of such a reactive metal as Al, is desired, the deposition can be performed in an pure Ar argon environment with the help of a special gas curtain. The tool provides deposition rate for metals as high as 1-5 um/min with high adhesion. The measured adhesion for copper on steel was at least 250 g/mm^2. The ECAP technology opens broad possibilities for surface processing at atmosphere without environmental impact.

6:00pm **SE+MS+TF-TuA12 Solid-state Dewetting: Control and Applications***,* ***Lukasz Borowik,*** *Y. Almadori, N. Chevalier, J.-C. Barbé,* CEA, LETI, MINATEC Campus, France

The dewetting of ultrathin silicon layers, induced by the thermal budget, is an issue to develop Silicon On Insulator (SOI) and Silicon Germanium On Insulator (SGOI) based technologies. However, dewetting can be controlled to obtain well-arranged agglomerates with similar size or even inhibited. This experimental study aims at demonstrating: the effect of the strain, surface contamination, ion sputtering on the dewetting mechanism, and further applications of dewetting thanks to interfacial reaction between agglomerates and the silicon dioxide. For that purpose, we present the results obtained on: (1) (001) oriented ultrathin (8-22 nm) silicon layers on silicon dioxide, (2) (001) oriented 12 nm silicon-germanium layers on silicon dioxide. In order to understand the dewetting mechanism, samples were heated up to ~800°C under ultra-high vacuum (1×10^{-9} mBar) during tens of minutes. The dewetted samples were characterized by Atomic Force Microscopy (AFM) to put in evidence the influence of the different factors on dewetting mechanism.

In first part of our presentation we will present various methods to control dewetting process by using different parameters such as: strained silicon, [1] surface contamination [2] or argon pre-sputtering. [3] These parameters allow tuning agglomerates size, shape and density. In second part of the talk we will show possible applications of dewetting to form porous silicon dioxide via agglomerates interfacial reaction, and finally how to master stoichiometry of silicon germanium agglomerates. [4] All these methods are promising since permit an easy and fast implementation, it is thus of real interest, since it opens up Si and SiGe agglomerates with tuned Ge concentration to application in innovative technologies.

This work was performed in the frame of the ANR LOTUS project. The measurements were realized on the CEA Minatec Nanocharacterization Platform (PFNC).

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

SE-TuP1 Room Temperature Bonding of Polymer and Silicon Wafer using Vacuum Ultraviolet Surface Activation*, **Yoshihiro Fujiwara**, T. Utsunomiya, T. Ichii, H. Sugimura,* Kyoto University, Japan

Vacuum ultraviolet (VUV; $\lambda < 200$ nm) light and active oxygen species generated by VUV light chemically introduce polar functional groups to the surface of organic materials, which are related to adhesive property and wettability. In our previous research [1][2], we investigated the VUV decomposition and chemical conversion of the chemisorbed self-assembled monolayers (SAMs) and polymers surfaces. Using the VUV treatment under the atmospheric pressure, we have succeeded in bonding of Cyclo-olefin polymer (COP) films, which is a nonpolar hydrocarbon polymer, and in bonding between the polymer film and metals such as copper and aluminum at temperature lower than the glass transition temperature of each polymer. However, because of the surface roughness, thermal stress and the presence of intermediate oxide layer, the bonding mechanism is still unclear. In this research, we carried out the surface activated bonding of COP and silicon(111) single crystal wafer as a model surface with atomic-scale flatness. The atomically flat surface enables us to bond different materials at room temperature. Bonding condition without roughness and thermal effects is desirable to reveal the effectiveness of VUV treatment of the surface. A bond strength test was conducted to elucidate the effect of surface modification and bonding conditions such as VUV-irradiation distance, VUV-irradiation time, terminal functional groups of SAMs.

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SE-TuP2 Improvement in Organic Solvent Resistance of Cyclo-Olefin Polymer by Coating with Silica-like Thin Film*, **Taiki Kanzawa**, T. Utsunomiya, T. Ichi, H. Sugimura,* Kyoto University, Japan

Cyclo-olefin polymer (COP) is an amorphous polymer and has the great optical properties like silica glass.[1] Therefore, COP is suitable for microfluidic devices with the optical detection. However, COP is not durable to many organic solvents such as toluene and ether. For utilizing COP to wider range of application fields, this problem must be solved.

Several methods for fabricating the silica-like thin film on polymer substrates have been reported.[2,3] We optimized the coating methods to improve organic solvents resistance of COP. Vacuum ultra-violet (VUV) light of 172 nm wavelength was used in order to photochemically activate the hydrophobic surface of COP plate. Then, tetramethylcyclotetrasiloxane (TMCTS), which has similar component to silica, was chemisorbed onto VUV light-irradiated COP surface by vapor phase deposition. Finally, the sample coated with TMCTS thin film was irradiated by using VUV light again.

The X-ray photoelectron spectroscopy (XPS) and the attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR) measurements clearly indicated that TMCTS thin film was converted to silica-like thin film after VUV light-irradiation. Then, we dropped some organic solvents onto the sample coated with silica-like thin film. After evaporation, there were no traces of osmosis, showing the no permeation of organic solvents to bulk polymer. These results showed that coating with silica-like thin film greatly improved the resistance to organic solvents.

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SE-TuP3 Microstructure and Properties of (ZrHf)N Thin Films Deposited by Sputtering at Room Temperature*, N.N. Chu, **Yu-Wei Lin**, C.-N. Hsiao,* ITRC, National Applied Research Laboratories, Tawain, Republic of China

This study investigated the microstructure and properties of nano-crystalline (ZrHf)N films on Si substrate at room temperature. (ZrHf)N films were prepared by reactive magnetron sputtering based on our previous optimum coating conditions (substrate temperature, system pressure, nitrogen flow etc.) for HfN and ZrN thin films. Based on the early studies, metal nitride coatings have attracted attention for good mechanical properties, hardness up to 30 GPa. In the study, we should have a generalized definition for substitutional solid solution. The addition of Hf into ZrN (or addition of Zr into HfN) forms the substitutional solid solution ZrHfN (or HfZrN). Different ratios of Hf/Zr will form various structure for $(Zr_xHf_{1-x})N$ with interesting properties, and many characteristics, such as nanostructure and hardness remain to be studied further. Characterizing the structure and properties of single ZrHfN layer coating with the different ratio of Hf-Zr to find out the optimum processing parameters, and further to tailor a variety of surface coating applications is the objective of this project.

SE-TuP4 Nanopatterned ZnO on Si-based Materials via Decoupled Ion Beam Modification and Metal Co-deposition*, **Zachariah Koyn**, B. Holybee, J.P. Allain,* University of Illinois at Urbana-Champaign

Ion beams have been shown to create nano-scale surface patterning on polycrystalline thin metal films, including ripples and dots [1,2]. Additionally, oxygen ion beams have been shown to induce fluence-dependent surface oxidation on metal surfaces [3]. This work seeks to unravel the directed irradiation synthesis of metal oxide thin-films and nanostructures, specifically ZnO, with irradiation-driven mechanisms on dissimilar, polymer-based substrates via in-situ, in-operando high-pressure XPS. This examines the dual effects of oxygen irradiation as a means to both oxidize and pattern 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. Recent work utilized a single ion beam to simultaneously irradiate and sputter deposit metal impurities on Si, creating nanostructures [4]. The work here decouples these processes by using two ion beams to independently control the metal deposition and surface modification fluxes and energy distributions. The ratio of these fluxes is the primary tool used to explore the creation and control over size and shape of nanostructures. Beam energies of 500-1500 eV are used at ambient temperatures to protect the substrate, with an inert beam used for metal sputter deposition and both inert and reactive (O_2^+) normal incidence beams used for surface modification. Both Si and PDMS substrates are explored with fluences of 1E16–1E18 ions/cm^2. Surface chemistry is monitored in-operando in the new Ion-Gas-Neutral Interactions with Surfaces (IGNIS) facility. XPS is performed at pressures up to 5 mTorr, allowing for the real-time monitoring of Zn deposition and oxidation. The ability to functionalize flexible, transparent substrates with metal-oxide nanostructures offers exciting applications in areas such as flexible and wearable electronics, gas sensors, biosensors, and photonics [5].

