

## Plasma Science and Technology Division Room B131 - Session PS1+SE-MoM

### Atmospheric-Pressure Plasmas

**Moderators:** Michael Gordon, University of California at Santa Barbara, François Reniers, Université Libre de Bruxelles, Belgium

8:20am **PS1+SE-MoM1 On the Versatility of Atmospheric Non-equilibrium Plasmas: Material Synthesis, Packaging Sanitation and Oncological Applications**, *Matteo Gherardi, V. Colombo, F. Barletta, A. Bisag, C. Bucci, F. Capelli, R. Laurita*, Alma Mater Studiorum-University of Bologna, Italy; *E. Mezzofanti*, AlmaPlasma srl; *T. Galligani*, Alma Mater Studiorum-University of Bologna, Italy, Italia; *G. Girolimetti, S. Coluccelli, L. Amato, G. Gasparre*, S.Orsola-Malpighi Hospital, Bologna, Italy; *M. Perrone*, S. Orsola-Malpighi Hospital, Bologna, Italy; *A.M. Porcelli*, Alma Mater Studiorum-University of Bologna, Italy; *P. De Iaco*, S. Orsola-Malpighi Hospital, Bologna, Italy

#### INVITED

Non-equilibrium atmospheric pressure plasmas (APPs) are an extremely versatile sources of reactive species, UV radiation, radicals and electrons, showing the promise of new medical therapies and offering innovative means to induce chemical reactions and synthesize materials. Trying to capture the versatility of this technology and to depict the current challenges, the presentation will deal with three different technological applications of APPs.

In the first part of the talk, APP biocidal potential is discussed in the industrial perspective of producers of food/beverage packaging and packaging machines. In this field, a fast and economic packaging sanitation is required in order to guarantee a sufficient shelf life to the product. Advantages and limitations of APPs with respect to conventional technologies, as well as the challenges of scaling plasma equipment up to the dimensions required by the industrial production volumes will be discussed.

In the second part of the talk, recent findings on the oncological applications of APPs will be presented. The discussion will focus in particular on Epithelial Ovarian Cancer (EOC), the fifth leading cause of cancer-related death among women and a disease characterised by the diffusion of nodules or plaques from the ovary to the peritoneal surfaces (carcinosis), with a poor prognosis at diagnosis (15-20% within 5 years) in advanced stages (III-IV). Due to the limitations of the currently available therapeutic options, the use of APPs is envisioned to produce plasma activated liquids (PALs) containing reactive oxygen and nitrogen species (RONS) to wash the intraperitoneal cavity with the aim of selectively provoking apoptosis in cancer cells without damaging the healthy ones.

Finally, the use of APPs for the synthesis of materials will be discussed in the frame of the development of an innovative multi-layer coating able to reduce biofilm proliferation onto a biomedical device, while at the same time preserving its bio- and hemo-compatibility, avoiding blood clots formation. An APP assisted process is here used to deposit all the different layers of the coating, composed by silver nanoparticles (AgNPs) embedded in a plasma polymerized HMDSO (ppHMDSO) matrix. The coating characteristics will be discussed in light of the results provided by chemomorphological analysis and cellular and anti-biofilm assays.

9:40am **PS1+SE-MoM5 Streamers Effects in Cold Atmospheric Plasma Applications: Coatings, Gas Conversion, Surface Chemistries**, *A. Ozkan, J. Mertens, François Reniers*, Université Libre de Bruxelles, Belgium

For a long time, research in atmospheric plasma dielectric barrier discharges (DBDs) focused on homogeneous discharges. However, most of the DBDs present inhomogeneities in the form of streamers.

In this presentation, we aim at showing the drastic effect of these streamers on the chemical reactivity of the discharges. Consequences can be found for instance on the chemistry and on the roughness of plasma deposited coatings, on the deposition rates, or on the conversion of gases inside the discharge. These streamers can be studied through a high speed/high sensitivity camera, and by recording the current – voltage curves with a Rogowski coil on an oscilloscope. The chemistry in the plasma phase is studied using mass spectrometry, optical emission spectroscopy and gas chromatography. Roughness can be measured using profilometry or AFM, and the surface chemistry is analyzed by XPS.

The effect of the streamers will be demonstrated using the following examples :

- the plasma polymerization of CFx coatings, in Argon or Helium leads to different coatings chemistries and roughnesses, induced by the streamers. This leads to coatings with contact angle varying from 110° (PTFE like) to more than 140°.

- the plasma polymerization of anhydrides shows that the number of streamers depends on the nature of the anhydride injected, and more specifically on the presence of double bonds, and their location. This affects the final chemistry of the coatings, but also the deposition rate.

- the conversion of CO<sub>2</sub> by a DBD is a highly filamentary discharge. Although this is due to the electronegative nature of CO<sub>2</sub>, we show that, by changing the dielectric, and by playing with the plasma parameters, one can significantly vary the number of streamers. We also show that this number of streamers seems to be a key factor for the gas conversion.

10:00am **PS1+SE-MoM6 Improved Water Intrusion Resistance on Adhesive Bonded Metals using Atmospheric CVD SiO<sub>2</sub> Barrier Coatings**, *Zachary Jeckell, D. Patel, T. Choi, M. Schmid, L. Bónová, D.E. Barlaz, D.N. Ruzic*, University of Illinois at Urbana-Champaign; *I.A. Shchelkanov, B.E. Jurczyk*, Starfire Industries LLC

Lightweight manufacturing, specifically the bonding of dissimilar metals is gaining traction lately as the automobile industry looks for new ways to reduce the weight of their vehicles without compromising the safety or performance. However, current technologies such as spot welding can either be difficult, as is the case for aluminum and magnesium, or impossible as is the case for carbon fiber reinforced polymers. The Center for Plasma Material Interactions (CPMI) has developed a scalable method for performing atmospheric plasma enhanced chemical vapor deposition (AP-CVD) using a 2.45 GHz microwave power supply and a torch design that allows for inline precursor delivery to the plasma. Atmospheric plasmas offer unique advantages for manufacturing, such as the potential to be directly integrated into an assembly line, as well as the ability to deposit on complex geometries. This research investigates the feasibility of depositing SiO<sub>2</sub>, using hexamethyldisiloxane (HMDSO) as the chemical precursor, onto materials commonly used in lightweight manufacturing and then applying an automotive adhesive to bond the materials together. The silica layer is intended to function as both an adhesion promoter as well as a water barrier coating. The composition of the film is verified using XPS, and the film morphology and thickness are observed using cross-sectional SEM to verify that the deposited film is dense and in the range of 10-100 nm. The robustness of these films is determined by adhesion testing following deposition of silica, as well as after water soak testing which are used to simulate prolonged exposure to realistic environments. Preliminary water soak testing on aluminum has shown a decrease in max stress of 2.5% after 168 hours of water soak at 55 °C, which is a significant improvement over the 25% benchmark currently used in the automotive industry.

10:40am **PS1+SE-MoM8 OES Imaging and Double Langmuir Probe Studies of Flow-through, Supersonic Microplasma Jet Sources**, *K.E. Mackie, Michael Gordon*, University of California at Santa Barbara

Spatially-resolved OES imaging and double Langmuir probe (DLP) measurements were carried out on flow-through supersonic microplasma jets to highlight how plasma operating conditions (e.g., pressure, current, presence of growth precursors/O<sub>2</sub>, distance from the nozzle) affect the local gas ( $T_{rot}$  and  $T_{trans}$ ) and electron ( $T_e$ ) temperatures in the plasma jet plume.  $T_{rot}$  and  $T_{vib}$  were estimated using semi-empirical and rigorous quantum mechanical fits to OES spectra of the first positive group of N<sub>2</sub> ( $B^2\Pi \rightarrow A^2\Sigma_u^+$ ), and  $T_e$  was obtained via fits to DLP IV curves. Experiments on Ar jets with downstream pressures in the 10-200 Torr regime yielded estimates of  $T_{rot} = T_e$  and  $T_{vib}$  of 500-700 K and 5000-6000 K, respectively, using two independent methods. DLP data gave estimates of  $T_e$  in the 1-3 eV range, which depended on the exact location in the expanding jet plume. The transition between a pre-discharge-like operating regime at low plasma currents to true hollow cathode operation at high currents was also observed in the plasma IV characteristic and companion OES measurements. The talk will highlight OES imaging and DLP results, as well as the effect of gas additives, i.e., the presence of film deposition precursors and/or oxidants in the jet feed vs. background gas, on jet operating characteristics ( $T_e$ ,  $T_{gas}$ , etc.).

11:00am **PS1+SE-MoM9 Time-resolved Optical Emission Spectroscopy of an Atmospheric Pressure Plasma Jet – Surface Interaction**, *Michael Johnson, D.R. Boris, Tz.B. Petrova, S.G. Walton*, U.S. Naval Research Laboratory

Atmospheric pressure plasma jets (APPJs) have become a valuable tool for the modification of surfaces. One of the large benefits of APPJs is their

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ability to generate a chemically-rich environment in open air, allowing for the modification of a broad range of surfaces including metals, polymers, ceramics, and biological materials. However, when an APPJ interacts with a surface, the surface will influence the structure of the plasma jet and thereby alter the chemistry of the jet. This is particularly vital because different chemical species important for surface modification will form in different quantities depending on the surface. Because of this, two different surfaces treated by the same plasma jet will undergo exposure to slightly different conditions. In this work, time-resolved measurements of the optical emission of a pulsed-DC plasma jet impinging on different surface is measured to investigate how the structure and chemistry of the plasma on the surface evolve in time. Initially, the plasma source emits a streamer which propagates out from the jet nozzle into the open air and eventually collides the surface. With a metal surface, a 'secondary stroke' forms on the surface and extends back towards the jet outlet. The formation, extension, and duration of the stroke are functions of the pulse width and frequency of the voltage waveform used to generate the plasma jet. The metal surface allows for the formation of a long-lived, surface plasma that exists for the duration of the pulse. If a dielectric surface is impinged with the APPJ, the streamer will strike the surface and produces an ionization wave that extends along the surface. The ionization wave is short-lived and not significantly affected by the length of the pulse. This work is supported by the Naval Research Laboratory base program.

11:20am **PS1+SE-MoM10 Atmospheric-Pressure Plasmas As Ionization Sources For Atomic, Molecular, And Biological Mass Spectrometry, *Jacob Shelley, S. Badal, C. Walton, G. MacLean***, Rensselaer Polytechnic Institute; *I. Ayodeji*, University of South Florida; *G. Chan*, Lawrence Berkeley National Laboratory; *T. Evans-Nguyen*, University of South Florida **INVITED**

Analytical plasmas that operate at ambient pressures and mass spectrometry (MS) have been in a symbiotic relationship since the near-coincident advent of the inductively coupled plasma (ICP) ionization source and atmospheric-pressure (AP) inlets for mass spectrometers. Preceding that discovery by only a few years, it was shown that low-power plasmas could be used for soft ionization of intact molecules through chemical ionization pathways. More recently, analytical plasma source development has seen a resurgence with the realization of a variety of low-power AP plasma designs useful as MS ionization sources. AP plasmas are unique in that they have the ability to create a wide-range of energetic species useful for desorption and/or ionization processes.

Plasmas produce highly energetic species (e.g., ions, metastable neutrals, fast electrons, etc.), which can lead to high-energy physical or chemical processes to fragment and ionize molecules. This fragmentation can be so extensive that molecules are broken down into bare elemental constituents. In addition, low-energy ionization reactions can also occur due to the abundance of collisional cooling that can take place at ambient pressures. For instance, the helium-based flowing atmospheric-pressure afterglow (FAPA) source has been shown to produce intact molecular ions of molecular species with quite high ionization efficiencies.

This presentation will demonstrate the broad utility and range of applications of low-power AP glow discharges, specifically the FAPA discharge, and the solution-cathode glow discharge (SCGD). The possibilities of these devices extend well beyond conventional atomic and small molecule detection. By tuning the chemistry of the discharge, we can alter conventional ionization modes to encompass elemental analysis to biomolecular detection to polymer analysis. For instance, our group has developed a method to detect elemental ions with FAPA-MS via online complexation reactions with volatile ligands. But, the open-air nature of FAPA can produce isobaric interferences from ambient species. To overcome this issue, differential mobility spectrometry was used as a post-ionization filter to remove background ions. Ultimately, FAPA-DMS may dramatically improve selectivity and sensitivity in fieldable MS applications. Meanwhile, it was found that SCGD-MS could be used for the detection of atomic, molecular, and biological species directly from solutions. Furthermore, it was found that peptides could be tunably fragmented at atmospheric pressure, which led to 100% sequence coverage for many of the peptides examined.

## Thin Films Division

### Room A122-123 - Session TF+SE-MoA

#### HiPIMS and Reactive HiPIMS for Novel Thin Films

**Moderators:** Joe Becker, Kurt J. Lesker Company, Megan Holtz, Cornell University

**1:40pm TF+SE-MoA1 The Influence of the Magnetic Field on the Deposition Rate and Ionized Flux Fraction in the HiPIMS Discharge, H. Hajihoseini, University of Iceland, Iceland; M. Cada, Z. Hubicka, Academy of Sciences of the Czech Republic, Czech Republic; S. Unaldi, LPGP Université Paris-Sud, France; M.A. Raadu, N. Brenning, KTH Royal Institute of Technology, Sweden; Jan Tomas Gudmundsson, University of Iceland, Iceland; D. Lundin, LPGP Université Paris-Sud, France**

Three different ways to quantify the degree of ionization in sputtering magnetrons are discussed [1]. Then we move on to explore the effect of the magnetic field strength  $|B|$  and geometry (degree of balancing) on the deposition rate and ionized flux fraction  $F_{flux}$  in dc magnetron sputtering (dcMS) and high power impulse magnetron sputtering (HiPIMS) when depositing titanium. The HiPIMS discharge was run in two different operating modes. The first one we refer to as 'fixed voltage mode' where the cathode voltage is kept fixed at 625 V while the pulse repetition frequency is varied to achieve the desired time average power (300 W). The second mode we refer to as 'fixed peak current mode' is carried out by adjusting the cathode voltage to maintain a fixed peak discharge current and by varying the frequency to archive the same average power. Our results indicate that the dcMS deposition rate is weakly sensitive to variations in the magnetic field while the deposition rate during HiPIMS operated in fixed voltage mode changes from 30% to 90% of the dcMS deposition rate as  $|B|$  decreases [2]. In contrast, when operating the HiPIMS discharge in fixed peak current mode the deposition rate increases only slightly with decreasing  $|B|$ . In fixed voltage mode, for weaker  $|B|$  the higher the deposition rate, the lower the  $F_{flux}$ . The measured quantities, the deposition rate and ionized flux fraction, are then related to the ionization probability  $\alpha_i$  and the back attraction probability of the sputtered species  $\beta_i$ . We show that the fraction of the ions of the sputtered material that escape back attraction increases by 30% when  $|B|$  is reduced during operation in fixed peak current mode while the ionization probability of the sputtered species increases with increased discharge current when operating in fixed voltage mode.