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SE-TuP5 Propagating Exothermic Reactions in Al/Pt Multilayers of Varied Stoichiometry*, D.P. Adams,* Sandia National Laboratories*; R.V. Reeves,* Lawrence Livermore National Laboratory*; M. Abere, **Cathy Sobczak**,* Sandia National Laboratories

Reactive bimetallic multilayers are a form of energetic material that can be ignited at a point and undergo rapid, exothermic, self-propagating reactions. Providing a burst of heat, these materials continue to find use for different joining, battery and fusing applications. Much has been learned about the properties of these materials, yet little is known about the compositional limits of reactivity. In this presentation, we describe the propensity of sputter-deposited Al/Pt multilayers to undergo rapid, self-propagating formation reactions. Reactivity has been evaluated across a broad range of stoichiometry (nAl:mPt) and layer periodicity. Experiments demonstrate self-propagating reactions in ~1.6 micron-thick Al/Pt multilayers when the molar ratio of reactants is in the range 4Al:1Pt to 1Al:4Pt. This rather large compositional range is characterized by different reaction rates and behaviors. High-speed photography shows that equimolar Al/Pt multilayers undergo the most rapid reactions with wavefront speeds as large as 80 m/s. Al- and Pt-rich multilayers react at reduced rates with speeds as low as 1 m/s. A previously developed, analytical method by Mann et al. (J. Appl. Phys. 1997) is utilized to reveal additional details of reactions in the various multilayers. Models that account for the reactant layer thicknesses, composition, the adiabatic temperatures, the flame temperatures, and the measured heats of reaction are used to predict wavefront speeds that closely match measured values. These results are further analyzed to extract information regarding the mass transport characteristics of reactant species.

This work was supported by a Sandia Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.

SE-TuP7 Time-resolved Ion Energies in the Pulsed Cathodic Arc Plasma from Composite Niobium-aluminum Cathodes*, Siegfried Zoehrer,* Montanuniversität Leoben, Austria*; A. Anders,* Lawrence Berkeley National Laboratory*; R. Franz,* Montanuniversität Leoben, Austria

Cathodic arc plasmas are utilized in industry to synthesize a wide variety of functional thin films and coatings. However, the plasma properties present during the deposition processes are not yet fully understood, in particular when composite cathodes are used.

For pulsed cathodic arc plasmas, it is known that the plasma properties like ion energies and ion charge states are time dependent, but the influence of the cathode composition is not much studied. We therefore recorded time-resolved ion energy distribution functions in vacuum arc plasmas from composite NbAl cathodes with the Nb/Al atomic ratios 75/25, 67/33 and 25/75, as well as from single-element Nb and Al cathodes. The mass and charge-state-resolved detection of ions was realized using a commercial mass-energy analyzer modified to allow us having a time resolution of 100 ns (Tanaka et al., 2015). Three dimensional data sets were obtained, where the intensity, that is proportional to the ion count rate, is displayed as a function of time and energy for Nb and Al ions with charge states up to 5+ and 4+, respectively.

Regardless of the cathode composition, the highest mean charge states and ion energies were observed in the beginning of the pulses. There is also a clear influence of the cathode composition. Namely, the fraction of higher ion charge states being significantly lower in the plasma from the composite compared to the single-element cathodes. The current results regarding the time dependence of the ion charge state and energy distributions represent a first step towards a comprehensive understanding of how the cathode composition is affecting the plasma properties.

Tanaka, K.; Han, L.; Zhou, X. & Anders, A. (2015), 'Adding high time resolution to charge-state-specific ion energy measurements for pulsed copper vacuum arc plasmas', Plasma Sources Science and Technology 24(4), 045010.

Advanced Surface Engineering
Room 101C - Session SE+TR-WeM

Protective Coatings for Tribological Applications in Surface Engineering

Moderators: Andrey Voevodin, University of North Texas, Michael Stueber, Karlsruhe Institute of Technology, Germany

8:00am **SE+TR-WeM1 Correlative Theoretical and Experimental Investigation of the Formation of $AlYB_{14}$ and Competing Phases***, **Oliver Hunold**, Y.T. Chen, D. Music,* RWTH Aachen University, Germany*; P.O.A. Persson,* Linköping University, Sweden*; D. Primetzhofer,* Uppsala University, Sweden*; M. to Baben,* GTT-Technologies*; J. Achenbach, P. Keuter, J.M. Schneider,* RWTH Aachen University, Germany

The phase formation in the boron rich section of the Al-Y-B system has been explored by a correlative theoretical and experimental research approach. The structure of coatings deposited via high power pulsed magnetron sputtering from a compound target was studied using elastic recoil detection analysis, electron energy loss spectroscopy spectrum imaging, as well as X-ray and electron diffraction data. The formation of $AlYB_{14}$ together with the $(Y,Al)B_6$ impurity phase, containing 1.8 at. % less B than $AlYB_{14}$, was observed at a growth temperature of 800 °C and hence 600 °C below the bulk synthesis temperature. Based on quantum mechanical calculations we infer that minute compositional variations within the film may be responsible for the formation of both icosahedrally bonded $AlYB_{14}$ and cubic $(Y,Al)B_6$ phases. These findings are relevant for synthesis attempts of all boron rich icosahedrally bonded compounds with the space group: *Imma* that form ternary phases at similar compositions.

8:20am **SE+TR-WeM2 Investigation of Friction and Wear for the Oxide-Oxide Contact in the Piston Ring–liner System***, P. Ernst, P. Luethy, Ch. Bohnheio,* Oerlikon Metco AG, Wohlen, Switzerland*; F. Seibert, B. Widrig, **Jürgen Ramm**,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

The reduction of friction and wear are important issues in the development and optimization of internal combustion engines increasing their efficiency and reducing the service interval times. One possibility to increase the efficiency of an engine is an operation at higher temperature. Surface coating could help to keep the standard materials and extend their operation range to higher temperatures. In this work, the friction and wear of oxide coatings are investigated and compared with coatings which are standard for an engine like Nikasil and Fe- based liner coatings and CrN for piston rings. The oxide coating material was first tested in a SRV test and the coefficient of friction against steel and alumina was measured for dry and lubricated conditions. In addition, the wear of the coatings and the steel or alumina counter-part was inspected. The most promising coating combinations were tested in a motor-bike engine configuration and compared with standard material.

8:40am **SE+TR-WeM3 Local Characterization Tools as the Key for Optimized Performance of Hard Coatings***, **Christian Mitterer**,* Montanuniversität Leoben, Austria **INVITED**

Advanced tribological hard coatings providing multi-functional properties like wear and oxidation resistance combined with high toughness require sophisticated selection and design of materials and architectures. For a knowledge-based development of such coatings, advanced characterization techniques on the nano-scale are needed to establish the necessary link of their microstructure to their properties. Within this contribution, recent progress in coating characterization techniques is highlighted. The application of focused ion beam techniques, electron backscatter diffraction and synchrotron X-ray nanodiffraction enables previously unrevealed insights in microstructure evolution. For the determination of mechanical and tribological properties at elevated temperatures, high-temperature nanoindentation and high-temperature ball-on-disk tests in combination with in-situ measurement techniques and site-specific sample preparation for damage analysis are discussed. Utilization of micromechanical tests for coatings provides information about their fracture toughness and rupture strength. The available portfolio of characterization techniques enables the determination of a complementary microstructural and mechanical fingerprint of tribological hard coatings, which allows to understand the complex structure–property relations in these materials and subsequently to further improve their performance.

9:20am **SE+TR-WeM5 High Temperature Oxidation in Pure Steam Environment of HIPIMS Deposited CrN/NbN Nanostructured Coatings***, **Papken Hovsepian**, A.P. Ehiasarian, Y. Purandare,* Sheffield Hallam University, UK*; F.J. Perez, M.I. Lasanta, M.T. de Miguel, A. Illana,* Universidad Complutense de Madrid, Spain*; J. Juez-Lorenzo,* Fraunhofer Instititute fur Chemische Technologie ICT, Germany*; A. Aguero,* Instituto Nacional de Tecnica Aeroespecial (INTA), Spain

The demand for new materials to be used in supercritical steam power plants for efficient and clean coal utilization is ever growing. A significant reduction of CO_2 emissions is expected by increasing the efficiencies of the steam turbines to $\eta > 50\%$ which can be achieved by moving from subcritical low pressure/ low temperatures, (180 bar/540 ^oC) to high pressure/high temperature, (300 bar/600-620 ^oC) ultra-supercritical regime of operation. The main challenges faced by different steel components of the power plant with this approach however, consist of material failure due to high temperature oxidation, and phenomenon such as creep, erosion and descaling after a stipulated period of time. Over the years considerable research has been done in finding solution to the above problems in terms of protective surface layers with limited success.

In the current work, 4 µm thick CrN/NbN coating utilising nanoscale multilayer structure with bi-layer thickness of $\Delta = 3.4$ nm has been used to protect low Cr content P92 steel widely used in steam power plants. The uniquely layered coatings have a combination of nitrides of chromium and niobium which are not only resistant to aqueous corrosion, corrosion erosion and excellent tribological properties, but also have oxidation resistant in dry air up to a temperature of 850 °C. The novel High Power Impulse Magnetron Sputtering (HIPIMS) deposition technology has been used to deposit CrN/NbN with enhanced adhesion (critical scratch adhesion value of Lc= 80N) and very dense microstructure as demonstrated by XTEM imaging. These superior coating properties are achieved due to the unique high metal ion content (up to 90%) in the HIPIMS plasma, which allows particle acceleration and trajectory control by external electrical and magnetic fields thus delivering highly energetic material flux on the condensing surface.

P92 bare and coated samples were oxidised at 650°C in 100% steam atmosphere up to 2000 h, in order to simulate the future operation conditions of steam turbines employed in power plants. The oxidation kinetics was evaluated by mass gain measurements in a five decimal balance. In these conditions CrN/NbN provided a reliable protection of the P92 steel and outperformed other coatings such as ceramic Al_2O_3 and intermetallic Fe44Cr5Al used for the same application. The paper also discusses the effect of the growth defects and high temperature crack formation analysed by SEM and FIB- SEM techniques on the high temperature corrosion resistance in pure steam atmosphere thus revealing the coatings failure mechanisms.

9:40am **SE+TR-WeM6 Improved Thermo-Mechanical Properties and Oxidation Resistance of Ti-Al-N Coatings by Alloying Ta and Modifying the Coating Architecture***, **Christian Martin Koller**, A. Kirnbauer,* Technische Universität Wien, Austria*; H. Bolvardi,* Oerlikon Balzers, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P.H. Mayrhofer,* Technische Universität Wien, Austria

In recent years, different approaches towards the enhancement of physical vapor deposited TiAlN hard coatings were made. Among these, the alloying of additional elements to form quaternary compounds proved to be extremely efficient. In addition to as-deposited film properties also the coatings' thermo-mechanical behaviour and the performance in oxidizing environments, both constitute fundamental requirements for cutting applications, can be significantly increased.

One example is the substitution of Ti or Al by Ta, which chemically strengthens the face-centred cubic cell, leading to higher hardness values and increased Young's moduli. Furthermore, Ta prevents the formation of anatase $TiO_2$by directly promoting rutile-structured TiO_2. Consequently, a thermal-induced phase transformation of anatase into rutile TiO_2 and its therewith associated generation of crack networks is avoided.

In the present study two subsets of multilayers based on TiAlN/TaAlN and TiAlTaN/TaAlN were investigated. The coatings were synthesised using powder-metallurgically manufactured $Ti_{0.5}Al_{0.5}$, $Ta_{0.9}Al_{0.1}$, $Ta_{0.75}Al_{0.25}$, $Ta_{0.5}Al_{0.5}$, $Ti_{0.475}Al_{0.475}Ta_{0.05}$, and $Ti_{0.45}Al_{0.45}Ta_{0.10}$ targets. The TiAlN and TiAlTaN-base layers were arc evaporated (arc), whereas the TaAlN layers were either arc evaporated or reactively sputtered (rsd) [1][2]. The multilayer architecture was realised by the use of a shutter system or through the continuous two-fold rotation of the substrate holder, resulting in sharp and slightly burred layer interfaces. The overall Ta-content and

TaAlN–layer thickness was varied by different power settings of the $Ta_{0.75}Al_{0.25}$ cathode and shutter-open times, respectively.

We can show that a coating architecture of $TiAlN^{arc}$ and $TaAlN^{arc}$ allows for thermo-mechanical properties comparable to TiAlTaN, whereas superior oxidation resistance only can be achieved by a $TiAlN^{arc}/TaAlN^{rsd}$ arrangement. For both rsd-multilayer arrangements the critical factor in terms of thermo-mechanical performance and oxidation resistance is the TaAlN layer thickness as well as the overall interface volume. Results are discussed based on X-ray diffraction and electron microscopy studies.

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11:00am **SE+TR-WeM10 Tribochemistry between Graphene and Fe, Fe_2O_3, and Fe_3C Surfaces***, **J. David Schall,*** Oakland University **INVITED**

Tribosystems containing both iron and hydrocarbon-based lubricants are ubiquitous and an understanding of the chemistry that takes place in such systems is essential to the development of new lubricant additives designed to reduce friction and wear. Graphene nanoparticle additives have been proposed by numerous researchers due to the excellent friction and wear properties of graphene. Recent experiments have shown that even single layers of graphene in the absence of lubricants on steel components can greatly reduce wear (Berman, Carbon, 54, 2013, 454). Berman *et al* have hypothesized that graphene forms a conformal protective layer on the steel surface with or without additional lubrication. Simulations show vanishingly small friction when continuous sheets of graphene are sandwiched between Fe surfaces; however, real graphene has various functional groups including –carboxyls, -alkyls, -hydroxyls among others along the edges. Graphene can also be oxidized. In this talk simulations that illustrate the triboinitated mechanochemistry between graphene with various functional edge groups and Fe, Fe2O3 and Fe3C surfaces will be presented. These molecular dynamics simulations were conducted with a REAX-FF interatomic potential function for Fe, O, C and H (Zou, *JOM*, 64, 2012, 1426) that includes terms for chemical reactivity with charge transfer enabling investigation of tribochemistry in the sliding interface.

11:40am **SE+TR-WeM12 Tribological Testing of Leather Treated with Ag/TiO_2 Nanoparticles for Footwear Industry***, M. Rebelo de Figueiredo,* Montanuniversität Leoben, Austria*; I. Carvalho, S. Carvalho,* Universidade do Minho, Portugal*; C. Gaidau,* Leather and Footwear Research Institute, Romania*; **Robert Franz,*** Montanuniversität Leoben, Austria

Ecologic and health effects of applying materials with advanced functions for leather surface finishing contribute to increasing the added value and durability of leather and fur articles. The innovative properties of Ag/TiO_2 nanoparticles on leather surface are due to their antimicrobial, self-cleaning and flame retardant characteristics. Furthermore, it leads to a reduction of chemicals with high pollutant potential, e.g. volatile organic biocides, organic solvents and halogenated flame retardants typically used during leather manufacturing.

The efficient anchoring of Ag/TiO_2 nanoparticles on leather surface ensures minimum risk of human skin penetration. To this aim, two different technologies for the functionalisation of the leather surfaces were explored: (1) physical mixing of Ag/TiO_2 nanoparticles with film forming polymers and leather surface covering by conventional technologies and (2) leather surface activation by cold plasma pre-treatment and magnetron sputter deposition of transparent Ag/TiO_2 nanoparticle layers.

In order to test the adhesion of the deposited Ag/TiO_2 nanoparticles to the leather substrates, a series of tribological tests in ball-on-disc configuration has been performed using different counterpart materials ranging from rubber (e.g. nitrile rubber) to polymers (e.g. PTFE, PUR or POM). The analysis of the coating wear by light optical and scanning electron microscopy as well as Raman spectroscopy revealed details regarding the adhesion of the Ag/TiO_2 nanoparticles depending on the deposition method and parameters applied. In a similar way, the sticking behaviour of the Ag/TiO_2 nanoparticles to the different counterpart materials was analysed to emulate the uptake of the released nanoparticles by the human skin. The conducted experiments represent a first step towards a systematic study of the mechanical performance of leathers treated with nanoparticles in order to evaluate their suitability for future applications in the footwear industry.