[1] A. Butler, N. Brenning, M. A. Raadu, J. T. Gudmundsson, T. Minea and D. Lundin, *Plasma Sources Science and Technology*, **27**(10) (2018) 105005

[2] H. Hajihoseini, M. Čada, Z. Hubička, S. Unaldi, M. A. Raadu, N. Brenning, J. T. Gudmundsson and D. Lundin, *Plasma*, submitted for publication, April 2019

**2:00pm TF+SE-MoA2 HIPIMS and Magnetron Sputtering of Niobium for use in Josephson Junctions, George Major, M.R. Linford, Brigham Young University**

Niobium (Nb) is a technology-critical element with superconductive properties, and applications in electronics, superconductors, and particle accelerators. Thin film niobium is commonly deposited by magnetron sputtering. Properties of Nb thin films must be precisely tuned for applications, e.g., Josephson Junctions, as surface roughness, crystallite size, and apparent elastic modulus can affect superconducting film properties. To create a Josephson Junction, a thin film of Al (4 to 10 nm) is deposited on top of a smooth Nb film (ca. 100 nm). The functionality of this Al film is inversely related to its thickness. The smoother the film onto which the Al is deposited, the thinner it can be. High-power impulse magnetron sputtering (HiPIMS) is an emerging method for physically depositing thin films. HiPIMS produces a high degree of ionization of sputtered material and a high rate of molecular gas dissociation, which results in high density films. Various metals, including Ti and Ta, have been successfully deposited by HiPIMS, showing dense, smooth microstructures free of large-scale defects. Here, Nb thin films are deposited using magnetron sputtering and HiPIMS. These films are characterized by AFM, TEM, XPS, and SEM. Ellipsometry is used to study their optical properties and to determine their optical constants. HiPIMS should result in lower surface roughness compared to magnetron sputtering. The resulting films will lead to improved superconductive devices.

**2:20pm TF+SE-MoA3 Thin Film Crystal Growth of Oxides, Nitrides and Carbides using High Impulse Magnetron Sputtering, Jon-Paul Maria, The Pennsylvania State University** INVITED

This presentation will discuss thin film crystal growth using reactive pulsed magnetron sputtering specifically in the region referred to as high power impulse magnetron sputtering, or HiPIMS. HiPIMS is characterized by duty cycles less than approximately 10%, and magnetron power densities in excess of 1 kW/cm<sup>2</sup>. These intense impulses produce high ionization fractions of both the gas and sputtered species, they can be sustained in atmospheres containing substantial fractions of O<sub>2</sub> or N<sub>2</sub> with only modest re-sputtering, and they can be tuned so as to minimize target poisoning. Pulsed dc plasmas have been applied routinely to promote thin film adhesion, to achieve high deposition rates, and to produce extremely hard and wear resistant coatings. Their introduction to electronic materials has been much less rapid.

The intent of this presentation is to demonstrate the utility of pulsed dc plasmas, and specifically the HiPIMS regime, for electronic materials, including oxides, nitrides and carbides which require reactive environments that can in many cases can be challenging to realize. Three case studies will be presented: 1) epitaxial growth of CdO thin films for IR optoelectronic applications, 2) epitaxial growth of GaN thin films for wide bandgap applications, and 3) entropy-stabilized carbides for extreme environments. The basic instrumentation of this interesting plasma method will be discussed, and how it offers advantages for controlling defect chemistry, and this transport properties, in CdO, for enabling epitaxy at surprisingly low temperatures in GaN, with excellent control of surface morphology, and for achieving high carbon content in rocksalt carbides, and thus high hardness. In all cases the specific connections between plasma parameters, temperature, pressure, growth mode, and ultimately physical properties will be stressed. The intent is to demonstrate how this less-well explored region of plasma processing space offers possible advantages to crystal growth of electronic materials of contemporary interest.

**3:00pm TF+SE-MoA5 Reactive Bipolar High Power Impulse Magnetron Sputtering (B-HiPIMS) for Deposition of High Entropy Carbides, Trent Borman, M.D. Hossain, J.-P. Maria, The Pennsylvania State University**

Sputtered carbide thin films frequently feature significant carbon stoichiometry irrespective of the source materials, while amorphous-C or a-C:H secondary phases begin to precipitate with as many as 1/3 or more of the carbon sites vacant in the rock salt structure. In reactive sputtering it is often necessary to sputter in the compound regime in order to achieve a higher carbon stoichiometry, however this comes with the penalty of reduced sputter yield. Reactive HiPIMS can avoid carburization of the target through gas rarefaction and high target etch rates. While this is beneficial for process stability, carbide microstructural evolution is still limited by the low homologous temperature achievable in thin film deposition (0.25-0.3T<sub>melit</sub>). Recently, bipolar-HiPIMS has been discussed as a means of tailoring the bombardment in order to drive microstructural development through momentum transfer and thermalization of kinetic energy.

The authors will discuss the reactive synthesis of high entropy carbide films from metal alloy targets using Bipolar High-Power Impulse Magnetron Sputtering (B-HiPIMS) in a mixed Ar/CH<sub>4</sub> atmosphere. The effects of bipolar pulse voltages and lengths on microstructural, compositional, and phase development will be discussed. Additionally, the impacts of order of magnitude changes in sputter pulse length on the formation of carbide thin films will be reported. This work investigates a broad range of carbon stoichiometries: from metallic films and carbon deficient carbides to near stoichiometric carbides and carbide/amorphous-carbon nanocomposites. This enables investigation of the property trends as a function of carbon content, as it is presently unclear if the diverse trends observed in the binary carbides persist in a high entropy system or are overshadowed by the high entropy metal sublattice.

This material is based upon work supported by the National Science Foundation Graduate Research Fellowship (DGE-1252376) and the Office of Naval Research (N00014-15-1-2863).

**3:20pm TF+SE-MoA6 High Density Titanium Oxide and Silicon Oxide Films Deposited by Current-Controlled High Power Impulse Magnetron Sputtering, Arutiun P. Ehasarian, P.Eh. Hovsepian, D.A. Loch, Sheffield Hallam University, UK**

High density transparent oxide layers on glass can improve the environmental viability of photovoltaics, displays, and low emissivity layers in glazing as well as aid the photocatalytic deactivation of organic

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contaminants. High Power Impulse Magnetron Sputtering (HIPIMS) produces high density microstructures and high hardness due to the delivery of an ionised metal and dissociated oxygen deposition flux to the substrates.

TiO<sub>x</sub> and SiO<sub>x</sub> films were produced in a cluster tool by reactive HIPIMS of a pair of metallic targets in an Ar-Oxygen atmosphere. The HIPIMS process was carried out by controlling the current within the pulse. This resulted in the elimination of stability issues associated with runaway currents for all target poisoning states from metallic to fully poisoned. TiO<sub>x</sub> was deposited by a fast plasma ignition and a constant current during pulses of up to 200 microseconds. Electron cooling and gas rarefaction were observed sequentially during the initial stages of the pulse. These were followed by a steady increase in metal ion emission at constant power input. SiO<sub>x</sub> was deposited using a current ramp and shorter pulses of up to 20 microseconds and a bipolar operation. In the transition mode oxygen was emitted mainly from the target whilst in the fully poisoned mode it was detected in the gas phase by time-resolved optical emission spectroscopy. TiO<sub>x</sub> films deposited without additional heating or substrate biasing had good transparency and a refractive index which increased continuously as the oxygen flow reduced from 45 to 13% reaching a maximum value of 2.55 at a wavelength of 550 nm. The films comprised a mixture of rutile and anatase phase with HIPIMS deposition producing higher fractions of rutile compared to bipolar pulsed DC operation. The HIPIMS films reached higher refractive index of 2.55 compared to 2.47 for bipolar pulsed DC. The hardness of the films and its relation to process conditions are discussed. The morphological density was extremely high as confirmed by a 2 orders of magnitude reduction in corrosion current in potentiodynamic polarisation tests on 304 stainless steel substrates. SiO<sub>x</sub> microstructural density, refractive index and hardness are discussed.

**4:00pm TF+SE-MoA8 Epitaxial Growth and Surface Morphology of Thin Film GaN via HIPIMS, Kevin Ferri, E. Runnerstrom, Pennsylvania State University; A. Klump, Z. Sitar, R. Collazo, North Carolina State University; J.-P. Maria, The Pennsylvania State University**

GaN is a desirable wide bandgap semiconductor for applications as blue and UV emitters as well as high temperature, high power, and high frequency electronic devices. In order to overcome the low reactivity of gallium with nitrogen at low temperatures, thin film GaN deposition techniques such as Metal Organic Chemical Vapor Deposition often use high pressure growth at temperatures in excess of 1000 °C. While higher temperatures allow for high crystal quality thin film GaN with favorable morphology, this presents challenges to abrupt junction formation due to fast diffusion rates that cause dopant migration during deposition. It is thus advantageous to find avenues to lower the deposition temperature for GaN to a region where controlled doping can occur. While doing so, it is imperative to maintain epitaxy and growth morphology for device fabrication.

In this presentation, we demonstrate that reactive High-Power Impulse Magnetron Sputtering (HiPIMS) is an effective low temperature alternative for depositing high quality, epitaxial GaN thin films. In contrast to conventional direct current (DC) or radio frequency (RF) sputtering, pulsed DC provides the needed kinetic energy and ionization fraction to establish a sufficiently reactive environment to promote full nitridation. This can be challenging with many other Ga sources. More specifically, the low duty cycle regime of pulsed DC known as HiPIMS provides access to kW/cm<sup>2</sup> peak power densities without target degradation and thus dramatically increased gallium reactivity. In addition, adding an opposite polarity voltage pulse between the target bombarding events, known as a kick pulses, further allows one to tailor both the adatom landing energy on the substrate surface, and mitigate target poisoning.

This unique capability set enables us to prepare high crystal quality epitaxial GaN thin films with smooth surface morphologies characterized by c/2 steps and terraces at temperatures below 500 °C. The presentation will focus on the relationships between sputtering parameters including voltage, kick pulse, pulse length, and duty cycle, on GaN thin film crystal quality, surface morphology, and growth rate. Preliminary transport properties will be reported.

**4:20pm TF+SE-MoA9 Reactive HiPIMS Deposition of a Thick Cu:CuCN<sub>x</sub> Multilayered Nano-composite Coating Material for Improving Machining Process Performance in Rough Turning, Md.Masud-Ur Rashid, C.M. Nicolescu, KTH Royal Institute of Technology, Plasmatrix Materials AB, Sweden; A. Archenti, KTH Royal Institute of Technology, Sweden; G. Shuai, KTH Royal Institute of Technology; R. Tomkowski, KTH Royal Institute of Technology, Sweden**

Vibrations in metal cutting process such as turning have detrimental effect on productivity, finished surface roughness of workpiece and cutting insert life. During machining process high frequency vibration (equal to or above 10000 Hz) causes micro cracks to the cutting insert, which facilitate the failure of cutting insert and consequently resulted in higher roughness on workpiece surface. In this study a reactive high power impulse magnetron sputtering (R-HiPIMS) deposition process was used to deposit a thick copper and copper-carbon nitride (Cu:CuCN<sub>x</sub>) multilayered nano-structured composite coating, with higher stiffness and damping properties, on the shim. This coated shim was then used to suppress the high frequency vibration during rough turning operation. Scanning electron microscopy (SEM) of the coating cross section as well as energy dispersive x-ray spectroscopy (EDS) mapping of the cross-section confirms the multilayered structure with the presence of different ratios of copper (Cu), carbon (C), and nitrogen (N). The Cu:CN<sub>x</sub> coating thickness was measured to be approximately 100 μm. The average surface hardness (SH) and cross-sectional hardness (CSH), measured by Vickers-microhardness indentation, were found to be 353.2 HV and 149.5 HV respectively. Insert wear measurement after 30 minutes of rough turning process, reveals that the studied 100 μm Cu:CuCN<sub>x</sub> multi-layered composite coating material can reduce the tool wear by 60.5%. The average roughness value (Ra) of the work piece material is also reduced by 8.76% in case of using Cu:CN<sub>x</sub> coated shim comparing to conventional shim.

**4:40pm TF+SE-MoA10 The Residual Stress Control in Hard Metal Films by Energetic Deposition, Y.G. Li, Y.Z. Qu, Z.T. Jiang, M.K. Lei, Dalian University of Technology, China**

For energetic deposition, ion bombardment was an important factor independent of grain size for influencing the residual stress, and the energy and flux were critical parameters to determine the residual stress evolution. In this work, modulated pulsed power magnetron sputtering (MPPMS) and deep oscillation magnetron sputtering (DOMS) were employed to control the energy and flux with or without bias to modulate the ion bombardment for intrinsic stress generation. The films thickness was selected at 0.2, 0.5, 1.5 and 3.0 μm to give a comparative study of the intrinsic stress, and thermal stress was not considered since the effect of thermal stress made no major influences. It was found that the thin films all showed compressive residual stress with thickness under 1 μm, and the residual stress of Cr thin film was lower than that of the Nb thin film under similar thickness. The residual stress of DOMS Nb thin film was always higher than MPPMS Nb thin film, however the residual stress of DOMS Cr thin film was equivalent to MPPMS Cr thin film. The ion irradiation effect should be the dominating effect responsible for the difference between Nb and Cr thin films, since Nb generated more Nb<sup>2+</sup> ions than Cr in energetic deposition. For Cr thin films, the grain size and deposition rate were also important influencing factors, fine grain size and high deposition rate promoted the formation of compressive residual stress. For energy deposition, the effect of secondly charged ions in the film growing front should be concentrated to establish a proper kinetic model for intrinsic stress generation.

**5:00pm TF+SE-MoA11 Advanced HIPIMS Coatings Through Kick Pulse Technology, Jason Hrebik, Kurt J. Lesker Company**

HIPIMS coating technology has been rapidly growing over the past few years due to the availability of R&D scale supply offerings. This has resulted in many new breakthroughs in application enhancement, production scalability, and efficiency. The number of applications where HIPIMS is now considered is also advancing. Breakthroughs in HIPIMS controllability have enabled researchers to find a variety of ideal operating parameter sets for various performance requirements. One of the most significant technical advances is a reverse positive kick pulse. This option provides a significant variable for driving out film stress in HIPIMS applications and increasing yield rates, which have been a major downside to HIPIMS in the past. These advances open up new possibilities for the technology and the enhancement of many thin film applications. This presentation will highlight examples of these applications along with the advantages associated with HIPIMS and the Kick pulse technology. It will show how these advances can be scaled to larger scale production applications and provide examples of what enhancements can be expected.

## Advanced Surface Engineering Division Room A215 - Session SE+AS+TF-WeA

### Nanostructured Thin Films and Coatings

**Moderators:** Mehran Golizadeh, Montanuniversität Leoben, Austria, Suneel Kodambaka, University of California, Los Angeles

3:00pm **SE+AS+TF-WeA3 Metallic Glass: From Coating to First-Ever Nanotube Arrays**, *Jinn P. Chu*, National Taiwan University of Science and Technology, Taiwan, Republic of China

Thin film metallic glass (TFMG) is a new class of multi-component metallic thin film with unique characteristics, including high strength, high ductility, smooth surface, absence of grain boundaries, low coefficient of friction, and corrosion resistance, though their bulk forms are already well-known for properties because of their amorphous structure. Thin films prepared by physical vapor-to-solid deposition are expected to be further from equilibrium than those prepared by liquid-to-solid melting or casting processes. This is expected to further improve the glass forming ability and widen the composition range for amorphization. In the first part of my talk, I will present some important TFMG properties and applications we have discovered in recent years. Then, the metallic glass nanotubes (MGNTs) on Si fabricated by a simple lithography and sputter deposition process for very large-scale integration is introduced. This first-ever metallic nanotube array is awarded by *American Chemical Society (ACS)* at nano tech Japan 2018 in Tokyo. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter [1]. The MGNT surface becomes hydrophobic, repelling water. By heating/cooling the array, the surface hydrophobicity is changed. Two examples will be presented in this talk based on modifications of this scheme. First, after modification of biotin, the array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin by monitoring the shift. The detection limit of the arrays for streptavidin is estimated to be 25 nM, with a detection time of 10 min. Thus, the arrays may be used as a versatile platform for high-sensitive label-free optical biosensing [2]. Second, the array is prepared on a heating device and, with an applied electric voltage to the heating device underneath, so that the arrays are functional as biomimetic artificial suckers for thermally adhesion response [3].

#### References

- [1] J. K. Chen, W. T. Chen, C. C. Cheng, C. C. Yu and J. P. Chu, Metallic glass nanotube arrays: preparation and surface characterizations, *Materials Today*, 21 (2018), 178-185.
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3:20pm **SE+AS+TF-WeA4 Tin Oxide Nanoaggregate Fragmentation and Restructuring during Supersonic Impaction based Thin Film Deposition Processes**, *Souvik Ghosh, X. Chen, C. Li, B. Olson, C.J. Hogan*, University of Minnesota, Minneapolis

Aerosol deposition (AD) is a versatile technique for printing thin films. During AD, gas-suspended particles are impacted inertially on a target surface at high velocities. Subsonic impaction processes often lead to highly porous, weakly bound depositions. High-speed supersonic deposition, however, can lead to denser, mechanically robust coatings of metals & metal oxides. Supersonic deposition is hence a potential low temperature route to the additive manufacturing of thin films (<1  $\mu\text{m}$  to >10  $\mu\text{m}$ ) of a variety of materials.

However, the mechanism of film densification & consolidation remains poorly understood, particularly because AD can function with spherical or fractal-like agglomerated particles, from both dry powder feeds & aerosol synthesis processes. In an effort to better understand AD, we examined the mechanism of thin film formation via supersonic impaction of  $\text{SnO}_2$  nanoaggregates on alumina, where we observed the formation of mechanically robust  $\text{SnO}_2$  thin films.  $\text{SnO}_2$  nanoaggregates were synthesized via flame spray pyrolysis (FSP) of Tin 2-Ethylhexanoate. These nanoaggregates characterized via differential mobility analysis shows a broad size distribution in the 40 nm -300 nm mobility diameter range. X-ray

diffraction analysis of as-collected powders confirmed the formation of nano-crystalline  $\text{SnO}_2$ . To understand morphological changes to aggregates during high speed deposition, a differential mobility analyzer was used prior to deposition to select aggregates within a prescribed mobility diameter. The aggregates were then deposited electrostatically at low velocity (at atmospheric pressure) & supersonic speeds after passing through a 200  $\mu\text{m}$  throat width, slit-type, conically contoured converging-diverging nozzle. With low speed deposition, we observed highly branched, chain like aggregates; while after supersonic deposition, we observed denser aggregates with significantly lower number of particles. Images hence suggest that the aggregates fragment & restructure during supersonic impaction.

Fragmentation & restructuring was quantified by image analysis of TEM images to determine their projected radii of gyration, perimeter, end-to-end distance, & projected area. These four parameters were then compared to those from in-silico projections of quasifractal aggregates, enabling extrapolation of the 3D architectures of deposited particles. Plots of the number of primary nanoparticles in aggregates as functions of their inferred radii of gyration confirmed that supersonic deposition leads to both (1) fewer primary particles per aggregate (fragmentation) & (2) for a given number of primary particles, smaller radii of gyration (restructuring).

4:20pm **SE+AS+TF-WeA7 From Gas-ion to Metal-ion-controlled Irradiation: A Paradigm Shift in the Thin Film Growth by Magnetron Sputtering**, *Grzegorz Greczynski*, Linköping University, Sweden; *I. Petrov, J.E. Greene*, University of Illinois at Urbana-Champaign; *L. Hultman*, Linköping University, Sweden

#### INVITED

Ion irradiation is a key tool for controlling the nanostructure, phase content, and physical properties of refractory ceramic thin films grown at low temperatures ( $T_s$ ) by magnetron sputtering. However, in contrast to gas-ion bombardment, the effects of metal-ion irradiation on properties of these films have not been extensively studied due to (i) low metal-ion concentrations during standard dc magnetron sputtering (DCMS), and (ii) difficulties in separating metal-ion from gas-ion fluxes. These issues were recently resolved with our development of high-power pulsed magnetron sputtering (HiPIMS), in which pulsed substrate bias is applied in synchronous to the metal-ion-rich portion of each pulse.<sup>1</sup> Careful choice of sputtering conditions allows exploitation of gas rarefaction effects such that the charge state, energy, and momentum of metal ions incident at the growing film surface can be tuned.

The results of time-resolved mass spectrometry analyses performed at the substrate position during HiPIMS and HiPIMS/DCMS co-sputtering of transition-metal (TM) targets in Ar and Ar/N atmospheres are reviewed. Knowledge of the temporal evolution of metal- and gas-ion fluxes is essential for precise control of the incident metal-ion energy and minimizing the role of gas-ion irradiation. Also, covered are the growth of TM nitride and boride alloys by metal-ion synchronized HiPIMS. In contrast to gas-ions, a fraction of which are trapped at interstitial sites, metal-ions are primarily incorporated at lattice sites resulting in much lower compressive stresses. In addition, the closer mass match with the film-forming species results in more efficient momentum transfer and provides the recoil density and energy necessary to eliminate film porosity at low  $T_s$ . Several novel film-growth pathways are described: (i) nanostructured N-doped  $\text{bcc-CrN}_{0.05}$  films combining properties of both metals and ceramics, (ii) fully-dense, hard, and stress-free  $\text{Ti}_{0.39}\text{Al}_{0.61}\text{N}$ , (iii) single-phase cubic  $\text{Ti}_{1-x}\text{Si}_x\text{N}$  with the highest reported SiN concentrations, (iv) unprecedented AlN supersaturation in single-phase NaCl-structure  $\text{V}_{1-x}\text{Al}_x\text{N}$ , (v) a dramatic increase in the hardness, due to selective heavy-metal-ion bombardment during growth, of dense  $\text{Ti}_{0.92}\text{Ta}_{0.08}\text{N}$  and  $\text{Ti}_{0.41}\text{Al}_{0.51}\text{Ta}_{0.08}\text{N}$  films deposited with no external heating, and (vi) simultaneous increase in both hardness and toughness of  $\text{Zr}_{1-x}\text{Ta}_x\text{B}$  layers deposited with synchronized  $\text{Ta}^+$  irradiation.

Finally,  $\text{Ti}_{1-x}\text{Ta}_x\text{N}$  alloys grown with no external heating are shown to produce high-quality Cu diffusion barriers and provide excellent corrosion protection for stainless-steel substrates.

<sup>1</sup> G. Greczynski, J. Lu, J. Jensen, I. Petrov, J.E. Greene, S. Bölz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *J. Vac. Sci. Technol. A* 30 (2012) 061504

5:00pm **SE+AS+TF-WeA9 Atomic Layer Deposition of Silver Thin Film on Polydimethylsiloxane (PDMS)**, *Sarah Hashemi Astaneh, C. Sukotjo, C.G. Takoudis*, University of Illinois at Chicago

Two types of samples were prepared in this work:

- 1- Silver coated PDMS

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2- Silver coated PDMS with interlayer of TiO<sub>2</sub>

For type 1 samples: Silver deposition was done in the custom-built ALD system. Ag(fod) (Pet<sub>3</sub>) was used as a silver precursor and dimethyl amineborane ((BH<sub>3</sub> (NHMe<sub>2</sub>)) was used as a reducing agent. Silver bubbler and dimethyl amineborane bubbler temperatures were kept at 96 °C and 50 °C, respectively. The reactor pressure and temperature was kept at 500 mtorr and 115 °C during deposition, respectively.

For type 2 samples: prior to silver coating, deposition of TiO<sub>2</sub> on PDMS was done in a commercial ALD system (Kurt J. Lesker 150 LE). Tetrakis (dimethylamido) titanium (IV) (TDMAT™) was used as the metal oxide precursor and maintained at 70 °C in the bubbler during all depositions. Ultra high purity N<sub>2</sub> was used as a carrier gas as well as purging gas. O<sub>3</sub> was used as an oxidizer for this ALD reaction and it was prepared using a UV-ozone generator placed immediately upstream of the deposition chamber to reduce ozone decomposition in delivery line as described in our previous studies. The reactor pressure and temperature was kept at ~1000 mtorr and 120 °C during TiO<sub>2</sub> deposition. This process leads to ~9 nm of TiO<sub>2</sub> interlayer on PDMS.

Right after this step, TiO<sub>2</sub> coated PDMS samples were transferred to the custom-built ALD system and silver deposition was carried on in the custom-built ALD system similar to type 1 samples.

In each of the above runs, simultaneously; same thin film was deposited on p-type Si (100) silicon wafer (University wafer Inc, USA) and used as a reference substrate to determine deposited film thickness.

The growth and composition of the silver on top of PDMS samples were analyzed with X-ray photoelectron spectroscopy (XPS) using Kratos AXIS-165 equipped with monochromatic Al K $\alpha$  X-ray source operating at 15kV and 10 mA. As can be seen in figure 1, Ag 3p, Ag 3d peaks appeared clearly on Si, TiO<sub>2</sub> coated Si and TiO<sub>2</sub> coated PDMS substrates.

5:20pm **SE+AS+TF-WeA10 Use of an Einzel Lens to Enhance Electrohydrodynamic Printing Technology, Matthew Strohmayer<sup>1</sup>, A. Dhall, P. Ramesh, N. Tokranova, C.A. Ventrice, Jr., SUNY Polytechnic Institute**

Additive manufacturing (AM) shows great promise for both research and industrial applications. The main advantages of AM include limited waste and the ability to build complicated structures. The most common techniques for AM are fused deposition manufacturing, digital light printing, and ink jetting. All of these techniques suffer from resolution and material limitations. Recently, a cost-effective, versatile method of high-resolution printing called electrohydrodynamic (EHD) printing has been introduced. This method allows for spatial resolution in the hundreds of nanometers. This process works similarly to a typical ink jetting system, except instead of the ink/polymer being pushed out of a tip, it is pulled out by an applied electric field. This allows for the resultant droplet to be smaller than the needle diameter. Electrostatic repulsion of the charged droplets limits the ultimate resolution of this technique. To overcome this resolution limitation, we have incorporated an Einzel lens into the system to focus the droplets. This helps the droplets overcome the repulsive Coulomb interaction, leading to better spatial resolution. To validate this approach, simulations were performed to test for different parameters, including droplet size changes and lens optimization. This was then used to build a real system.

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<sup>1</sup> ASSD Student Award Finalist

## Advanced Surface Engineering Division Room A215 - Session SE+PS-ThM

### Plasma-assisted Surface Modification and Deposition Processes

**Moderators:** Robert Franz, Montanuniversität Leoben, Austria, Jianliang Lin, Southwest Research Institute

**8:00am SE+PS-ThM1 Core/Shell Particles using a Plasma-based Reactors, Santiago Vargas-Giraldo, D. Galeano-Osorio, C. Castano,** Virginia Commonwealth University

Nano-size and micro-size manufacturing have found an invaluable tool in plasma-assisted materials deposition techniques. Primarily, plasma-assisted physical vapor deposition (PAPVD) methods are clean, reliable and flexible to develop films and coatings. Materials produced by PAPVD may lead to stable structures and stoichiometries that are not possible on other processes. On the other hand, core/shell systems have dragged high attention due to their unique properties. These structures exhibit high surface area, and the interfacial interaction between the core and the shell leads to complex chemistries and transfer phenomena. This work presents an innovative approach to synthesize shells for existing particles using sputtering equipment. It demonstrates the challenges for the direct implementation of magnetron sputtering to obtain single and double shells on glass microspheres. First, a simple flat sample stage was used to discuss the prominent structural and conformability imperfections due to shadowing effects on 3D cores. To overcome this limitation, a new sample stage to manipulate the core particles under vacuum for more uniform shell formation was designed. As proof of concept, various metals and metal oxide shells over glass micro-size spheres were obtained. Extensive materials characterization of the newly formed structures was performed. The results are the groundwork for a myriad of technological applications.

**8:20am SE+PS-ThM2 Formation Mechanisms of Converted Layer During Erosion of Composite Al-Cr Arc Cathodes, Mehran Golizadeh, F. Mendez Martin, B. Rashkova,** Montanuniversität Leoben, Austria; **S. Kolozsvári,** Plansee Composite Materials GmbH, Lechbruck am See, Germany; **R. Franz,** Montanuniversität Leoben, Austria

Cathodic arc deposition (CAD) is a well-established physical vapor deposition technique which is characterized by a highly ionized plasma emitted from the cathode. The energy of the ions in the plasma ranges from 20 to some 100 eV, depending on the cathode material and the discharge conditions. These energetic and highly ionized plasmas significantly influence film growth mechanism and, e.g., high-temperature phases can be stabilized at typically low deposition temperatures in CAD. The plasma properties are influenced by the properties of the converted layer which forms on the surface of composite cathodes due to local consecutive melting-solidification cycles caused by the motion of the cathode spot over the cathode surface. Therefore, a detailed understanding of the formation mechanism and properties of the converted layer is essential to understand and manipulate plasma properties.

Within the current work, composite cathodes with composition of  $Al_{0.5}Cr_{0.5}$  but different grain size, namely 80 and 1200  $\mu\text{m}$ , were eroded in inert Ar gas at a pressure of 1 Pa applying a current of 60 A. A short erosion time of 30 s enabled us to capture single craters left behind by a cathode spot. A cross-section of the crater prepared using focused ion beam (FIB) showed the liquid pool formed by the cathode spot was violently deformed by plasma pressure, pushing the liquid out of the crater to the rim and surrounding space (macroparticles). The leftover liquid was rapidly quenched and there was almost no heat-affected zone below the crater. This finding shows that solid-state diffusion plays a negligible role in the formation of the converted layer.

Further, cross-sections of the cathodes eroded for 1h were prepared by conventional metallography and FIB. Detailed microstructural and phase analysis using transmission electron microscopy and transmission Kikuchi diffraction together with cross-sectional study of single craters revealed that the converted layer is formed in a way that the rim of a crater fills the neighbouring craters due to step erosion. The splashes ejected from craters by plasma pressure also contribute to forming the converted layer. The later mechanism can be dominating depending on the topography of the cathode surface, which was confirmed by the erosion of the cathodes with 1200  $\mu\text{m}$  grain size.

**8:40am SE+PS-ThM3 Self-organization of Plasma in RF Magnetron Sputtering, Matjaz Panjan,** Jozef Stefan Institute, Slovenia

Self-organization of magnetron plasma in so-called spokes has been previously reported for pulsed [1, 2] and continuous magnetron discharges [3]. In this presentation, we will demonstrate that spokes also form in oscillatory RF magnetron sputtering regime [4]. We used an ICCD camera and electrical probes to investigate the rotating plasma patterns. The spokes in RFMS were compared to the spokes in classical DCMS at similar discharge conditions. In both regimes, stable plasma patterns were observed for a wide range of discharge parameters. For similar gas pressures and discharge powers, the number of spokes in the RFMS regime was always larger than in the DCMS regime. The number of spokes changed sequentially with the increasing working gas pressure for both magnetron operations. In the DCMS regime, a single spoke was observed at the lowest argon pressure (0.25 Pa) and a second spoke was observed only at the highest pressure (2 Pa). In the same pressure range, the plasma in the RFMS regime displayed four spokes at the lowest pressure and six or seven spokes at the highest pressure. The influence of discharge power on the number of spokes was less pronounced for both magnetron regimes. Spoke patterns were analyzed by examining the inelastic collisions between electrons and argon atoms. For this purpose, we simulated the dissipation of electron energy in the drift direction and compared the calculations to the length and number of spokes for particular discharge conditions. Overall, the simulations agree well with the observed plasma patterns in DCMS and RFMS.