12:00pm **SE+TR-WeM13 Phase Formation of Cathodic Arc Evaporated Al_xCr_{1-x} and $Al_xCr_{1-x}O_\delta$ Thin Films***, **Valentin Dalbauer,*** CDL AOS TU Wien, Austria*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; C.M. Koller,* CDL AOS TU Wien, Austria*; P.H. Mayrhofer,* Vienna University of Technology, Austria

Aluminium-based oxides and oxide scales are highly valued for various demanding applications due to their outstanding thermo-mechanical properties as well as their superior resistance in oxidising and chemically hazardous environments. However, the polymorphic character of Al_2O_3 (and consequentially also $(Al_xCr_{1-x})_2O_3$) synthesised at deposition temperatures lower than 800 °C is impeding its large-scale utilisation. Especially high Al–containing films, being dominated by transient oxides, are susceptible for thermally-induced phase transformations, which are associated with the formation of crack networks. Therefore, the growth of the thermodynamically stable α-Al_2O_3 at deposition temperatures ~ 400-600 °C has been in the focus of research for many years. Although considerable advances were made, none of them proved to be applicable to industrial utilisation. A comprehensive and in-depth understanding of mechanisms, leading to the growth of transient oxides within the quasi-binary system Al_2O_3–Cr_2O_3 synthesised by cathodic arc evaporation is therefore still of major interest, as this knowledge is crucial for being able to grow coatings with dedicated crystallography and microstructure.

In the present work, we approach this issue by investigating the structural evolution of intermetallic Al_xCr_{1-x} and $Al_xCr_{1-x}O_\delta$ films synthesised by arc evaporation. Depositions were carried out in non-reactive as well as reactive atmosphere, using low to intermediate O_2 flow rates to examine its impact on film morphology and phase composition. In order to correlate the chemical aspect and process conditions (i.e., Cr-content and O_2 partial pressure) with the accessible microstructure and crystallographic evolution, powder-metallurgically manufactured Al_xCr_{1-x} targets with different compositions were selected. By this, the significant phase regimes within the binary Al-Cr phase diagram are accessible.

In detail, arc evaporation of $Al_{0.9}Cr_{0.1}$, $Al_{0.7}Cr_{0.3}$, $Al_{0.5}Cr_{0.5}$, and $Al_{0.25}Cr_{0.75}$ targets leads to the formation of intermetallic films dominated by $Al_{13}Cr_2$, Al_8Cr_5 or $AlCr_2$ phases, which well–agrees with the equilibrium Al-Cr phase diagram. Chemical analyses demonstrate that differences in the Al/Cr-ratio between targets and films increase towards the Cr-rich side, which decrease by introducing O_2 to the deposition process. Furthermore, the simultaneous broadening and intensity reduction of dominant intermetallic XRD peaks is accompanied by the emergence of weak broad signals indicative for the development of X-ray amorphous areas. Between 70 and 90 at.% Al we find a compositional window, which is characterised by a maximum target evaporation and minimum film growth rate.

Advanced Surface Engineering
Room 101D - Session SE+2D+EM-WeA

Multifunctional Thin Films and Coatings

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Michael Stueber, Karlsruhe Institute of Technology, Germany

2:20pm **SE+2D+EM-WeA1 Investigation of H_2S Poisoning Process on Composite Material Made of Metal Oxides and Carbon Nanotubes**, ***Yichen Duan**, A.V. Teplyakov,* University of Delaware

The composite material based on a combination of SnO_2, CuO and acid-treated carbon nanotubes is considered to be promising for H_2S sensing applications. By applying large dosage of H_2S (1% in volume) to the composite and evaluating the chemical changes spectroscopically via XPS, SEM and EDS, the poisoning mechanism of this type of sensing material is revealed. Specifically, metal sulfides (CuS and SnS_2), metal sulfate ($Sn(SO_4)_2$) and thiols are formed as the products following the introduction of H_2S. In fact, all the three components of the material are affected by H_2S. Moreover, when oxygen is present, metal sulfides can be reoxidized back into metal oxides while metal sulfate and thiols remain unchanged. The measurements of the model sensor response also support the assessment of the poisoning process.

2:40pm **SE+2D+EM-WeA2 Graphene-family Nanomaterials Co-assembled with Nanostructured Cobalt Oxide Polymorphs as Hybrid Supercapacitive Electrodes and Enzymeless Glucose Detection Platforms**, ***Sara Carrizosa**, B. McDonald, S. Gupta,* Western Kentucky University

Graphene-family Nanomaterials Assembled with Cobalt oxides and Cobalt Nanoparticles As Hybrid Supercapacitive Electrodes and Enzymeless Glucose Detection PlatformsWe developed graphene/cobalt oxides and graphene/cobalt nanoparticles hybrid assembly highlighting the impacts of nanoscale surface morphology and microstructure producing tailored interfaces for improved electrochemical and electroanalytical properties. Molecular electrodeposition and facile hydrothermal synthesis techniques followed by thermal treatment are demonstrated to be effective approaches for nanoengineered electrochemical electrodes. Hybrid electrodes consisting of supercapacitive graphene nanosheets and pseudocapacitive nanostructured cobalt oxide polymorphs (CoO and Co_3O_4) as well as cobalt nanoparticles (CoNP) synthesized on two- and three-dimensional graphene nanosheets facilitate chemically bridged (covalently and electrostatically anchored) yet tunable graphene-cobalt interfaces. The intrinsic microstructure and surface of these hybrids were characterized by electron microscopy combined with elemental mapping, X-ray diffraction and Raman spectroscopy. The graphene/cobalt hybrid composites were investigated as asymmetric supercapacitor cathodes and as electroanalytical platforms for enzymeless detection of glucose. We demonstrate that Co3O4/ErGO and Co3O4/multilayer graphene hybrids are capable of delivering high specific capacitance of > 600 F g-1 at a current density of 10 A g-1 is achieved when the mass ratio of Co3O4 to ErGO is equal to 80:20 as compared with other hybrids with excellent cycling stability in voltage range 0–1.2 V. It can also detect glucose with ultrahigh sensitivity of 4.57 mA mM-1 cm-2 and a remarkable lower detection limit of < 50 nM in the following order Co_3O_4/rGO_{HT} < CoO/ErGO < CoNP/ MLGNiFoam < Co_3O_4/MLGNiFoam . We attribute all of these remarkable findings due to interplay of (a) open pore system beneficial to ion diffusion and transport kinetics owing to larger accessible geometric surface area, (b) three-dimensional topologically multiplexed and highly conductive pathways provided by MLG, ErGO and rGO_{HT} nanoscaffold architectures to ensure rapid charge transfer and electron/ion conduction (< 10 ms), and (c) synergistic integration of functional nanomaterials devoid of graphene sheets agglomeration with optimal transition metal (oxides) nanoparticles loading.

3:00pm **SE+2D+EM-WeA3 Cross-Bonding between Silicon, Silica and III-V Surfaces at the Nano-Scale Using Energy Analysis via Three Liquid Contact Angle Analysis (3LCAA) to achieve Hermetic Wet NanoBonding™**, ***Ashley Mascareno**,* SiO2 NanoTech LLC/Arizona State University Physics Dpt*; N.X. Herbots,* SiO2 NanoTech LLC*; C.F. Watson,* SiO2 NanoTech LLC/Arizona State University Physics Dpt

Mobile ions such as Na, percolate from saline environments into marine and atmospheric sensors and limit their reliability to less than a week. Implantable glucose monitors for diabetics require replacement about every 3-7 days, with finger blood samples re-calibration daily. Hermetic bonding can yield economic, medical, and human benefits by extending lifetime of such integrated sensors from days to years. Si-based surfaces such as thermally-grown amorphous a-SiO_2 on Si(100), and on III-V surfaces can be hermetically bonded with Wet NanoBonding™ to yield dense, hermetic cross-bonding. In Wet Nonbonding™, planarization is first accomplished at the nano-scale, then a-SiO_2 is etched with HF, while a 2 nm precursor β-$cSi_2O_4H_4$ phase is grown on Si(100) to initiate cross-bonding. Next, both surfaces are put into mechanical contact in a class 10 clean-room and nano-bonded under low temperature (T<180° C) steam pressurization.