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[3] M. Panjan *et al.*, *Plasma Sources Sci. Technol.*, **24** (2015) 065010

[4] M. Panjan accepted for publication in *J. Appl. Phys.* (2019)

**9:00am SE+PS-ThM4 Study of High Power Pulsed Magnetron Sputtering Discharge with Positive Bias on the Target after the Main Pulse, Ivan Shchelkanov, T.J. Houlahan, J. McLain, I.F. Haehnlein, B.E. Jurczyk, R. Stubbers,** Starfire Industries LLC; **D.E. Barlaz, D.N. Ruzic,** University of Illinois at Urbana-Champaign

Low-pressure magnetron sputtering is a well-established industry standard for high quality thin film deposition. Among different types of magnetron sputtering, High Power Pulsed Magnetron Sputtering (HPPMS), also called High Power Impulse Magnetron Sputtering (HIPIMS), offers the highest ion fraction of sputtered material, which dramatically increases the options available for thin film synthesis. The highly ionized sputtered material assists in multilayer film growth leading to more adhesive, dense, and smoother films as compared to conventional DC Magnetron Sputtering (dCMS) techniques, without the need for extra plasma-assisting elements and techniques in the process. Unfortunately, HPPMS typically suffers from low deposition rates as compared to dCMS[1]. Various attempts have been made to overcome this drawback, among them are: more efficient magnetic field configurations [2-6], HPPMS operation with extreme target conditions [7,8], or the application of a pulsed positive bias onto the sputtered target to control the plasma potential after the main HPPMS pulse [9]. Operation with a positive voltage KICK at the end of the main HPPMS pulse allows for the deposition of multilayer coatings onto a cold, grounded substrate with better adhesion than is typical of a simple HPPMS discharge. Furthermore, for grounded substrates positioned at glancing angles with respect to the sputtered magnetron cathode, the deposited coatings exhibit a very dense structure and great adhesion to the substrate even when deposited onto the inside wall of high aspect ratio vias. To fully understand limits, effects, and drawbacks of the positive KICK, its influence on plasma parameters, deposition rate, coatings structure, and adhesion are discussed.

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[7] A.V.Tumarkin, *et al.*, *Surface and Coatings Technology*. 2016. Vol. 293. P. 42-47

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[8] A.V.Kaziev et al., Surface and Coatings Technology. 2016. Vol. 293. P. 48–54

[9] B. Wu et al., Vacuum, Volume 150, Page 216-221 (2018)

9:20am **SE+PS-ThM5 Innovative PVD Strategies for the Design of Novel TiO<sub>2</sub>-based Photoanode Utilized in Dye-sensitized Solar Cells**, *Rony Snyders*, University of Mons, Belgium

INVITED

In view of the environmental challenges that our societies face, it is accepted that the development of alternative and renewable energy sources is a must. If solar energy is recognized as one of the most promising, it is still necessary to improve the solar cell technologies. Among others, Dye Sensitized Solar Cells (DSSC) are often seen as one of the ideal technological approach if several issues are fixed. One of the key problem associated with the implementation of these cells if related to the photoanode performances, specifically in terms of charge transport. Indeed, the standard photoanode based on TiO powder often exhibit a too high electrical resistivity associated with the intrinsic properties of the material.

During the past years, we have worked on the development of alternatives TiO<sub>2</sub>-based material in order to solve the encountered problems. More precisely we have studied the growth of (N-doped) nano-sculpted TiO<sub>2</sub> films by using reactive magnetron sputtering in glancing angle deposition. Concerning the doping, co-reactive deposition as well as ion implantation have been evaluated. All samples have been thoroughly characterized by state-of-the-art techniques and, for most of them, tested in DSSCs.

The results demonstrate that our approach is versatile allowing to control the morphology of the TiO<sub>2</sub> films at the nanoscale, and therefore to tune the capability of the material to adsorb the active dye. Specifically, we showed that a combination of our films with conventional TiO<sub>2</sub> nanoparticles could be a promising approach. In addition, we also demonstrate that the phase constitution of the nano-sculpted films can be optimized in the form of a core-shell anatase/rutile structure in order to improve the charge transport. On the other hand, the study of the N doping reveals that it is possible to finely control the position of the N atom (substitutional vs interstitial) as a function of the experimental parameters. In this context, we demonstrated that the O vacancies density favor the substitutional doping. Finally, we even showed that p type TiO<sub>2</sub>:N films presenting good electrical and optical properties can be synthesized. This last result is of particular interest for the development of “full TiO<sub>2</sub>” tandem DSSCs.

11:00am **SE+PS-ThM10 Enhancing the Far Ultra-Violet Optical Properties of Aluminum Mirrors with a Single Step Approach to Oxide Removal and Fluorine Passivation**, *David Boris*, U.S. Naval Research Laboratory; *A.C. Kozen, S.G. Rosenberg*, American Society for Engineering Education (residing at U.S. Naval Research Laboratory); *J. del Hoyo, J.G. Richardson, M.A. Quijada*, NASA Goddard Spaceflight Center; *S.G. Walton*, U.S. Naval Research Laboratory

Astronomical measurements in the Far Ultra-Violet (FUV, 90-200nm) require the use of aluminum thin films due to aluminum’s high reflectivity over this wavelength range. Unfortunately, the native aluminum oxide layer formed in atmosphere is strongly absorbing in this wavelength range, requiring that the aluminum films be passivated with a dielectric that inhibits oxidation. Due to the fast oxidation of aluminum, a simultaneous etch and deposition process is desirable to both eliminate the native aluminum oxide after growth and replace it with a different passivation coating layer. Optical measurements in the FUV range are some of the most challenging due to limited selection of low reflectivity coatings available for use on aluminum thin films. Typically magnesium fluoride (MgF<sub>2</sub>) or lithium fluoride (LiF) coatings are used for these passivation purposes but each has its problems. MgF<sub>2</sub> has an absorption cutoff at 115 nm occluding a critical part of the FUV spectrum. LiF has a lower absorption cutoff at 102.5 nm, but is hygroscopic and thus susceptible to degradation in ambient conditions. A promising alternative to these coating materials is AlF<sub>3</sub>, which theoretically can provide reflectivity greater than 50% down to 100 nm if the coating is sufficiently thin. In this work, we explore the use of electron beam generated plasmas to simultaneously etch the native oxide layer from aluminum thin films while depositing an AlF<sub>3</sub> capping layer to passivate the aluminum metal reflector. XPS measurements indicate that this approach is capable of producing very thin (<5 nm) AlF<sub>3</sub> films with some mild (<10%) oxygen contamination. We will discuss the impact of plasma power, plasma chemistry, and plasma exposure time on the composition and structure of the passivation layer and how those parameters effect the optical properties. This work is partially supported by the Office of Naval Research, the Naval Research Laboratory base program,

and NASA Strategic Astrophysics Technology (SAT) grant No. NNH177ZDA001N

11:20am **SE+PS-ThM11 Improving the Crystallinity of Inorganic Coatings Synthesized by Atmospheric Plasma using a New Device for Heating the Substrate**, *Antoine Remy, M.S. Fall, F. Reniers*, Université Libre de Bruxelles, Belgium

The deposition of good quality crystalline inorganic coatings by atmospheric pressure dielectric barrier discharge remains a challenge. Thanks to an original coupling of a substrate heating device based on an inductive current loop and located under the dielectric and an atmospheric pressure dielectric barrier discharge, we show that one can deposit in one step crystalline vanadium oxide and titanium oxide, with grain sizes bigger than those achieved by post-deposition annealing. As case study, vanadium oxide and titanium oxide are chosen. The respective precursors (vanadium oxytriisopropoxide - VOTP and titanium tetraisopropoxide – TTIP) are injected as vapors in a home made reactor with argon acting as carrier gas and main plasma gas. Oxygen is injected as reactant in the chamber. The DBD operates using a G10S-V AFS generator, at a frequency of 19 kHz, and with an injected power comprised between 0 and 80 W. The heating unit consists in a inductively coupled device located under the bottom electrode and dielectric and a susceptor place between the substrate and the dielectric. Thanks to a modified design of the bottom electrode, the induction loop does not heat said electrode, but the Eddy current heats only the susceptor, and the substrate. It is shown that this device allows the direct synthesis of crystalline orthorhombic V<sub>2</sub>O<sub>5</sub> at 300°C, and of anatase TiO<sub>2</sub> at 400°C. A comparison with coatings deposited at room temperature and annealed at 300 and 400°C respectively shows that the coatings deposited on the heated substrate exhibit larger grain sizes. This original combination of an atmospheric pressure plasma DBD and a device to heat inductively the substrate shows that one can obtain good crystallinity for inorganic coatings, and opens potentially new opportunities for the deposition of such coatings by atmospheric plasma.

11:40am **SE+PS-ThM12 Improved Nitride Formation on Titanium Substrates by Femtosecond Laser Processing with Secondary Plasma**, *Jeremy Mettler, D.E. Barlaz*, University of Illinois at Urbana-Champaign; *B.E. Jurczyk*, Starfire Industries LLC; *D.N. Ruzic*, University of Illinois at Urbana-Champaign

We discuss the development of a plasma-enhanced, laser-induced surface conversion process for forming TiN, a common coating favored for its hardness and corrosion resistance. This process uses a pulsed femtosecond laser to provide localized energy deposition at the Ti surface, along with a secondary plasma to supply reactive N species. This method allows the surface conversion to be conducted in a single pass, rather than requiring a pretreatment step in Ar atmosphere for oxygen removal. The nitrogen radicals react preferentially where the laser provides sufficient energy to cause conversion of the native oxide layer. The conversion efficiency was investigated for DC and RF plasmas, as well as for different plasma powers, pressures, N precursors, and sample biases. Preliminary results with no secondary plasma achieved surface conversions of up to 9% TiN, measured using XPS. The inclusion of a secondary plasma provides a marked improvement over this previous result, both in terms of oxide removal and nitride formation. Laser powers for this work were between 3-5 W. A Langmuir probe diagnostic was used to compare plasma density at different powers (on the order of 100 W) and for different compositions.

12:00pm **SE+PS-ThM13 Characterizing the Spatially Dependent Properties of Plasma Polymerized Acrylic Acid Films**, *Karyn Jarvis, S.L. McArthur*, Swinburne University of Technology, Australia

Plasma polymer films have been deposited on planar surfaces for a wide variety of applications, such as controlling cell growth or adding linker molecules for biosensors. They can however also be deposited onto three dimensional objects, such as tissue engineering scaffolds, biomedical implants or 3D printed devices. Coating three dimensional objects however is more complex as greater monomer fragmentation occurs closer to the electrode. It is therefore important to understand the properties of the plasma polymer films that will be deposited when a sample is different distances from the electrode. The use of plasma polymer films in biomedical applications also requires suitably stable films under physiological conditions, which will also be influenced by the distance from the electrode. Significant changes in film properties in aqueous conditions have serious implications on the incorporation of these films in biomedical devices.

Acrylic acid is a commonly used monomer for plasma polymerization to produce negatively charged carboxylic acid terminated surfaces, which



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have been used for a number of biomedical applications by manipulating cell growth. To gain a greater understanding of the spatially dependent behavior of plasma polymerized acrylic acid (ppAAc) films deposited in our custom-built stainless steel T-shaped reactor, ppAAc films were deposited at varying distances from the electrode (30 – 190 mm) at different deposition powers (5 – 80 W). The surface chemistry was analysed with X-ray photoelectron spectroscopy (XPS) while the film thickness was determined using spectroscopic ellipsometry. Aqueous stability was determined via immersion in Milli-Q. The film thicknesses decreased while the carboxyl group concentrations increased as the distance from the electrode increased and/or the deposition power decreased due to reduced monomer fragmentation further from the electrode and at lower powers. The aqueous stability of the films deposited further from the electrode increased as the deposition power increased. At 10 W, the film 30 mm from the electrode showed no decrease in film thickness after aqueous immersion while the films deposited 110 and 190 mm from the electrode were completely removed. Minimal film loss for the films deposited at 110 mm required a deposition power of 30 W while 60 W was required for minimal film loss for films deposited at 190 mm from the electrode. This work highlights the importance of having a spatially well characterized plasma reactor to enable the deposition of plasma polymer films with the desired properties, which has significant implications on the incorporation of these films into a number of applications.

## Advanced Surface Engineering Division Room A215 - Session SE-ThA

### New Challenges and Opportunities in Surface Engineering

**Moderators:** Jolanta Klemberg-Sapieha, Polytechnique Montreal, Matjaz Panjan, Jozef Stefan Institute, Slovenia

2:20pm **SE-ThA1 Evaluating Electro-Mechanical Reliability using In-Situ Methods**, *M.J. Cordill, O. Glushko*, Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria; *Patrice Kreiml*, Montanuniversitaet Leoben Erich Schmid Institute for Materials Science, Austria

**INVITED**

Electrical, mechanical and interfacial properties of thin metal films on compliant polymer substrates are important to understand in order to design reliable flexible electronic devices. Thin films of Cu and Au on polyimide and polyethylene terephthalate substrates were examined for their use as interconnects in flexible electronic devices. Using in-situ tensile straining with atomic force microscopy (AFM), X-ray diffraction (XRD), and confocal laser scanning microscopy (CLSM) mechanical and interfacial behavior can be examined. AFM and CLSM can provide information about crack spacing and film delamination, while XRD experiments are utilized to determine the lattice strains and stresses present in the films. If these in-situ techniques are combined with in-situ 4-point-probe (4PP) resistance measurements, the influence of the mechanical damage on the electrical properties can be correlated. This combination of multiple in-situ investigations are particularly useful when studying the electro-mechanical behavior under cyclic loading conditions where some materials can have an improvement of the electrical conductivity after a few hundred cycles. Mechanism behind these phenomena as well as methods to measure the adhesion of metal-polymer interfaces found in flexible electronic devices will be discussed.

3:00pm **SE-ThA3 Surface Engineering for Bearing Applications: Present Status and (Near)-Future Needs**, *Esteban Broitman*, SKF - RTD - Research & Technology Development Center, Netherlands

**INVITED**

Machines with rotating components usually rely on bearings to reduce friction in moving its parts around a fixed axis. The increasing demand for more precise bearings to lower power consumption and heat generation, while simultaneously support increasing applied loads and/or higher speeds, has given place to the use of surface engineering processes.

In the case of bearings, it is widely accepted the advantages of using coatings as the surface process to improve its performance. During the last three decades, advanced coatings have enjoyed a growing interest in several industrial applications because they can be engineered to provide different properties like electrical insulation, low friction, and resistance to corrosion, surface initiated rolling contact fatigue, abrasive wear, and plastic deformation. The main surface engineering processes to deposit these coatings include traditional technologies such as dipping and liquid spraying, chemical conversion, galvanizing and electroless processes, as well as more sophisticated technologies such as thermal spraying, physical vapor deposition, diffusion, and ion implantation. However, the special characteristics of the bearing steel and the need to limit the deposition costs reduce the number of methods that can be practically used.

In this talk I will first introduce the four main areas where coatings can contribute to improve the performance of bearings made of standard bearing steel: lower friction, decreased wear, corrosion resistance, and electrical insulation. For each area I will review which coatings are industrially used, their possible industrial deposition methods, and their main mechanical and tribological properties. Examples of SKF coatings used to extend maintenance and life expectancy of specialized bearings will be described, like NoWear® (carbon-based nanostructured coating), Black Oxide (iron oxide conversion film), INSOCOAT® (aluminum oxide coating), and manganese phosphate films. I will finish the presentation visioning which the (near)-future needs of specialty surface-treatment coatings are in response to bearing application challenges, including a novel fifth area of sensorized coatings.