Modifying the surface energy components of 2 surfaces can help optimize hermerticity by increasing the density of cross-bonding. Surface energy γ^T can be measured via 3 Liquid Contact Angle Analysis (3LCAA) using the the Van-Oss theory, which models γ^T for semiconductor and insulators in 3 interactions : (1) Lifschitz-Van der Waals molecular dipole interactions γ^{LW}, (2) electron donor interactions γ^+, and (3) electron acceptor interactions γ^-. Successful NanoBonding™ can occur between one surface with high γ^+ and one with high γ^-. 3LCAA extracts these from contact angles between several liquids with known surface energies and the surface. Sessile drop analysis with water, glycerin, and α-bromonaphthalene is conducted in a Class 100 hood using 4-8 drops per liquid for statistical accuracy. RCA cleaned Si(100) and Si(100) terminated with 2-nm β-$cSi_2O_4H_4$ via the Herbots-Atluri (H-A) process are used, in combination with Rapid Thermal Anneal and Oxidation (RTA and RTO), to grow a-SiO_2 [3]. The γ^T of hydrophilic RCA-cleaned Si(100) is 47.3±0.5 mJ/m^2 , 25% higher than the γ^T of ordered, hydrophobic β-$cSi_2O_4H_4$ Si(100) , 37.3±1.5mJ/m^2, and 30% higher than RTO oxides 34.5±0.5 mJ/m^2. Interactions from γ^{LW} account for 90-98±2% of γ^T in ordered oxides, but only 76.5±2.0% of those in hydrophilic surfaces. Thus, 3LCAA detects changes in surface reactivity from defects, impurities, and dangling bonds. While γ^+ accounts for little to none of γ^T for all but one surface, 180° C annealing during Wet NanoBonding significantly increases γ^+ in β-$cSiO_2$. Conversely, HF etching significantly increases γ^- for a-SiO_2. When matching acceptor with donor interactions between surfaces via 3LCAA, cross-bonding density appears to increase, and NanoBonding™

3:20pm **SE+2D+EM-WeA4 Porous Materials for Solid Phase Microextraction by Sputtering and Chemical Vapor Deposition**, ***Tuhin Roychowdhury**, A. Diwan, B. Singh, M. Kaykhaii, M.R. Linford,* Brigham Young University

Solid phase microextraction (SPME) is an important sampling tool. It consists of placing a coated fiber above a sample (headspace mode) or immersing it in a liquid such that molecules (analytes) of interest can be selectively extracted and concentrated. The captured species are then released by heating into a chromatograph for separation and identification. It is a ‘green’ method because no additional solvent is used in this process. We have developed a new class of SPME fibers that offer extraordinary capacity and speed. They are prepared by sputtering a material under conditions that lead to a nanoporous coating on the fiber. When silicon is sputtered under these conditions, its outermost surface can be additionally oxidized, leading to a high density of silanol groups than can be subsequently silanized. For example, the fibers can be derivatized with octadecyldimethylmethoxysilane by chemical vapor deposition (CVD), which creates a hydrophobic extraction medium. The performance of our 2 micron sputtered coatings has been compared to that of thicker (7 micron) commercial coatings. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity for alcohols, amines, aldehydes, and esters. Real world samples, e.g., hops and PAH from water, have also been analyzed. Different coating thicknesses have been prepared and evaluated. Sputtered coatings have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and wetting.

4:20pm **SE+2D+EM-WeA7 Ferroelectric Thin Films for Memory Applications**, ***Joyprokash Chakrabartty**,* Institut national de la recherche scientifique (INRS), Canada

Ferroelectric (FE) oxides draw attention in science community because of its spontaneous switchable polarization often used in electronic devices. FEs are earth abundant, easy to synthesis and low degradation of electronic properties while exposed to room atmosphere. One of its promising applications is in computer memory devices. FEs function as memory by storing data in its two polarization states normally defined as up and down state. However the challenges lie in enhancing data bit density at room temperature. Here we show four step ferroelectric polarization switching in $BiFeO_3$(BFO)/$SrRuO_3$(SRO)/$BiMnO_3$(BMO) heterostructure thin films which act as FE memory devices. All crystalline films are grown on (100) oriented

Niobium doped SrTiO3 (NSTO) single crystal substrates by pulsed laser deposition. Our experimental results show a promising device concept, unique in FE memories that can enhance the data storage capacity in heterostucture capacitor devices at room temperature.

4:40pm **SE+2D+EM-WeA8 Thermoelectric and Optical Properties of Advanced Thermoelectric Devices from Ni/Bi_2Te_3/Ni and Ni/Sb_2Te_3/Ni Thin Films***, **Satilmis Budak**, Z. Xiao, J. Cole, A. Kassu, D. Price, T. Davis, T. Strong, J. Gray,* Alabama A&M University

Thermoelectric devices were prepared from Ni/Bi_2Te_3/Ni and Ni/Sb_2Te_3/Ni thin films using DC/RF magnetron sputtering and E-beam deposition systems. Thermoelectric devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase both the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The thin film devices were characterized using Seebeck coefficient measurement systems; four probe van der Pauw measurement system to measure resistivity, sheet resistance, density, mobility and type of the charge carrier concentration. In addition to the Seebeck coefficient and van der Pauw measurements, the laser thermal conductivity system was used for the thermal conductivity measurements. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM). Raman Spectroscopic technique is used for identification of inherent molecular specificity and analysis of chemical compositions of the films. The resonant features of the scattering spectra measured under the 532 nm and 785 nm wavelength excitation lasers are analyzed.

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, NSF-EPSCOR-R-II-3-EPS-1158862, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687, Department of Homeland Security-Scientific Leadership Award, Grant No. DHS-SLA 2014-ST-062-000060.

5:00pm **SE+2D+EM-WeA9 Effects of Composition and Strain on Band Gaps of Pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge***, **Nalin Fernando**,* New Mexico State University*; R. Hickey, J. Hart, R. Hazbun, D. Zhang, J. Kolodzey,* University of Delaware*; S. Zollner,* New Mexico State University

Ge-Si-Sn alloys are interesting for CMOS applications for a variety of reasons. For example, adding Sn to Si-Ge lowers the band gap, which reduces parasitic contact resistance. Also, the lattice constant of Ge-Sn alloys increases when adding Sn. Therefore, such alloys could be used to impart strain on PMOS devices with Ge channels. We used deformation potential theory to determine the compositional dependence of the direct, indirect, E_1, and $E_1+\Delta_1$ band gaps of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge and theoretical predictions are validated through spectroscopic ellipsometry measurements of the band gaps of pseudomorphic $Ge_{1-y}Sn_y$ on Ge grown by MBE.

The band structure of Ge is a strong function of strain and alloy composition, and a transition from an indirect to a direct band gap has been observed for y~6-10% for relaxed $Ge_{1-y}Sn_y$ indicating the possibility of widespread applications of Ge-based photonic devices. The pseudomorphic nature of the Ge-based alloy layer on a substrate is important to keep dislocation densities low at the interface to improve the performance of the device. Band gap engineering of Ge by controlling strain and alloying with Si and Sn has attracted great interest since a $Ge_{1-x-y}Si_xSn_y$ ternary alloy with two compositional degrees of freedom allows decoupling of the lattice constant and electronic structures.

The pseudomorphically grown $Ge_{1-x-y}Si_xSn_y$ layer on Ge experiences a biaxial stress due to the lattice mismatch between the alloy layer and the Ge. The strain resulting from the stress affects the band structure of the alloy. Deformation potential theory is used to determine the compositional dependence of the band gaps of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge as a function of Si (x) and Sn (y) compositions. The predictions of the deformation potential theory are validated for pseudomorphic $Ge_{1-y}Sn_y$ (for Si=0) on Ge through measurements of the optical properties. The complex pseudodielectric functions of pseudomorphic $Ge_{1-y}Sn_y$ alloys grown on Ge by MBE were measured using ellipsometry in the 0.1-6.6 eV energy range for Sn contents up to 11%, to investigate the compositional dependence of the band gaps. Critical point energies (CP) and related parameters were obtained by analyzing the second derivative spectrum of the dielectric function. Our experimental results for E_g^{dir}, E_1 and $E_1+\Delta_1$ gaps are in good agreement with the theoretically predicted CP energies. We will discuss the strain and compositional dependence of the band gaps and the effects of the growth temperature of the Ge buffer layer on Si to the band gaps.

This work was supported by AFOSR (FA9550-13-1-00222). FTIR measurements were performed at CINT.

5:20pm **SE+2D+EM-WeA10 MBE Growth of Hexagonal Boron Nitride for use in Novel Electronic Devices***, **Adam Barton**, R. Yue, C.M. Smyth, R. Addou, L. Cheng, R.M. Wallace, J. Kim, M. Kim, J. Hsu, K.J. Cho,* The University of Texas at Dallas*; L. Colombo,* Texas Instruments*; C.L. Hinkle,* The University of Texas at Dallas

2D materials offer unique opportunities in device fabrication due to the weak van der Waals interaction between crystalline layers that allows for the growth of high-quality heterostructures with significantly less impact from lattice mismatch with the substrate. Hexagonal boron nitride (hBN) has a honeycomb structure similar to graphene except with alternating boron and nitrogen atoms. The hexagonal rings are composed of six sp^2-hybridized atoms (three boron atoms and three nitrogen atoms). The electronic structure results in a bandgap of 5-7eV, a low-κ dielectric constant of $2-4\varepsilon_o$, and an electron affinity of roughly 2 eV. These electronic properties make hBN an exciting material for a wide range of applications in electronic devices. In particular, we are interested in coupling hBN with transition metal dichalcogenides (TMDs) for low-power tunnel FET applications. Previous publications have primarily utilized chemical vapor deposition (CVD) to grow hBN on catalyzing transition metal substrates (Co, Ni, Cu, etc.) at growth temperatures ranging from 800-1200°C. However, these substrates and growth temperatures are not practical for the majority of device applications. Chalcogen loss in TMDs, for example occurs well below those temperatures.

In this work we report on our recent findings on the growth and characterization of hBN thin films grown by molecular beam epitaxy (MBE). This will include a detailed discussion of the growth mechanism on a variety of substrates (MoS_2, HOPG, WSe_2, Bi_2Se_3, and sapphire) using substrate growth temperatures ranging from 300-800°C. The impact of the source fluxes, substrate temperatures, and in particular, the presence of atomic hydrogen during growth will be presented. The hexagonal phase of BN is achieved as determined by diffraction, Raman, and XPS. AFM, TEM, and RHEED are also used to assess film quality and the experimentally determined bandgap and band alignment will be presented. We will also present our recent work on coupling hBN with ALD-deposited Al_2O_3 to enable higher-k gate dielectrics on top of 2D materials heterostructures.

This work is supported in part by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST. This work was also supported in part by the Texas Higher Education Coordinating Board's Norman Hackerman Advanced Research Program.

5:40pm **SE+2D+EM-WeA11 Passivation of Interfaces Between High-k Dielectrics and SiGe: *Ex Situ* Wet Sulfur Clean vs. *In Situ* Plasma Nitridation***, **Kasra Sardashti**[*], M.S. Clemons,* UC San Diego*; M. Yakimov,* SUNY College of Nanoscale Science and Engineering*; K. Tang,* Stanford University*; S. Oktyabrsky,* SUNY College of Nanoscale Science and Engineering*; P.C. McIntyre,* Stanford University*; L. Dong, N. Yoshida,* Applied Materials, Inc.*; A.C. Kummel,* UC San Diego

Silicon-Germanium is a promising channel material to be used in novel CMOS device architectures such as FinFET and Nanowire FET, due to its high hole mobility. Moreover, it enables control of carrier mobility by mechanical stress and band gap by variation in Si/Ge content in multilayer design. One of the important issues to address in the integration of SiGe in the MOS devices is formation of low-defect interfaces with very thin high-k gate dielectrics such as Al_2O_3, HfO_2 and ZrO_2. Due to adverse effect of Ge sub-oxide (GeO_x) formation and subsequent Ge out-diffusion on the performance of the devices, robust strategies to control the Ge reactions during and after oxide deposition are essential to further the development of SiGe FETs. This study determines the effects of two passivation methods on the quality of the interfaces between SiGe and high-k dielectrics: 1) Ex-situ wet sulfur passivation using $(NH_4)_2S$ solution; 2) In-situ NH_3 plasma nitridation. Al_2O_3 and HfO_2 were deposited on SiGe surfaces by atomic layer deposition (ALD). Electrical and chemical properties of the interfaces were evaluated by capacitance-voltage (C-V) spectroscopy, angle-resolved photoelectron spectroscopy (AR-XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). Both sulfur passivation and plasma nitridation resulted in smaller density of interface traps with a large majority of the trap energy levels adjacent to the valence band edge. Ex-situ sulfur passivation was found to improve the interface quality by reducing the extent of GeO_x formation at the high-k/SiGe interface, therefore constraining the extent of Ge out-diffusion within the oxide. The

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[*] **National Student Award Finalist**

mechanism is distinct; sulfur forms much stronger bonds to Ge than to Si due to the d-orbitals on the Ge; this promotes selective oxidation of the Si and prevents formation of GeOx. Using plasma nitridation, a thin layer of SiON forms selectively at the high-k/SiGe interfaces, preventing the presence of thermally-unstable species such as GeOx and GeON. In addition, SiON can act as a physical diffusion barrier to Ge out-diffusion. The nitridation is selective due to the higher enthalpy of formation for Si vs Ge oxynitrides. Both ex-situ sulfur passivation and in-situ NH_3 plasma nitridation were found to be effective approaches in preparing low-defect Al_2O_3/SiGe and HfO_2/SiGe interfaces; the different chemical mechanisms show there are multiple paths to selective bond formation to SiGe which can be utilized to engineer low-defect stable interfaces.

6:00pm **SE+2D+EM-WeA12 Enhanced Voltage Control of Perpendicular Magnetic Anisotropy in Magnetic Tunnel Junctions Using Ultrathin PZT Composite Oxide Tunneling Barriers***, **Kevin Fitzell**, X. Li, K. Wong, G. Yu, S. Robbennolt, S.H. Tolbert, P.K. Amiri, K.L. Wang, J.P. Chang,* University of California at Los Angeles

In contrast to manipulating magnetization with applied current, using an applied electric field can significantly reduce the required energy and result in less heat generation, leading to increased energy density. This can be accomplished using the voltage-controlled magnetic anisotropy (VCMA) effect, which forms the basis of next-generation magnetoelectric MRAM devices. Specifically, applying an electric field across a CoFeB/MgO interface can decrease the perpendicular magnetic anisotropy field as a result of the altered electron density at the interface, thus destabilizing the magnetization state and allowing for its efficient and deterministic reorientation with a small applied magnetic field. This operation principle stands in contrast to that of STT-RAM, which uses upwards of 100 fJ to write a single bit (300,000 times more energy than the actual energy barrier to switching).

Previous research on CoFeB/oxide interfaces has shown that increasing the dielectric constant of the oxide layer also increases the sensitivity of the interfacial magnetic anisotropy energy to an applied electric field. Lead zirconate titanate (PZT), having excellent ferroelectric properties including a large dielectric constant, is therefore a prime candidate for integration into such oxide layers in an attempt to maximize the VCMA effect. Using atomic layer deposition (ALD), PZT was thus incorporated into magnetic tunnel junctions having MgO/PZT/MgO multilayer composite tunneling barriers. Our group has shown that MRAM devices fabricated using these MgO/PZT/MgO tunneling barriers resulted in a 40% increase in the VCMA coefficient (and thus substantial energy savings) over magnetic tunnel junctions simply employing MgO tunneling barriers, despite the PZT layer being amorphous. Our most recent work has focused on the crystallization of these ultrathin PZT layers, which would cause an even larger dielectric response (even greater energy savings) and open an avenue toward four-state memory devices relying on the ferroelectric polarization of the PZT.