4:00pm **SE-ThA6 In situ Scanning Electron Microscopy based Uniaxial Compression of sub-micrometer-size NbC(100) Single-crystalline Pillars**, *A. Aleman, K. Tanaka, H. Zaid, J.-M. Yang, Suneel Kodambaka*, University of California, Los Angeles

Cubic group 4 and 5 transition-metal carbides (TMCs), such as HfC and TaC, are hard (>20 GPa) and strong (moduli >270 GPa) solids with high melting

points (> 2900 K) that exhibit superior strengths at elevated temperatures and excellent resistance to wear, ablation, and corrosion. They are attractive for applications in cutting tools, hard protective coatings, advanced propulsion systems, spacecrafts, rockets, and hypersonic jets that operate under extreme environments, e.g. at ultra-high temperatures (> 2000 K) and highly corrosive atmospheres. The realization of enhanced ductility, especially at low temperatures could potentially enable new applications for this class of materials. Our recent efforts have focused on understanding the mechanical behavior of group 5 TMC single-crystals, VC, NbC, and TaC.

Here, we report on the room-temperature mechanical behavior of 100-oriented NbC single-crystalline pillars of diameters between 330 and 830 nm. We prepared the pillars via focused ion beam milling of bulk, commercially-available, NbC single-crystals. We carried out uniaxial compression of the pillars using Hysitron PI-85 picoindenter *in situ* in a scanning electron microscope. We find that all the pillars exhibit plastic deformation with strains up to 26%. Load-displacement curves obtained during the compression tests reveal multiple displacement bursts, indicative of sustained slip. Interestingly, yield strengths vary non-monotonically with pillar diameter between 8 GPa and 12 GPa and by up to 40% among the pillars of the same diameter. From the post-compression images of the pillars, we identify {110}<110> and {111}<110> as the two likely slip systems operating within these pillars. We suggest that the observed size-dependence in NbC(100) pillars is a consequence of the activation of these two slip systems. We observe a similar size-dependence in VC(100) pillars based upon which we suggest that the observed mechanical behavior is characteristic of group 5 TMCs.

4:20pm **SE-ThA7 Thermal Stability of MoNbTaVW High Entropy Alloys Thin Films Deposited by Cathodic Arc**, *A. Xia, Robert Franz*, Montanuniversität Leoben, Austria

High entropy alloys (HEAs) are a new emerging class of materials typically consisting of 5 to 13 metallic elements in an approximately equimolar ratio. Studies conducted on HEA bulk materials revealed promising combinations of properties, such as high strength, ductility, corrosion resistance, wear resistance, hardness, low diffusion and thermodynamic stability. While research on bulk high entropy alloys has seen quite a boost over the past years, investigations on thin films are still a relatively unexplored area.

Within the current work, the thermal stability of refractory MoNbTaVW HEA thin films was studied up to an annealing temperature of 1600 °C. The thin films with a thickness of about 1 µm were synthesized on sapphire substrates by cathodic arc deposition. The samples were annealed in a vacuum furnace for 1 hour at temperatures ranging from 1000 to 1600 °C in steps of 100 °C. After annealing, scanning electron microscopy images were recorded indicating changes in the film morphology at 1200 °C and above. Analysis by X-ray diffraction revealed the formation of new phases at 1500 °C. Nanoindentation tests were performed to assess possible changes in the mechanical properties of the films. A decrease from about 20 GPa for the as-deposited films to about 9 GPa after annealing at 1600 °C was noticed. The electrical conductivity of the MoNbTaVW thin film slightly decreased due to annealing as the measured resistivity increased from 5·10<sup>-7</sup> Ωm to 1.5·10<sup>-6</sup> Ωm.

4:40pm **SE-ThA8 Erosion Resistant Coatings Inside Narrow Tubes to Protect Aircraft Engine Components**, *A. Kilicaslan, O. Zabeida, E. Bousser, L. Martinu, Jolanta Klemberg-Sapieha*, Polytechnique Montreal, Canada

There is an ever-growing interest in the use of functional coatings to protect surfaces of materials and workpieces against harsh environments such as corrosion, abrasion or solid particle erosion (SPE), making surface engineering solutions a very attractive balance between performance and cost. Numerous vapor-based fabrication techniques have been developed, namely PVD, CVD and PECVD, that can be used to achieve high hardness and high wear resistance, while being compatible with substrate materials such as metals, and different substrate shapes. This is increasingly important in the case where there is a need for protective coating solutions for inner surfaces of tubular components, such as parts of aircraft engines, oil pipelines, mining components, and numerous others. Specifically, certain aircraft diffusers are designed to conduct the air to the combustion chamber by means of many narrow gas inlets arranged around a circular frame. In such case, SPE arising from dust particles and volcanic ashes present in the air can result in an increase of the gas inlets diameter, leading to back streaming of air into the compressor (known as the compressor surge), which can give rise to significant aircraft engine damage and catastrophic consequences.

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In response, we propose a novel Non-Line-Of-Sight (NLOS) technique to coat the inner parts of non-linear surfaces and cavities with hard, wear- and erosion-resistant coatings possessing high erosion resistance, hardness significantly higher than the hardness of the particles impacting the surface, as well as a large thickness (preferably 8  $\mu\text{m}$  and more).

Specifically, we review, study and demonstrate the fabrication process of hard SPE-resistant TiN protective coatings on the inner surfaces of narrow tubes using a non-obvious NLOS approach yielding a uniform film thickness and properties along the tube axis (better than 20%). The deposition process indicates the importance of applying pulsed-DC PECVD, when uniform hard TiN films are prepared at low-frequency in the several kHz range. The TiN films (about 12  $\mu\text{m}$  thick), exhibit high hardness and Young's modulus (25 and 225 GPa, respectively), corresponding to the (111) preferred crystallographic orientation. We show that the SPE resistance on the inner surface decreased by a factor of more than 15 compared to the bare substrate, and that the process is well suited for the protection of aerospace, manufacturing, 3D printed and other critical components with a complex shape of inner surfaces.

## Surface Science Division

### Room A220-221 - Session SS+2D+AP+AS+OX+SE-ThA

#### Dynamics at Surfaces/Reactions and Imaging of Oxide Surfaces

**Moderators:** Irene Groot, Leiden University, The Netherlands, William E. Kaden, University of Central Florida

2:20pm **SS+2D+AP+AS+OX+SE-ThA1 Adsorption, Reaction, and Diffusion of Energetic Reagents on Morphologically Diverse Thin Films, Rebecca Thompson<sup>1,2</sup>**, M.R. Brann, S.J. Sibener, The University of Chicago

I present work from two studies illustrating the impact of condensed-phase film morphology on reaction kinetics and surface adsorption. To begin, I will discuss the **oxidative reactivity of condensed propene films**. This work is conducted in a state-of-the-art ultra-high vacuum chamber equipped for operation at cryogenic substrate temperatures. Time-resolved reflection absorption infrared spectroscopy (RAIRS) is used to track propene reactivity when films are exposed to a supersonic expansion of ground state oxygen atoms,  $\text{O}(^3\text{P})$ . I demonstrate that propene reacts significantly on exposure, producing primarily propylene oxide and propanal. Oxide production is significant; partial oxidation products are rarely observed in gas phase studies and olefin oxides are incredibly important chemical intermediates in a variety of industrial processes. Regardless of initial film thickness, the reaction follows zero order kinetics, with a calculated activation energy of 0.5 kcal mol<sup>-1</sup>. This low barrier closely matches that reported in gas phase studies, suggesting that the condensed-phase reaction is likely diffusion-limited. I also highlight that the propene deposition temperature has a substantial impact on reactivity. Films deposited below 50 K produce dramatically different RAIR spectra that correspond to a more amorphous film composition. These films are nearly unreactive with  $\text{O}(^3\text{P})$ , indicating that oxygen diffusion is directly tied to the density and ordering in the more crystalline film.

This dependence on film structure is also observed in the second study, which explores **embedding in and adsorption on crystalline, non-porous amorphous, and porous-amorphous water ice films**. Using a combination of supersonic molecular beams, RAIRS and King and Wells mass spectrometry techniques, I demonstrate that direct embedding into the bulk is remarkably insensitive to film structure; the momentum barrier is identical between amorphous and porous-amorphous ice films. Below this barrier, however, sticking probabilities differ considerably between the different films, suggesting that the pore structure is more efficient at dissipating incident energy. These discoveries are critical for the accurate quantitative modeling of molecular uptake and reactivity on icy astrophysical bodies such as comets and planetesimals. When taken together, these two studies provide fundamental mechanistic insight into the sticking, diffusion, and reactivity of small molecules on complex films, with a specific emphasis on the impact of film morphology and organization.

2:40pm **SS+2D+AP+AS+OX+SE-ThA2 Oxidation of Semiconductors and Semimetals by Supersonic Beams of  $\text{O}_2$  with Scanning Tunneling Microscopy Visualization, Ross Edel<sup>3</sup>, T. Grabnic, B. Wiggins, S.J. Sibener**, The University of Chicago

Our research examines the oxidation of semiconductor and semimetal surfaces using a novel, one-of-a-kind instrument that combines a supersonic molecular beam with an in-line scanning tunneling microscope (STM) in ultra-high vacuum. This new approach to surface reaction dynamics provides spatiotemporal information on surface oxidation over nanoscopic and mesoscopic length scales. We have uncovered the kinetic and morphological effects of oxidation conditions on three technologically relevant surfaces: Si(111)-7 $\times$ 7, highly oriented pyrolytic graphite (HOPG), and GaAs(110). A complete understanding of the oxidation mechanism of these surfaces is critical due to their technological applications and roles as model systems. Samples were exposed to  $\text{O}_2$  with kinetic energies from 0.4-1.2 eV and impingement angles 0-45° from normal, with STM characterization between exposures. In some cases, we were able to monitor the evolution of specific features by revisiting the same nanoscopic locations. Our study of Si(111)-7 $\times$ 7 revealed two oxidation channels, leading to the formation of dark and bright reacted sites. The dark sites dominated the surface and exhibited almost no site selectivity while the bright sites preferred the corner sites of the 7 $\times$ 7 unit cell. Our observations suggest that two adsorption pathways, trapping-mediated and direct chemisorption, occur simultaneously. On HOPG, we found that different oxygen energies, incident angles, and surface temperatures produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. Finally, oxidation of GaAs(110) was found to proceed by two morphologically distinct, competing mechanisms: a homogeneous process leading to layer-by-layer oxide growth, and a heterogeneous process with oxide islands nucleating from surface defects. The rates of both mechanisms change with  $\text{O}_2$  kinetic energy, with homogeneous oxidation dominating at lower energies (<0.7 eV) and heterogeneous oxidation with higher energies ( $\geq 1.0$  eV). The results obtained in this work provide vital information about the morphological evolution and kinetics of semiconductor and semimetals, offering a comprehensive overview of the spatiotemporal correlations that govern oxidation dynamics on surfaces.

3:00pm **SS+2D+AP+AS+OX+SE-ThA3 Studying Molecule-Surface Interactions using Rotational Orientation Control of Ground-State Molecular Beams, Gil Alexandrowicz**, Swansea University, UK **INVITED**

Performing quantum state selective experiments of molecule-surface collisions provides unique insight into the interaction potential. One particularly tricky molecular property to control and measure is the rotational projection states, i.e. the orientation of the rotational plane of the molecule. Previous data was mostly restricted to photo-excited/paramagnetic species. In this talk, I will describe the molecular beam apparatus which allows to control and measure the rotational orientation of ground state molecules [1], present new experimental results for  $\text{H}_2$  colliding with ionic surfaces and discuss the future of this new technique in terms of studying molecule-surface interaction-potentials and modifying the outcome of reactive molecule-surface collisions.

[1] Nature Communications, 8, 15357 (2017).

4:00pm **SS+2D+AP+AS+OX+SE-ThA6 Diffusion of (100)-epitaxially Supported 3D fcc Nanoclusters: Complex Size-dependence on the Nanoscale, King Chun Lai, J.W. Evans**, Iowa State University

Diffusion of supported 3D nanoclusters (NCs) followed by coalescence leads to coarsening of ensembles of supported NCs via Smoluchowski Ripening (SR) which is a key pathway for degradation of supported metal catalysts. The dependence of the NC diffusion coefficient,  $D_N$ , on size  $N$  (in atoms) is the key factor controlling SR kinetics, and traditional treatments assumed simple monotonic decrease with increasing size. We analyze a stochastic model for diffusion of (100)-epitaxially supported fcc NCs mediated by diffusion of atoms around the surface of the NC. Multiple barriers for surface diffusion across and between facets, along step edges, etc. are chosen to accurately describe Ag [Lai and Evans, Phys. Rev. Materials 3 (2019) 026001]. KMC simulations reveal a complex oscillatory variation of  $D_N$  with  $N$ . Local minima  $D_N$  sometimes but not always correspond to  $N = N_c$  where the equilibrium Winterbottom NC structure is a closed-shell. Local maximum generally correspond to  $N = N_c + 3$ . The

<sup>1</sup> Morton S. Traum Award Finalist

<sup>2</sup> National Student Award Finalist

<sup>3</sup> National Student Award Finalist

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oscillatory behavior is expected to disappear for larger N above  $O(10^2)$ . Behavior has similarities to but also basic differences from that for 2D supported NCs [Lai et al Phys. Rev. B 96 (2017) 235406]. Through detailed analysis of the energetics of the 3D NC diffusion pathway (which involves dissolving and reforming facets), we can elucidate the above behavior as well as observed trends in effective diffusion barrier.

**4:20pm SS+2D+AP+AS+OX+SE-ThA7 Oxide Surface Formation on Rh Nanoparticle during O<sub>2</sub> Exposures Observed by Atom Probe Microscopy, Sten Lambeets**, Pacific Northwest National Laboratory; *T. Visart de Bocarmé*, Université Libre de Bruxelles, Belgium; *N. Kruse*, Washington State University; *D.E. Perea*, Pacific Northwest National Laboratory

Metallic surfaces may undergo a series of surface and subsurface structural and chemical transformations while exposed to reactive gases that inevitably change the surface properties. Understanding such dynamics from a fundamental science point of view is an important requirement to build rational links between chemical/structural surface properties and design new catalysts with desired performance or new materials with enhanced resistance to corrosion. The research presented here addresses the early oxide formation dynamics on a rhodium (Rh) single nanoparticle during O<sub>2</sub> exposures and reveals the inter-facet cooperation between Rh{012} and Rh{113} facets, as well as the important role that the subsurface plays.

Field Ion and Field Emission Microscopies (FIM and FEM) enable correlative atomic to nanoscale imaging of the surface of a very sharp Rh needle, the apex size and shape of which models that of a Rh nanoparticle. FIM is used to map, with atomic lateral resolution, the Rh surface revealing a complex network of crystallographic facets, while FEM is used to observe and record O<sub>2</sub> dissociative adsorption and subsequent reaction with H<sub>2</sub> over this same surface of Rh in real-time with nano-scale lateral resolution. Since FEM imaging relies on local work function variations, it notably can be used to follow the fate of adsorbed oxygen atoms (O(ads)) on the Rh surface. As a result, we directly observe that the O<sub>2</sub> dissociative adsorption is mainly active on the Rh{012} regions. The application of Atom Probe Tomography (APT) provided a means to map the fate of the adsorbed oxygen leading to bulk oxide formation through Rh{113} facets. Thus the correlative combination of FIM, FEM, and APT provides unique insight into the mechanism of bulk oxide formation starting from the dissociative oxygen absorption occurring at {012} facets and subsurface penetration of the adsorbed oxygen occurring through {113} facets. leading to a preferential accumulation of the oxygen within the bulk along the [111] direction. This work offers a unique methodology to explore the interactions between the different crystal facets of a complex surface, to explore the complex dynamics linking the surface and the bulk, and finally, offers exciting perspectives leading to a better understanding of heterogeneous catalysis and corrosion dynamics.

**4:40pm SS+2D+AP+AS+OX+SE-ThA8 Noncontact AFM on Oxide Surfaces: Challenges and Opportunities, Martin Setvin**, TU Wien, Austria **INVITED**

Recent development of the noncontact atomic force microscopy (nc-AFM) has opened new possibilities in different fields – imaging of organic molecules [1], controlling the charge state of adsorbed species [2], or enhanced chemical resolution of surface atoms [3]. I will focus on the emerging possibilities and opportunities in the field of oxide surfaces and their surface chemistry.