Tribology Focus Topic
Room 101A - Session TR+BI+SE+TF-ThA
Materials Tribology

Moderator: Michael Chandross, Sandia National Laboratories

2:20pm **TR+BI+SE+TF-ThA1 Reaction Pathways and Tribofilm Formation Kinetics at a Solid-Solid Interface***, H.L. Adams,* University of Wisconsin-Milwaukee*; A. Martini,* University of California Merced*; **Wilfred Tysoe**,* University of Wisconsin-Milwaukee **INVITED**

Perhaps the most difficult surface-science challenge is to monitor reaction pathways and kinetics at sliding solid-solid interfaces, in particular for opaque contacting materials [1]. Optical techniques can be used to interrogate the interface when one of the contacting surfaces is transparent, but they are often not sensitive to the first monolayer. Strategies for measuring reaction pathways and their kinetics for well-defined surfaces in ultrahigh vacuum (UHV) are described using the example of sliding-induced decomposition of adsorbed methyl thiolate species, formed by exposure to dimethyl disulfide, on copper. Surface science experiments show that methyl thiolates are stable up to ~425 K on copper, but decompose during rubbing; the effect of the external force is to lower the reaction activation barrier so that it proceeds at room temperature. The surface reaction products can be monitored immediately after sliding in UHV using surface spectroscopies (for example, Auger spectroscopy). However, the reaction kinetics can also be monitored in situ first, by measuring the gas-phase species evolved as a function of the number of times the surface is rubbed, where methane and ethane are detected and second, by measuring the change in friction force due to the evolution of the nature of the species present on the surface. This allows the elementary steps in the tribofilm formation pathway to be identified and their rates measured.

[1] Heather L. Adams, Michael T. Garvey, Uma Shantini Ramasamy, Zhijiang Ye, Ashlie Martini, and Wilfred T. Tysoe, Journal of Physical Chemistry C, **119**, 7115–7123 (2015)

3:00pm **TR+BI+SE+TF-ThA3 Nanotribology of Graphene Revisited: The Influence of Contact Size and Substrate Topography***, A. Balkanci,* Bilkent University, Turkey*; Z. Ye, A. Martini,* University of California Merced*; **Mehmet Z. Baykara**,* Bilkent University, Turkey

Two-dimensional (2D) materials have been the focus of intense research in recent years thanks to their outstanding electronic and mechanical attributes. In particular, graphene exhibits exceptional potential as a solid lubricant appropriate for use in nano-/micro-scale mechanical systems. As such, a comprehensive evaluation of its frictional properties on such small length scales is of crucial concern. While pioneering studies toward this purpose have revealed strongly layer-dependent frictional behavior [1], the precise roles that contact size and substrate topography (important design parameters for mobile components in nano-/micro-scale devices) play in the lubricative nature of graphene have not been explored yet in detail.

In this contribution, we present a combined experimental and numerical study aimed at evaluating the influence of contact size and substrate topography on the nanotribological characteristics of graphene. In particular, atomic force microscopy (AFM) is employed under ambient conditions to measure friction forces on mechanically-exfoliated graphene as a function of applied load, number of graphene layers, and contact size. To study the influence of contact size on measured frictional properties, AFM probes with different tip apex sizes are obtained by thermal evaporation of gold and platinum onto the probes. In conjunction with the experiments, molecular dynamics (MD) simulations are performed that involve the calculation of friction forces experienced by model tip apexes of varying size on single- and few-layer graphene. Moreover, substrates with various RMS roughness and correlation length values are employed in the MD simulations to investigate the effect of substrate topography on frictional behavior. Results reveal that a subtle interplay between contact size and substrate topography determines the layer-dependent frictional behavior of graphene, providing a new perspective to the nanotribology of this remarkable material.

[1]: C. Lee *et al.*, Science **328**, 76 (2010)

3:20pm **TR+BI+SE+TF-ThA4 Iron-Doped Diamond-Like Carbon Coatings (Fe-DLCs): Synthesis, Characterization, and Tribology--Seminal Results***, **Parag Gupta**,* Northwestern University/Argonne National Lab.*; M.E. Graham,* Northwestern University

Iron-doped diamond-like carbon coatings (Fe-DLCs) of ≈ 0.1 to 35 at.% Fe content have been synthesized, characterized, and tribologically tested. Coatings were deposited on Si(111), 52100 steel ball, and H-13 steel flat substrates using a closed-field unbalanced magnetron sputter deposition process with unmodified and modified graphite target states, the latter with press-fit cast gray iron slugs. Process parameters of target modification, target power, acetylene flowrate, and substrate bias were varied and used in establishing a process-conditioning window to create predictable coatings.

Mechanical characterization was done to determine deposition rate, thickness, internal stress, and hardness. Cross-sectional characterization was done to determine coating uniformity, to understand coating adhesion and morphology, and to confirm interlayer presence and morphology (if deposited). Surface characterization was done to determine surface roughness and mechanical anisotropy. Chemical characterization was done to determine elemental concentration and chemical anisotropy. Finally, structural characterization was done to determine carbon bond order.

Using a ball-on-flat reciprocating tribometer, highly-doped Fe-DLCs were studied at either room temperature or ≈ 100 °C and with either coating / coating or steel / coating contact. Electrical contact resistance between interfaces was measured *in situ*. A contact pressure of ≈ 1 GPa was employed alongside an average sliding speed of 1.0 cm / s, except when non-monotonic sequential speed stepping was prescribed. The boundary-lubricated sliding tests were conducted in the presence of poly-alpha-olefin SAE grade 30 synthetic base stock oil (PAO10) with and without molybdenum dithiocarbamate (MoDTC) and zinc dialkyldithiophosphate (ZDDP) additives, both at 0.5 wt.%. Coatings were also tested in unlubricated conditions.

Friction responses were determined, and wear assessments were conducted. Tribofilm and debris analyses were done. The results were compared to those from DLC, CrN + DLC, Si-DLC, and W-DLC coatings obtained from Oerlikon Balzers. Results indicate that Fe-DLC samples containing between 12 and 35 at.% Fe exhibit negligible wear in the presence of PAO10 with MoDTC and ZDDP, affirming the influence of iron in catalyzing protective tribofilms. Additionally, wear on such samples in both lubricated and unlubricated conditions is far lower than that observed for other coatings, indicating that these Fe-DLCs are robust in any conditions.

4:00pm **TR+BI+SE+TF-ThA6 Tribo-Rheometry of Soft Matter***, J. Kim, **Alison Dunn**,* University of Illinois at Urbana-Champaign **INVITED**

Hydrogel surfaces are biomimics for sensing and mobility systems in the body such as the eyes and large joints due to their compliance, controllable chemistry, permeability, and integrated aqueous component. Recent studies have shown that polymer concentration gradients in the top microns of crosslinked hydrogel surfaces result in a less dense surface region. In addition, the lubrication of hydrogel interfaces is driven by the effective mesh size, a parameter which follows from the local density. Given the similarity of a dilute crosslinked hydrogel surface with a dilute polymer solution, we probe the surface of a polyacrylamide hydrogel using stepped-velocity tribo-rheometry over 5 decades of sliding speed, with an annular aluminum countersurface. Three distinct lubricating regimes emerge based on a) hysteretic torque response depending upon increasing or decreasing sliding speeds, and b) characteristic torque overshoot following velocity step changes. This evidence supports the analogy of a rheology-like lubrication response. We postulate that the mechanisms of hydrogel-against-hard material lubrication are due to distinct complex fluid behavior characterized by weakly or strongly time-dependent response. Tribo-rheometry is particularly suited to uncover the lubrication mechanisms of complex interfaces such as are formed with hydrated hydrogel surfaces and biological surfaces.

4:40pm **TR+BI+SE+TF-ThA8 Friction Coefficient Lowering in High-hardness Boron Nitride Films Under Ultra-high Vacuum***, **Masao Noma**,* Shinko Seiki Co., Ltd, Japan*; K. Eriguchi,* Kyoto University, Japan*; M. Yamashita,* Hyogo Prefectural Institute of Technology, Japan*; S. Hasegawa,* Osaka University, Japan

Solid lubricant material with low friction coefficient is of technological interest for its usage under harsh environments such as ultra-high vacuum. At present, MoSi -containing films [1] are the most widely employed for space applications because of their low friction coefficients (0.02–0.05) in vacuum [2]. However, the mechanical hardness and the oxidation resistance temperature are 10–20 GPa [3] and 360 °C [4], respectively, inapplicable to a long term operation in space. Boron nitride (BN) films have been considered an alternative material because of their superior high hardness and oxidation resistance temperature, 45 GPa and 1200 °C, respectively [5]. We have proposed a novel reactive plasma-assisted coating technique (RePAC) for forming 1-µm-thick high-hardness BN films (~50 GPa) [6][7]. In this study, we present "friction coefficient lowering" phenomena in the high-hardness BN films under ultra-high vacuum ($\sim 10^{-6}$ Pa), which is in sharp contrast to "friction coefficient increase" usually observed for other hard coating materials. The time-dependent high-vacuum friction measurement revealed that the friction coefficient decrease from 0.1 to 0.03 was found for the substrate bias voltage from −90 to −180 V in the RePAC. In this (incident ion energy) region, the cubic BN phase was formed in the turbostratic BN background, leading to the high-hardness of ~50 GPa at atmosphere [7]. Moreover, the obtained low friction coefficient was confirmed to be stable (<0.05) for long time exposures to the vacuum (~96 hrs). The friction coefficients of the present BN films are comparable to widely reported values of MoS_2 films. The BN film prepared by the RePAC is one of promising hard coating materials for harsh environment (e.g., space) applications.