The limits of atomic resolution will be illustrated on clean and water-exposed binary oxides like TiO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> or iron oxides. The enhanced chemical resolution of nc-AFM offers a unique opportunity for approaching complex materials with ternary chemical composition. This will be demonstrated on bulk-terminated perovskites SrTiO<sub>3</sub> and KTaO<sub>3</sub>. A dedicated cleaving procedure [4,5] allows preparing flat regions terminated by domains of SrO/TiO<sub>2</sub> (or KO/TaO<sub>2</sub>) with a well-defined atomic structure. The surface stability, point defects, electronic structure, and chemical properties of such surfaces will be discussed and linked to the incipient-ferroelectric character of these materials.

[1] Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G., *Science* 2009, 325, 1110

[2] Gross, L.; Mohn, F.; Liljeroth, P.; Repp, J.; Giessibl, F. J.; Meyer, G., *Science* 2009, 324, 1428

[3] Sugimoto, Y.; Pou, P.; Abe, M.; Jelinek, P.; Perez, R.; Morita, S.; Custance, O., *Nature* 2007, 446, 64

[4] I. Sokolovic, M. Schmid, U. Diebold, M. Setvin, *Phys. Rev. Materials* 3, 034407 (2019)

[5] M. Setvin, M. Reticcioli, F. Poelzeleitner, J. Hulva, M. Schmid, L. A. Boatner, C. Franchini, U. Diebold, *Science* 359, 572-575 (2018)

**5:20pm SS+2D+AP+AS+OX+SE-ThA10 Edge-Enhanced Oxygen Evolution Reactivity at Au-Supported, Ultrathin Fe<sub>2</sub>O<sub>3</sub> Electrocatalysts, Xingyi Deng**, D. Kauffman, D.C. Sorescu, National Energy Technology Laboratory

Transition metal oxides have been emerging as promising candidates to replace the state-of-the-art IrO<sub>2</sub> electrocatalysts for oxygen evolution reaction (OER) in alkaline electrolyte, but their key structure-property relationships are often shadowed by heterogeneities in the typical catalyst samples. To circumvent this challenge, we have combined ultrahigh vacuum surface science techniques, electrochemical measurements, and density functional theory (DFT) to study the structure-dependent activity of well-defined OER electrocatalysts. We present direct evidence that the population of hydroxylated Fe edge-site atoms correlates with the OER activity of ultrathin Fe<sub>2</sub>O<sub>3</sub> nanostructures (~0.5 nm apparent height) grown on Au(111) substrates, and the Fe<sub>2</sub>O<sub>3</sub>/Au catalysts with a high density of edge sites can outperform an ultrathin IrO<sub>x</sub>/Au OER catalyst at moderate overpotentials. DFT calculations support the experimental results, showing more favorable OER at the edge sites along the Fe<sub>2</sub>O<sub>3</sub>/Au interface with lower predicted overpotentials resulted from beneficial modification of intermediate binding. Our study demonstrates how the combination of surface science, electrochemistry, and computational modeling can be used to identify key structure-property relationships in a well-defined electrocatalytic system.

# Thursday Evening Poster Sessions, October 24, 2019

**Advanced Surface Engineering Division  
Room Union Station B - Session SE-ThP**

## **Advanced Surface Engineering Poster Session**

**SE-ThP2 Plasma and Heat Treatment Response of Carborane Self-Assembled Monolayer on Copper, *Rupak Thapa, L. Dorsett, S. Malik, R. Bale, S. Wagner, D. Bailey, A.N. Caruso***, University of Missouri-Kansas City; *J.D. Bielefeld, S.W. King*, Intel Corporation; *M.M. Paquette*, University of Missouri-Kansas City

Self-assembled monolayers (SAMs) have a wide variety of applications. These include modifying the properties of metal surfaces to act as protective layers or to enable molecular recognition for sensors. Here, we investigate copper surfaces modified by thiol-carborane SAMs. We use carborane-based boron carbide due to its excellent chemical, thermal, and mechanical properties along with its symmetrical icosahedral shape and capacity to cross-link under the influence of heat or plasma. It has been shown that carborane-based SAMs provide better corrosion resistance on silver and have the ability to change the electronic properties (e.g., work function) of gold and silver. Here, we investigate the influence of plasma and heat on carborane SAMs on copper using in situ ellipsometry, in situ x-ray photoelectron spectroscopy, and water contact angle measurements. We use various plasmas (N<sub>2</sub>, O<sub>2</sub>, and Ar) at different conditions (power, pressure, and time) to determine how these stabilize, degrade, and/or otherwise modify the SAMs. We also heat the samples to various temperatures and investigate their growth properties and thermal stability. Results suggest that SAMs based on 1,2-dithiol-o-carborane containing two thiol groups are more stable than those based on 9-thiol-m-carborane containing one thiol group.

## Chemical Analysis and Imaging Interfaces Focus Topic Room A226 - Session CA+AS+NS+SE+SS-FrM

### Novel Applications and Approaches in Interfacial Analysis

**Moderators:** Paul Dietrich, SPECS Surface Nano Analysis GmbH, Germany, Jeong Young Park, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

8:20am **CA+AS+NS+SE+SS-FrM1 Chemical Reactions on Bimetal Surfaces with Operando Surface Techniques, Jeong Young Park**, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea **INVITED**

The origin of the synergistic catalytic effect between metal catalysts and reducible oxide has been debated for decades. Clarification of this effect, namely the strong metal-support interaction (SMSI), requires an understanding of the geometric and electronic structures of metal-metal oxide interfaces under operando conditions.[1] A bimetallic platinum (Pt) alloy catalyst is an excellent platform to uncover the contentious role of the metal-metal oxide interface because the alloyed transition metal can coexist with the Pt surface layer in the form of an oxidized species on the bimetal surface during catalytic reactions.

**In this talk, I present in-situ observation results of structural modulation on Pt-Ni metastable and Ni (111) surfaces at 0.1 Torr pressure of CO, O<sub>2</sub>, and CO oxidation conditions with ambient-pressure scanning tunneling microscopy (AP-STM) and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS).[2] We show that the stable Pt-skin covered Pt<sub>3</sub>Ni(111) surface is broken by segregation of dissociative oxygen-induced Ni oxides under elevated oxygen pressure environment, which evolved clusters could have a crucial relation with enhanced catalytic activity. We show that NiO<sub>1-x</sub>/Pt-Ni nanostructures are on the Pt<sub>3</sub>Ni(111) surface under CO oxidation and these metal-oxide interfaces provide more efficient reaction path for CO oxidation [2]. Furthermore, I will show the research efforts for understand the catalytic behavior of bimetal PtCo and PtNi nanocatalysts using in-situ surface techniques including catalytic nanodiode and transmission electron microscopy. The catalytic nanodiode that consists of metal catalyst film, semiconductor layers, and Ohmic contact pads revealed the strong correlation between the hot electron flux (chemicurrent) and catalytic activity under CO oxidation and hydrogen oxidation. Using this approach, the catalytic activity and hot electron generation on PtCo bimetal nanoparticles were investigated. In-situ transmission electron microscopy reveals the formation of metal oxide layers on bimetal nanoparticle surfaces under oxygen conditions. We show that formation of interface between Pt and CoO enhances both of catalytic activity and chemicurrent yield [3].**

[1] J. Y. Park et al. Chemical Reviews 115, 2781-2817 (2015)

[2] J. Kim et al. Science Advances 4, eaat3151 (2018).

[3] H. Lee et al. Nature Communications 9, 2235 (2018).

9:00am **CA+AS+NS+SE+SS-FrM3 Principal Component Analysis to Reveal Camouflaged Information in Spectromicroscopy of (complex) Oxides, David Mueller, M. Giesen, Forschungszentrum Juelich GmbH, Germany; D. Stadler, University of Cologne, Germany; T. Duchon, F. Gunkel, V. Feyer, Forschungszentrum Juelich GmbH, Germany; S. Mathur, University of Cologne, Germany; C.M. Schneider, Forschungszentrum Juelich GmbH, Germany**

Spectroscopic imaging techniques are becoming more and more accurate and available, which results in an increase of data to handle and analyze. Near Edge X-Ray absorption spectroscopy, especially in the soft X-Ray regime, has the ability to identify inhomogeneities in chemistry and electronic structure, which is mostly done by fingerprinting or using internal standards. In a spectromicroscopic image, each pixel contains such a spectrum, and by the lack of rigorous fitting routines that are for example present in XPS, reduction and preevaluation of data is needed. Principal Component Analysis (PCA) of X-PEEM data affords this in an unambiguous and unbiased way by identifying and highlighting spectroscopic features which contribute to a spectrum.<sup>1</sup>

Two cases where PCA revealed information that might have been missed otherwise are presented here: Firstly, iron oxide thin films grown by CVD showed a considerable influence of an external magnetic field on chemistry and crystallinity. Combination of O-K- and Fe-L-Edge X-PEEM unambiguously identified different iron oxide polymorphs (Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) depending on field strength during deposition. The former XAS Edge showed subtle spatial variations in the EXAFS regime that could be

identified as the breakdown of long-range ordering, pointing to incomplete crystallization when films are deposited without magnetic field assistance.<sup>2</sup>

The second example is the surface decomposition of Pr<sub>0.5</sub>Ba<sub>0.5</sub>CoO<sub>3- $\delta$</sub>  (PBCO), a promising material for the use as water splitting catalyst and solid oxide electrochemical cell electrode. Using spatially resolved O-K-, Co-L-, and Ba- and Pr-M-Edge XAS, changes in surface chemical composition upon annealing and its impact on the electronic structure were observed. Laterally resolved by X-PEEM, PCA could reveal that exposing thin films of the material to technologically relevant conditions (1073 K, 20 mbar of O<sub>2</sub>) leads to a more complex decomposition pathway than simple spinodal unmixing to the end members BaCoO<sub>3</sub> and PrCoO<sub>3</sub> as the spectromicroscopic dataset could only be described satisfactory by a linear combination of three components.

9:20am **CA+AS+NS+SE+SS-FrM4 In situ Electron Microscopy of Catalysts with Atomic Resolution under Atmospheric Pressure, Xiaoqing Pan**, University of California Irvine **INVITED**

Understanding the atomic structures of catalysts under realistic conditions with atomic precision is crucial to design better materials for challenging transformations. For example, under reducing conditions, certain reducible supports migrate onto supported metallic particles and create strong metal-support states that drastically change the reactivity of the systems. The details of this process are still unclear and preclude its thorough exploitation. In the past decade, most of atomic-scale transmission electron microscopy (TEM) studies involving gas-solid interactions were conducted in an environmental TEM, where the gas pressure is typically limited to less than 1/100 of atmosphere. Recently, it has become possible to overcome this limitation through a MEMS-based, electron-transparent closed cell with a heating stage.

In this talk, I will present our recent results using this device (the Protophysics Atmosphere™ system) in selected catalyst systems. In a palladium/titania (Pd/TiO<sub>2</sub>) catalyst, we directly observed the formation of the oxide overlayers on the supported Pd particles with atomic resolution under atmospheric pressure and high temperature. It shows that an amorphous reduced titania layer is formed at low temperatures, and that crystallization of the layer into either mono- or bilayer structures is dictated by the reaction environment. This transition occurs in combination with a dramatic reshaping of the metallic surface facets. *In-situ* TEM observations of a modular Pd-ceria core-shell nanostructured catalyst (Pd@CeO<sub>2</sub>) showed that an unexpected structural transformation occurs upon heating at high temperatures. The system reaches to a stable state with the mixture of nanoparticles with two different sizes, which accounts for the exceptional catalytic properties that have been reported. Using the similar techniques, we also studied the core-shell platinum-metal (Pt-M) nanoparticles which show a catalytic performance in the oxygen reduction reaction (ORR) superior to that of pure Pt nanoparticles. To understand the formation mechanism of the Pt shell, we studied thermally activated core-shell formation in Pt<sub>3</sub>Co nanoparticles via *in-situ* electron microscopy with the gas cell. The disordered Pt<sub>3</sub>Co nanoparticle was found to transform into an ordered intermetallic structure after annealing at high temperature (725°C) in 760 Torr O<sub>2</sub>, followed by layer-by-layer Pt shell growth on (100) surfaces at low temperature (300°C). The apparent 'anti-oxidation' phenomenon promoted by the ordered Pt<sub>3</sub>Co phase is favorable to the ORR catalyst, which operates in an oxidizing environment.

10:00am **CA+AS+NS+SE+SS-FrM6 Exposing Buried Interfaces in Thin Film Photovoltaics through Thermo-mechanical Cleaving, Deborah McGott**, Colorado School of Mines; C.L. Perkins, W.K. Metzger, National Renewable Energy Laboratory; C.A. Wolden, Colorado School of Mines; M.O. Reese, National Renewable Energy Laboratory

Thin film solar cells, such as cadmium telluride (CdTe) and Cu(In,Ga)Se<sub>2</sub> (CIGS), contain buried interfaces that are critical to carrier transport, recombination, and device performance, yet are poorly understood due to their inaccessibility within the device stack. In particular, accessing the interface in a way that preserves the chemical structure has historically been extremely difficult. Here, we describe an innovative technique to expose buried interfaces through a two-step thermo-mechanical cleaving process. First, a stressor layer (typically an epoxy or commercially available polymeric backsheet) is applied to the solar cell. Then, the stack is submerged in a cold bath (T  $\leq$  -30°C) to thermally shock the system. This causes the stressor to contract quickly and pull the polycrystalline film cleanly off of its substrate at an interface that is weakened by a monolayer accumulation of 2-D material (CdCl<sub>2</sub> in CdTe and MoS<sub>2</sub> in CIGS).

Focusing on CdTe solar cells, we then use X-ray photoelectron spectroscopy to probe the oxidation states at the newly exposed SnO<sub>2</sub> interface. We

show that the tin oxide front electrode promotes the formation of nanometer-scale oxides of tellurium and sulfur. Most oxidation occurs during  $\text{CdCl}_2/\text{O}_2$  activation. Surprisingly, we show that relatively low-temperature anneals (180–260°C) used to diffuse and activate copper acceptors in a doping/back contact process also cause significant changes in oxidation at the front of the cell, providing a heretofore missing aspect of how back contact processes can modify device transport, recombination, and performance. Device performance is shown to correlate with the extent of tellurium and sulfur oxidation within this nanometer-scale region. Mechanisms responsible for these beneficial effects are proposed.

## 10:20am CA+AS+NS+SE+SS-FrM7 Switchable Dopants on Percolation Networks of 2D Materials for Chemiresistive Sensing Applications in Aqueous Environments, Peter Kruse, McMaster University, Canada

Permanent doping of semiconductors and low-dimensional structures to modulate their electronic properties is a well-established concept. Even in cases where doping of thin films by analytes (e.g. carbon nanotubes by ammonia) is applied in sensors, it is only reversed by physical removal of dopant molecules, e.g. heating. We have introduced the concept of molecular switches as chemical dopants for thin nanocarbon (or other 2D-materials) films. These molecules can be switched between doping and non-doping states in the presence or absence of a particular analyte. They impart selectivity not only due to their change in doping behavior, but also by physically blocking other potential dopants in the analyte solution from interacting with the conductive film. The resulting structures can act as chemiresistive films. Chemiresistive sensors are a well-established technology for gas-phase sensing applications. They are simple and economical to manufacture, and can operate reagent-free and with low or no maintenance. Unlike electrochemical sensors they do not require reference electrodes. While in principle they can be made compatible with aqueous environments, only a few such examples have been demonstrated. Challenges include the need to prevent electrical shorts through the aqueous medium and the need to keep the sensing voltage low enough to avoid electrochemical reactions at the sensor. We have built a chemiresistive sensing platform for aqueous media. The active sensor element consists of a percolation network of low-dimensional materials particles that form a conducting film, e.g. from carbon nanotubes, pencil trace, exfoliated graphene or  $\text{MoS}_2$ . The first member of that platform was a free chlorine sensor. We are currently working to expand the applicability of our platform to other relevant species, in particular anions and cations that are commonly present as pollutants in surface and drinking water. Our sensors can be incorporated into a variety of systems and will also be suitable for online monitoring in remote and resource-poor locations.