[1] M. Chhowalla, and G. A. J. Amaratunga, *Nature***407** (2000) 164.

[2] G. Colas et al., *Wear***305** (2013) 192.

[3] N. M. Renevier et al., *Surf. Coat. Technol.***142-144** (2001) 67.

[4] K. C. Wong et al., X. Lu, *Wear***264** (2008) 526.

[5] C. B. Samantaray and R. N. Singh, *Int. Mater. Rev.***50** (2005) 313.

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

[7] K. Eriguchi et al., AVS 61st Int. Symp. & Exhibition, SE+NS+TR-TuM3 (2014).

5:00pm **TR+BI+SE+TF-ThA9 Nanoscale Friction Properties of Water Intercalated Graphene on Mica and its Isotope Effects*, Hyunsoo Lee,*** Institute for Basic Science (IBS) & Korea Advanced Institute of Science and Technology (KAIST)*; J.-H. Ko,* KAIST, Republic of Korea*; J.S. Choi,* Electronics and Telecommunications Research Institute, Republic of Korea*; J.H. Hwang,* IBS & KAIST, Republic of Korea*; Y.-H. Kim,* KAIST, Republic of Korea*; M.B. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)*; J.Y. Park,* IBS & KAIST, Republic of Korea

We demonstrate that the frictional behavior of hydrophobic graphene on hydrophilic mica is affected by water intercalation after exposure to humid air using atomic force microscopy. The single- and multi-layer graphene were formed by mechanical exfoliation on freshly cleaved muscovite mica. The adsorption of the ice-like water layer between graphene and mica led to friction enhancement, as compared with a pristine graphene/mica sample, which is presumably due to additional frictional energy dissipation at the solid–liquid interface. Moreover, friction on the graphene increased as the number of stacking water layers increased. The magnitude of friction increase was, on the other hand, reduced as following increase of the number of covering graphene layer above intercalated water layer, and then the friction is eventually not distinguished from the multi-layer graphene stack excluded water adsorption. Using the first-principle density functional theory calculations we explain this unexpected behavior by the increased spectral range of vibration modes of graphene caused by water, particularly the low frequency flexural modes, and by the better overlap of the graphene vibration modes with the mica phonons, which favors a more efficient dissipation of the frictional energy. Additionally, we found that the intercalation of deuterium oxide (D_2O) leads to the lower friction, compared to H_2O intercalated graphene on mica. We attribute this isotope effect with to the low vibrational frequency of D_2O adsorbate, which results in the low rate of frictional energy dissipation at the interface.

5:20pm **TR+BI+SE+TF-ThA10 The Remarkable Friction Behavior of Copper at Cryogenic Temperatures*, Andrew Kustas,*** Sandia National Laboratories*; J. Curry,* Lehigh University*; T. Babuska, M. Chandross, P. Lu, T.A. Furnish, N. Argibay,* Sandia National Laboratories

It is commonly accepted that unlubricated, self-mated pure metal contacts over the course of sliding invariably cold-weld and gall, leading to undesirably high friction and wear. Recent work with nanostructured pure metals has shown that in fact it is possible to obtain low friction ($\mu < 0.5$) with pure bare metals such as pure Cu and Au at room temperature. Here we discuss those findings, and more recent work that shows the impact of temperature, stress and microstructure evolution on friction of self-mated pure metals. Variable temperature friction experiments were used to show the existence of a temperature-dependent transition for Cu from high ($\mu > 1$) to low ($\mu = 0.25$) friction, achieved by sufficiently reducing temperature and promoting the development of nanocrystalline surface films that are unachievable at room temperature at the relatively high applied stresses imposed. In-situ electrical contact resistance (ECR) measurements were used to indirectly measure the evolution of the microstructure (grain size) at the interface throughout the experiment. Microscopy was then used to verify claims of nanocrystalline surface film formation at low temperatures. Lastly, an analytical model based exclusively on materials properties is presented that incorporates stress and temperature over time to predict grain size, connecting grain size to friction behavior, for pure FCC metals. While more work is needed to develop the proposed framework, a model that intrinsically connects grain size to friction behavior of metals based exclusively on materials properties is transformational to alloy design, and raises a number of compelling and highly fundamental questions for further research.

5:40pm **TR+BI+SE+TF-ThA11 Understanding Friction in MoS2, Part 1: Stress, Time and Temperature*, Tomas Babuska,*** Sandia National Laboratories*; J. Curry,* Lehigh University*; M. Chandross, M.T. Dugger,* Sandia National Laboratories*; B. Krick,* Lehigh University*; N. Argibay,* Sandia National Laboratories

In the 90 years since the first patent was issued for molybdenum disulfide (MoS_2) as a friction and wear reducing additive, great strides have been made in understanding its remarkable lubricity. However, much remains to be understood about the mechanisms of friction at the molecular scale. Firstly, we present results of investigations into the origins of the well-known non-Amontonian behavior of MoS_2. We show that the apparent return to Amontonian behavior previously reported with steel is in fact associated with an elasto-plastic transition of the contact, and that the stress-dependent friction predictable varies as a function of substrate composition and microstructure (hardness). Time-dependent friction evolution (i.e. run-in behavior) was also found be strongly a function of substrate material composition and stress; these results imply a potentially useful connection between stress and microstructure evolution in both film and substrate that is discussed. We also report on investigations into the temperature-dependent friction and wear behavior of pure MoS_2. In the range -150 to 250°C, we report dramatic deviations from previous literature, as well as the existence of transitions between thermal and athermal behavior as a function of temperature. Evidence of deviations from classical Arrhenius behavior is presented, and the implications of these findings discussed in the context of thermally-activated friction models at the molecular scale. Finally, we end with a discussion of how these findings collectively advance our ability to develop a practical predictive friction model for MoS_2 that includes temperature, stress, substrate effects, defect density and commensurability as their foundation.

6:00pm **TR+BI+SE+TF-ThA12 Understanding Friction in MoS2, Part 2: Water, Oxidation and Run- in*, John Curry,*** Lehigh University*; M. Chandross, T. Babuska,* Sandia National Laboratories*; N.C. Strandwitz, H. Luftman,* Lehigh University*; M.T. Dugger, N. Argibay,* Sandia National Laboratories*; B. Krick,* Lehigh University

Effects of water vapor and oxidation resistance for amorphous (sputtered) and highly ordered (N_2 sprayed) MoS_2 were investigated with a high-sensitivity, low energy ion scattering (HS-LEIS) spectrometer, molecular dynamics simulations and accompanying tribological testing in each environment of interest. Recent studies have shown that N_2 sprayed MoS_2 coatings possess a preferential surface parallel basal plane texture as deposited due to the kinetic energy imparted during spraying, effectively shearing MoS_2 particles onto the surface. As such, the highly ordered structure of the sprayed coatings both at the surface and throughout the bulk of the film are hypothesized to act as a diffusion barrier to environmental contaminants. Coatings were exposed to molecular oxygen at 250°C and atomic oxygen at 20°C for 30 minutes each and subsequently depth profiled in the HS-LEIS. Results show that N_2 sprayed coatings were successful in limiting the depth of oxidation for both types of exposure. The main contributor, however, to increased initial friction post exposure was the type of coating (amorphous vs highly oriented). Tribological experiments in dry and humid nitrogen showed the initial friction response to be unaffected for sprayed samples while greatly affected for sputtered. Spiral orbit tribological testing was utilized in dry and humid nitrogen environments to further assess the effect of prolonged sliding on purely amorphous MoS_2 with and without formation of a transfer film. It is hypothesized that water does not poison friction behavior of established films of highly oriented MoS_2, but it does poison the ability to form long range order and sintering of crystallites.

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