## 10:40am CA+AS+NS+SE+SS-FrM8 Analysis Of Radioactive Materials In Liquid Using In Situ Sem And Tof-Sims, Jennifer Yao, X.-Y. Yu, Z.H. Zhu, E.C. Buck, Pacific Northwest National Laboratory

Characterization of nuclear materials in solid particles or particles in liquid slurry, particularly in high level waste, can establish the elemental, organic, and isotopic compositions that effect the properties of the materials during nuclear fuel cycle activities and processes. Techniques to evaluate such detailed information, even at small concentrations, can support nuclear materials and science programs by increasing our ability to manage and control nuclear materials. However, radioactive materials analysis in liquids and slurries can be challenging using bulk approaches. We have developed a vacuum compatible microfluidic interface, system for analysis at the liquid vacuum interface (SALVI), to enable surface analysis of liquids and liquid-solid interactions using scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In this work, we illustrate the initial results from the analysis of liquid samples of importance in the geologic disposal of  $\text{UO}_2$  spent nuclear fuel in a repository environment using in situ liquid SEM and SIMS. Our results demonstrate that multimodal analysis of  $\text{UO}_2$  materials is possible using SALVI. Both in situ liquid SEM and SIMS can be used as new approaches to analyze radioactive materials in liquid and slurry forms of high level nuclear waste.

## 11:00am CA+AS+NS+SE+SS-FrM9 Interactions between Synthetic Bilgewater Emulsion and Biofilms, Jiyoung Son, Earth and Biological Sciences Directorate; J. Yao, Earth & Biological Sciences Directorate; X.-Y. Yu, Pacific Northwest National Laboratory

### Presentation Summary:

This presentation will showcase our latest results of the interaction between biofilms and synthetic bilgewater using a surface chemical imaging technique.

### Abstract

Bilgewater, an oil-in-water (O/W) emulsion, is a persistent pollutant released to the ocean from the lowest part of ships. Microbes play an important role in the ocean. It is hypothesized that microbes release organics that can act as surfactants that affect bilgewater formation or weakening. We present the first systematic study of emulsions and biofilms and investigate the effects of biofilms on bilgewater emulsions. Three strains were selected *Pseudomonas*, *Arthrobacter*, and *Cobetia marina*. A Navy O/W emulsion consisting of three oils and a detergent mixture was used as the synthetic bilgewater model [1]. Biofilms were cultured in a microchannel to allow healthy culture [2]. Once a thick layer of biofilms was formed, the medium solution was changed to a mixture consisting of 50 % bilgewater emulsion. Dispersed biofilms were collected at 24 hrs. and 48 hrs. after emulsions were introduced into the channel. Bilgewater emulsions, biofilms, and mixtures of bilgewater emulsions and biofilms were analyzed using multiple *in situ* and *ex situ* techniques including time-of-flight secondary ion mass spectrometry (ToF-SIMS), scanning electron microscopy (SEM), and optical microscopy. Our findings indicate that biofilms change the chemical makeup of the emulsion surface compositions and emulsion droplet size distribution, confirming the hypothesis that extracellular polymeric substance (EPS) related components released from biofilms can function as surfactants and change the oil-in-water interfaces.

**Key words:** bilgewater emulsion, oil-in-water, microfluidics, biofilm, EPS, surfactant

### Reference

1. Church, J., D.M. Paynter, and W.H. Lee, *In Situ Characterization of Oil-in-Water Emulsions Stabilized by Surfactant and Salt Using Microsensors*. Langmuir, 2017. **33**(38): p. 9731-9739.
2. Yao, J., et al., *In Situ Characterization of Boehmite Particles in Water Using Liquid SEM*. J Vis Exp, 2017(127).

## 11:40am CA+AS+NS+SE+SS-FrM11 Artificial Intelligence—An Autonomous TEM for In-situ Studies, Huolin Xin, University of California Irvine INVITED

Deep learning schemes have already impacted areas such as cognitive game theory (e.g., computer chess and the game of Go), pattern (e.g., facial or fingerprint) recognition, event forecasting, and bioinformatics. They are beginning to make major inroads within materials science and hold considerable promise for materials research and discovery. In this talk, I will introduce deep convolutional neural networks and how they can be applied to the computer vision problems in transmission electron microscopy. I will also discuss the development and application of liquid TEM to the study of solid/liquid interfaces at the nanoscale.

## Plasma Science and Technology Division

### Room B130 - Session PS+2D+SE+TF-FrM

## Plasma Deposition and Plasma-Enhanced Atomic Layer Deposition

**Moderators:** David Boris, U.S. Naval Research Laboratory, Chenhui Qu, University of Michigan

## 8:20am PS+2D+SE+TF-FrM1 Plasma-based Synthesis of 2D Materials for Devices on Flexible Substrates, N.R. Glavin, Air Force Research Laboratory; Christopher Muratore, Department of Chemical and Materials Engineering, University of Dayton INVITED

Synthesis of flexible two-dimensional electronic devices using low-cost, naturally abundant materials (e.g.,  $\text{MoS}_2$ ) directly onto inexpensive polymeric materials at economically viable scales enables use of their unique characteristics in grand challenge areas of energy, healthcare, and national security. Recently-proven approaches for low temperature, plasma-based 2D synthesis suitable for flexible substrates developed by the authors include growth of amorphous materials with subsequent photonic annealing to access crystalline domain sizes up to several microns. This approach has been demonstrated for synthesis of large area ultrathin monolithic layers as well as  $\text{MoS}_2/\text{WS}_2/\text{BN}$  multilayers with pristine interfaces, allowing interrogation of intrinsic properties of 2D materials and their heterostructures as they apply to diverse optoelectronic devices, with a current focus on molecular sensing. Advantages of plasma-based approaches will be discussed in terms of detailed kinetic studies of crystal formation and compositional evolution on the substrate surface. Correlations of structure, especially defect densities, to materials properties and device performance will be discussed in the context of

diverse device applications including photodetectors and molecular sensors.

## 9:00am PS+2D+SE+TF-FrM3 Homogeneous Ternary Oxides of Aluminum with Silicon, Molybdenum, and Niobium by Plasma Enhanced ALD by Sequential Precursor Pulses, Steven Vitale, MIT Lincoln Laboratory

Deposition of ternary oxide films by ALD is well known. In the vast majority of cases ternary films are deposited by sequential deposition of thin layers of the constituent binary oxides, such as  $\text{Al}_2\text{O}_3$  /  $\text{SiO}_2$ . This nanolaminate approach allows for precise control of the global film stoichiometry and is a good solution for many applications, including optical coatings where the wavelength of light is much greater than the nanolaminate thickness thus the film appears quasi-uniform. The nanolaminate approach is less desirable for electronic applications which are sensitive to surface defect sites in the material which may act as charge traps. For these applications a truly homogeneous film which does not possess internal interface states is preferred. True homogeneous ternary oxide growth by sequential precursor pulses before the oxidation step is much less well explored. In this work we grow homogeneous ternary oxides of  $\text{Al}_x\text{Si}_y\text{O}_z$ ,  $\text{Al}_x\text{Nb}_y\text{O}_z$ ,  $\text{Al}_x\text{Mo}_y\text{O}_z$  by plasma enhanced ALD using sequential precursor pulses. The stoichiometry of the films is measured by XPS. Using this data we propose models of how the precursors interact with the surface under competitive adsorption. It is found that trimethyl aluminum (TMA) is so strongly adsorbed to the surface at unity surface coverage that ternary oxide growth is not possible if the surface is first exposed to TMA. However if the surface is exposed to the Si, Nb, or Mo precursor first, ternary oxide growth is achieved. The growth kinetics for the three films are markedly different, however, and we explain this through models of the adsorption energy of each precursor.

## 9:20am PS+2D+SE+TF-FrM4 Piezoelectric Response of ZnO Thin Films Grown by Plasma-Enhanced Atomic Layer Deposition, Julian Pilz, T. Abu Ali, Graz University of Technology, Austria; P. Schöffner, B. Stadler, Joanneum Research Forschungsgesellschaft mbH, Austria; A.M. Coclite, Graz University of Technology, Austria

ZnO is a direct band gap semiconductor with attractive piezoelectrical, optical, and electrical properties, particularly appealing for a variety of functional devices. Especially the utilization of piezoelectric properties of ZnO nanostructures for transforming mechanical to electrical energy has attracted much research interest. For most of these so called nanogenerators, solution based deposition methods have been applied to create the desired nanostructures, often lacking a precise control of the deposition parameters. Atomic layer deposition, on the other hand, allows conformal and uniform deposition on high aspect ratio structures with Å-level thickness control.

In this study, we investigate the piezoelectric response of ZnO thin films on flexible substrates as a starting point for piezoelectric nanostructures. The films are grown by plasma-enhanced atomic layer deposition (PE-ALD) to thicknesses below 100 nm by adapting diethylzinc and  $\text{O}_2$ -plasma as reactants. In comparison to thermal ALD (where diethylzinc and water are used as reactants), PE-ALD allows the deposition of films with higher resistivity, an important property to minimize the leakage of piezoelectric charges. Commercially available Polyethylenterephthalat (PET) coated with Indium Tin Oxide (ITO) serves as the flexible substrate and bottom electrode, respectively. The deposition of ZnO thin films is carried out at substrate temperatures between room temperature and 100 °C, as a change in preferential crystal orientation from (100) to (002) can be observed in this temperature range. The macroscopic piezoelectric characterization is performed in a home-built stamp station, in which a defined periodic force is exerted onto the samples and the generated piezoelectric charges are measured. Out of this, the longitudinal piezoelectric coefficient  $d_{33}$  can be obtained. Preliminary results show  $d_{33}$  coefficients  $> 7$  pC/N, which is comparable to literature results. The piezoelectric characterization is made for the different samples to understand how the  $d_{33}$  coefficient changes for films deposited at different substrate temperatures and thus having different crystal orientation. Since the [002] is the polar axis in the ZnO wurtzite crystal structure, films with preferred orientation in this direction are therefore expected to show higher  $d_{33}$  coefficients.

The work lays the basis for developing functional piezoelectric generators and sensors in thin film form. However, the concepts can be easily transferred to depositions on lithographically defined templates in order to create nanostructured ZnO, which exhibits increased piezo response.

## 10:00am PS+2D+SE+TF-FrM6 Plasma-enhanced Molecular Layer Deposition of Boron Carbide from Carboranes, Michelle M. Paquette, R. Thapa, L. Dorsett, R. Bale, S. Malik, D. Bailey, A.N. Caruso, University of Missouri-Kansas City; J.D. Bielefeld, S.W. King, Intel Corporation

Atomic layer deposition (ALD) research has exploded in this era of electronic miniaturization, smart materials, and nanomanufacturing. To live up to its potential, however, ALD must be adaptable to many types of materials growth. To extend the reach of this layer-by-layer deposition framework, researchers have begun to explore molecule based processes. Still relatively rare, existing molecular layer deposition (MLD) processes are limited and typically based on the condensation of "linear" 2D or "brush-type" organic polymer chains. To this end, icosahedral carborane ( $\text{C}_2\text{B}_{10}\text{H}_{12}$ ) molecules provide an interesting target. Carboranes have been used in the plasma-enhanced chemical vapor deposition of boron carbide films for low- $k$  interlayer dielectrics, neutron detection, and a variety of protective coatings. These are symmetric twelve-vertex molecules, known to form close-packed monolayers and to possess labile H atoms at each of the vertices capable of cross-linking in the presence of heat, plasma, or other energy source. As such, the carborane molecule is particularly intriguing as a novel MLD precursor for 3D growth, possessing unique symmetry, reactivity, and volatility properties not commonly encountered in traditional organic molecules. However, a challenge in developing a layer-by-layer process lies in achieving the selective coupling chemistry required, which in the case of molecular reagents requires typically exotic bifunctional derivatives. Herein we describe progress in developing a plasma-enhanced molecular layer deposition process based on carborane derivatives, where the plasma is exploited to create the surface functionalization necessary for selective coupling and to cross-link carborane layers. We investigate the deposition of several carborane derivatives on different functionalized surfaces with the application of various types of plasmas toward achieving controlled layer-by-layer growth of thin boron carbide films.

## 10:20am PS+2D+SE+TF-FrM7 Gas Phase Kinetics Optimization Study for Scaling-up Atmospheric Pressure Plasma Enhanced Spatial ALD, Yves Creighton, Holst Centre / TNO, The Netherlands, Netherlands

DBD plasma sources have been successfully integrated in spatial ALD equipment for low-temperature ALD ( $<120$  °C) of metal-oxides. Applications involving (semi)conductive substrates require remote plasma operation. Radical losses during transport from remote plasma limit substrate speeds or demand excessive plasma flow rates. Proximity remote plasma sources were developed with sufficient radical flux even at low gas flow rates. The sources were demonstrated for ALD of InZnO for high mobility thin film transistors. Further optimization asks for deeper understanding of radical kinetics. In this contribution experimental and calculated data will be presented which allow insight in the radical gain and loss processes. A reference temperature of 100 °C and gas flows in the range 2-10 slm (for a 4 cm wide source) were applied. Alumina depositions were carried out using TMA and 2%  $\text{O}_2$ - $\text{N}_2$  plasma gas. Deposited layers obtained for different relative height positions of the plasma source were analyzed. Growth per cycle (GPC) values indicate a strong decay of plasma reactivity for gaps  $> 0.5$  mm. As  $\text{O}_3$  should not decay over such small distance, this indicates that the process is radical based. Surprisingly the GPC also shows a peak value at 0.1 mm (Fig. 1).  $\text{O}_3$  and  $\text{NO}_x$  were measured in the plasma exhaust gas as a function of %  $\text{O}_2$  (Fig. 2). The 1-2%  $\text{O}_2$  for maximum NO appears to correspond with the optimal gas composition for both high GPC values and refractive index values close to 1.58 indicating high layer quality. This result suggests NO plays a role in downstream plasma radical formation. Further understanding of the role of plasma species such as N, metastable  $\text{N}_2(\text{A})$  and NO has been obtained by modelling. Kinetic data sets for optimization of  $\text{O}_3$  production have been implemented in a CFD model for the transport of plasma species from the remote plasma. For the analysis of modelling results, the reaction volume has been divided in 3 parts (1) the plasma ionization zone itself, (2) the flow dominated plasma source aperture and (3) the diffusional transport dominated surface reaction zone. The dominating reactions for gain and loss of O radicals differ much between zones (Fig. 3). As the main O radical formation in zone (2) is due to metastable excited  $\text{N}_2(\text{A})$ , in zone (3) reactions between N radicals and NO are the main source of O radical generation. In both zones, the main O radical loss process is due to generation of  $\text{O}_3$ . The experimentally validated model has been used for finding improved plasma process settings (source geometry, frequency, flow) allowing the further optimization of high-throughput plasma enhanced spatial ALD of metal oxides.



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10:40am **PS+2D+SE+TF-FrM8 Taking Plasma ALD to the Next Level: From Fundamental Understanding to Selective 3D Processing**, *T.F. Faraz, K. Arts, Eindhoven University of Technology, The Netherlands, Netherlands; L. Martini, R. Engeln, H.C.M. Knoop, Eindhoven University of Technology, The Netherlands; Erwin Kessels, Eindhoven University of Technology, The Netherlands, Netherlands*

INVITED

Current trends in semiconductor device manufacturing impose extremely stringent requirements on nanoscale processing techniques, both in terms of accurately controlling material properties and in terms of precisely controlling nanometer dimensions. Plasma-based processing remains key in next-generation device manufacturing with plasma-enhanced atomic layer deposition (PE-ALD or plasma ALD) being a method that has obtained a very prominent position in obtaining ultrathin films with atomic scale precision [1]. In this contribution the state-of-the-art of PE-ALD will be presented including latest insights into reaction mechanisms as well as some developments in plasma ALD equipment and emerging applications. Aspects such as the role of (energetic) ions, conformality in high aspect ratio structures, and selective processing will be discussed [2].

[1] H.C.M. Knoop, T. Faraz, K. Arts, and W.M.M. Kessels, *J. Vac. Sci. Technol. A* 37, 030902 (2019)

[2] T. Faraz, K. Arts, S. Karwal, H.C.M. Knoop, and W.M.M. Kessels, *Plasma Sources Sci. Technol.* 28, 024002 (2019).

11:20am **PS+2D+SE+TF-FrM10 Computational Investigation of Plasma Enhanced ALD of SiO<sub>2</sub>**, *C. Qu, University of Michigan; P. Agarwal, Y. Sakiyama, A. LaVoie, Lam Research Corporation; Mark J. Kushner, University of Michigan*

Plasma enhanced atomic layer deposition (PE-ALD) of dielectric films typically consists of two steps – precursor deposition and oxidation. For example, in a SiO<sub>2</sub> PE-ALD process, the Si-containing precursor is often deposited in the feature without use of plasma while the oxidation step is performed by an oxygen containing plasma. In principle, the surface kinetics of both steps are self-terminating. Although the plasma step is performed using gas pressures of several to 10 Torr, in addition to O-atoms the fluxes onto the wafer contain energetic particles in the form of ions, photons, hot-neutrals and excited states. When performing PE-ALD in high aspect ratio (HAR) features, transport of these species into the feature determine the quality of the deposition. Optimizing the PE-ALD depends on control of these fluxes.

In this work, results from a computational investigation of reactor and feature scale processes in idealized PE-ALD of SiO<sub>2</sub> will be discussed. Reactor scale simulations of a capacitively coupled plasma sustained in Ar/O<sub>2</sub> mixtures were performed using the Hybrid Plasma Equipment Model (HPEM); and provided fluxes and energy distributions of radicals, ions, excited states and photons onto the wafer. Feature scale simulations were performed with the Monte Carlo Feature Profile Model (MCFPM). The idealized ALD process consists of a non-plasma first step using an Si-R (R indicates organic) precursor. The second step uses fluxes from the Ar/O<sub>2</sub> plasma to remove the organic and oxidize the Si site. The base-case features are moderate to high aspect ratio (AR = 7-20) vias and trenches. The metrics to evaluate the process are surface coverage of Si, O, R, stoichiometry, defect density, surface roughness and deposition rate.

In self-terminating processes, many of these metrics should scale with  $pt$ , where  $p$  is the probability of reaction and  $t$  is the step length. For example, a given surface coverage of Si-R or Si-O should depend on first order on  $pt$ . However, as deposition proceeds and a feature fills, the effective AR increases. When coupled with conductance limited transport into the feature, with increasing AR the value of  $pt$  to produce a given surface coverage increases. As the deposition proceeds and AR increases, stoichiometry and defect density begins to have a dependence on height inside the feature, as surfaces deep in the feature receive less exposure to the reactive fluxes. The consequences of ion- and photon-induced damages will also be discussed.

\* Work supported by LAM Research Corp. and the DOE Office of Fusion Energy Science.

11:40am **PS+2D+SE+TF-FrM11 Analyzing Self-limiting Surface Reaction Mechanisms of Metal Alkyl Precursors and Nitrogen Plasma Species: Real-time In-situ Ellipsometric Monitoring of III-nitride Plasma-ALD Processes**, *Ali Okyay, OkyayTech Inc., Turkey; A. Mohammad, D. Shukla, S. Ilhom, University of Connecticut; B. Johs, Film Sense LLC; B.G. Willis, N. Bijykli, University of Connecticut*

ALD-grown films are vastly characterized via ex-situ measurements to quantify various material properties. However, gaining insight into the

saturation surface reactions and growth mechanisms is only possible with real-time in-situ process monitoring of individual ALD cycles. While several in-situ measurement techniques have been employed in ALD research, in-situ ellipsometry stands out as one of the best options for real-time monitoring surface reactions. The promising potential of in-situ spectroscopic ellipsometry has already been demonstrated for a number of materials grown by remote plasma-ALD. Here, we verify that cost-effective multi-wavelength ellipsometer (MWE) can also be used effectively for real-time in-situ analysis of plasma-ALD growth cycles. We demonstrate for the first time that real-time dynamic in-situ MWE measurements convey not only accurate film deposition rate, but as well resolve single chemisorption, ligand removal, and nitrogen incorporation events with remarkable clarity. Moreover, forcing the limits for fitting the acquired in-situ MWE data, we were able to track the evolution of the optical constants of III-nitride films along the ALD cycles which indeed showed thickness-dependent behavior.

Our main motivation behind this study was twofold: (i) Analyze and compare the self-limiting growth characteristics of binary III-nitride (AlN, GaN, and InN) thin films via real-time in-situ ellipsometry and to gain insight into the ALD surface reaction mechanisms including chemical adsorption, ligand removal, and nitrogen incorporation steps. (ii) Performance evaluation of our custom designed ALD reactor featuring improved hollow-cathode plasma source by comparing our results with previous plasma-ALD grown III-nitrides.

Despite using the conventional alkyl metal precursors (trimethylaluminum, trimethyl/ethylgallium, trimethylindium) utilized also widely in MOCVD epitaxial growth, their solid-gas surface interactions with nitrogen plasma species shows notable differences, particularly with respect to substrate temperature, plasma power, plasma exposure time, and plasma gas composition. In terms of substrate temperature, AlN exhibited crystallinity at lower temperatures when compared to GaN and InN. Even at 100 °C, AlN showed crystalline behavior whereas GaN displayed amorphous character up to 200 °C. While Ar/N<sub>2</sub>/H<sub>2</sub> composition is optimal for AlN, N<sub>2</sub>/H<sub>2</sub> and Ar/N<sub>2</sub> mixtures proved to be better for GaN and InN. InN experiments revealed that the inclusion of H<sub>2</sub> gas led to mixed phase growth with substantial c-In<sub>2</sub>O<sub>3</sub> phase. The possible surface reaction mechanisms that lead to these different growth behaviors will be discussed in detail.

12:00pm **PS+2D+SE+TF-FrM12 Tribological Properties of Plasma Enhanced Atomic Layer Deposition TiMoN with Substrate Bias**, *Mark Sowa, Veeco ALD; A.C. Kozen, University of Maryland; N.C. Strandwitz, T.F. Babuska, B.A. Krick, Lehigh University*

In our previous study, we demonstrated a tertiary plasma enhanced atomic layer deposited transition metal nitride (TiVN) with exceptional wear rates and friction coefficients. We have extended that work with an investigation of another tertiary transition metal nitride system, Ti<sub>x</sub>Mo<sub>y</sub>N<sub>z</sub>. For films deposited at 250°C and 300W on a Veeco CNT G2 Fiji PEALD system, we have demonstrated how the ratio of TiN:MoN cycles (1:0, 2:1, 1:1, 1:2, 0:1) provides linear control of the Ti:Mo in the resulting film. Through application of an 13.56MHz RF substrate bias (0-188V) during the plasma step, ion bombardment energy of the substrate can be varied, providing a means for tweaking the films physical and chemical characteristics which in turn are shown to impact the resulting film's tribological properties. As PEALD metal nitrides have broader interest than wear layers and to gain insights on the interrelationships of the mechanical properties, the processing details, and other film properties, we also report on the resulting film composition/impurities, density, crystallinity, optical properties, resistivity, and morphology.

## Advanced Surface Engineering Division Room A215 - Session SE+AS+SS-FrM

### Tribology: From Nano to Macro-scale

Moderator: Robert Franz, Montanuniversität Leoben, Austria

8:20am **SE+AS+SS-FrM1 The Scaling of Tribological Effects from Nano- to Macro-scale**, *Peter Lee, Southwest Research Institute*

INVITED

The last few decades has seen the advancement of technologies such as atomic force microscopes (AFM), scanning force microscopes (SFM) and friction force microscopes (FFM) to measure friction, wear and adhesions at the nano- and micro-scale, leading to the study of nano- and micro-tribology. The study of two surfaces at the nano- and micro-meter scale has led to the advancement of small scale engineering devices such as nano- and micro-electromechanical systems (NEMS and MEMES). However, it has also led to the study of materials used in macro-engineering in an attempt

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to understand the fundamentals of lubrication, friction and wear at the asperity scale in macro-systems.

Macro-tribology involves large apparent areas of contact where only a fraction of the asperity tips are in contact, whereas nano-tribology usually involves studying a single asperity contact where the actual contact is the same as the apparent contact. Consequently, roughness and actual contact shape plays a more significant role in the tribological behavior, which in turn means significant effects on forces such as friction, adhesion and surface tension. Tribology at the macro-scale is governed by complex phenomena such as ploughing, abrasive, and adhesive wear. Friction at the nano-scale is often studied purely in the wearless (interfacial) regime, where adhesion is substantial but wear is minimal.

This presentation will explore current research at the nano-scale and discuss how this has the potential to help in understanding and modeling at the macro-scale.

9:00am **SE+AS+SS-FrM3 Nanotribology of Graphene in Organic Solvents**, *Prathima Nalam, B. Sattari Baboukani*, University at Buffalo, State University of New York; *Z. Ye*, Miami University

Two-dimensional (2D) materials such as graphene, etc. are emerging as friction-reducing additives for transmission fluids and lubricating oils to enhance the service life of sliding metallic components. Here in this work, we investigate the dissipative mechanism for a supported (on silica substrate), monolayer of graphene when immersed in organic solvents such as *n*-hexadecane and cyclohexane. Nanoscale friction measurements on graphene conducted using atomic force microscope showed a non-monotonic variation *i.e.* a decrease and then an increase in friction forces as a function of immersion time in organic solvents. This behavior was attributed to the re-arrangement of organic molecules at the 2D confinement formed between the graphene and the underlying substrate. The oscillatory forces measured at the interface showed an increased packing order of the solvent molecules under 2D confinement and with equilibration time lead to a higher dissipative interface. The diffusion of organic molecules to the 2D confinement also results in a partially-suspended graphene layer and the interfacial friction is discussed by understanding the quality (local pinning states of individual atoms) of the contact made by the AFM probe while sliding on graphene.

9:20am **SE+AS+SS-FrM4 Measuring Atomic-scale Surface Friction of a Molecular Vehicle on Au(111)**, *K.Z. Latt, Sanjoy Sarkar, K. Kottur, M. Ræis*, Ohio University; *A. Ngo*, Argonne National Laboratory; *R. Tumbleson, Y. Zhang, E. Masson, S.-W. Hla*, Ohio University

Designing molecules with technomimetic properties has been actively pursued in the past decade. Among these, molecules specially designed for translational motion, dubbed as nanocars or molecular vehicles, are particularly appealing as they could ultimately be used to transport a molecular cargo or some specific chemical information from a start to an end point on a surface and on demand. Here, we have designed and assembled an electric nanovehicle using four molecular wheels and a molecular chassis as separate modules. An 'H' shape chassis is formed by two benzimidazolium groups linking the front and the rear axles to a terphenyl drive shaft. Final assembly of the nanovehicle is realized by attaching four pumpkin shaped cucurbituril molecular wheels. The chassis of the nanovehicle includes positive charges, which are used for the controlled lateral movement of the vehicle by scanning tunneling microscope tip induced electric field manipulation. The threshold voltage required to drive the nanovehicle is determined from the Vaussian-fit of the data. Moreover, we have determined lateral force to move the nanovehicle on a Au(111) surface at 5K and it is found to be in superlubricity regime.

9:40am **SE+AS+SS-FrM5 The Use of the Nanocomposite Concept in Hard Coatings for Improving the Frictional Performance**, *Albano Cavaleiro*, University of Coimbra, Portugal

INVITED

Nanocomposite thin films based on a structural arrangement consisting of grains of a transition metal nitride enrobed in a thin layer of silicon nitride, have been developed in last decades with the final aim of maximizing the mechanical strength. This specific arrangement was proved to be efficient regarding the oxidation resistance and the structural stability at high temperatures as well as the wear resistance, reason why these coatings are commercially available in the market. However, their performance in applications requiring low friction, against specific materials, is very inefficient. On the other hand, in last years the addition of elements, able to provide low friction, such as Ag or V, to traditional hard coatings (TiN, TiAlN, TiCrN,...) has been deeply studied. Results were very successful from

the lubrication point of view but the wear resistance was clearly reduced, due to either a decrease of the global mechanical strength of the coatings or the rapid depletion of the lubricant element from the coating by out diffusion to the contact zone.

In this talk an overview of the influence of the addition of lubricant elements to Ti-Si-N system will be presented. The coatings were deposited by conventional magnetron sputtering as well as by using HiPIMS power supplies. The importance of the type of the structure of the deposited coatings (nanocomposite or supersaturated solid solution) on their thermal stability, including oxidation resistance, will be discussed based on the diffusion of the lubricant elements. A comparison of the mechanical properties of the coatings deposited by both methods will be performed and the results will be interpreted based on the (micro)structure and residual stresses. Results on the tribological behaviour achieved by tests at room and high temperatures (up to 900 °C) against different balls (steel, alumina and Ti-alloy) will be presented and commented. Generally, results show that a decrease of the mechanical performance of the coatings is obtained with that elements addition. However, in relation to tribological performance, significant improvements could be reached although under specific testing conditions (type of ball, temperature, ...). In many cases, no improvements were observed.

10:20am **SE+AS+SS-FrM7 Development of Ultra-thick CrAlAgN Coatings by HiPIMS for Self-lubrication at Elevated Temperatures**, *Jianliang Lin*, Southwest Research Institute; *X. Zhang*, Southeast University, China

The pursuit of advanced coating systems to provide sufficient oxidation resistance and self-lubrication for high temperature tribological application continues. One of the approaches is to dope traditional hard transition metal nitride coatings with solid lubricants, e.g. Ag, Au, which diffuses towards coating surface to provide lubrication at elevated temperatures. However, the long term performance of these self-lubricating coatings at high temperatures in ambient air is limited by the rapid out diffusion of Ag, which is strongly affected by many factors, e.g. the volume fraction of the dopant and the density of the coating. It is expected that dense coating structure combined with increased coating thickness is helpful for achieving long term lubrication performance. In this paper, ultra-thick CrAlAgN coatings (50 μm) are deposited on steel and cement carbide substrates using high power impulse magnetron sputtering (HiPIMS) by carefully control the processing parameters. The structure and composition of the coatings were first tailored to achieve a combination of good adhesion, high density and good mechanical strength with HiPIMS deposition. The Ag concentration in the coatings is varied in the range of 3-10 at.%. For the coating performance, the oxidation resistance of the coating were studied in ambient air using isothermal test. The high temperature wear resistance of the coating was measured using a high temperature pin-on-disc tribometer in the ambient air from 500 °C to 900 °C. It was found that Ag doping degrades the mechanical strength and oxidation resistance of the CrAlN coatings, but the ultra-thick CrAlAgN coating show robust self-lubricating performance at high temperatures.

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