Plasma Science and Technology Division
Room: 21 - Session PS+AS+SE-MoM

Atmospheric Pressure Plasmas
Moderators: Olivier Guaitella, Ecole Polytechnique - CNRS, France, Seiji Samukawa, Tohoku Univeversity, AIST, Japan

8:20am **PS+AS+SE-MoM1 Study of Atmospheric-pressure kHz Multi-jet Plasma System**, ***Vladimir Milosavljevic***, *J. Lalor, L. Scally, P.J. Cullen*, Dublin Institute of Technology, Ireland

Non thermal plasmas can be generated in laboratory conditions using generic, readily available and easily sourced components. Examples include glass tubing, copper or stainless wire electrodes, metal mesh, plastic enclosures, and step-up transformer based power supplies. Such sources, although effective, may not offer optimised conditions or efficiencies. In many cases they may not sustain extended operation due to excess thermal and electrical breakdown. Second-generation laboratory apparatus and scaled up designs involve selected materials, custom machined components, electrodes based on calculated requirements, and suitably designed or sourced power supplies. These assemblies will offer a more accurate theoretical and empirical view of the plasma performance. The inclusion of a material selection software tool for the rational selection of engineering materials can provide detailed information relating to the mechanical thermal and electric properties. Developing a non-thermal atmospheric plasma source involves three important factors for material selection. Firstly the application and operating conditions of the design needs to be examined; is it to be handheld, exposed to ambient air or contained in an enclosure. For many plasma sources, certain polymers offer an ideal material, for other configurations, composites or metals may be best. Secondly, does the source need to facilitate a controllable environment in which to generate the plasma, in other words, is it necessary to purge or evacuate the enclosure in order to accurately control the gas chemistry, if this is the case, a choice of material for this housing and containment area must be considered. The third factor is the material selection for the conducting elements, namely the cables, electrodes and grounding components. Typical electrode metals include copper, aluminium, brass and stainless steel.

In this work 12 circular plasma jets are presented. They are designed and built in-house, and power up with a single phase generator of 10-30 kV, at 10-100 kHz that powers up to 2 kW. Voltage-current measurements and optical emission spectroscopy (OES) are applied for optimization of transient discharges operated for several different gas chemistry at atmospheric pressure. The influence of applied voltage, frequency, gas flow rate and gas chemistry in relation with the OES signal, plasma plume formulation, gas velocity and electrical properties of plasma jets are the objectives of this study.

This work was funded under the 'PlasmaGrain' project funded by the SFI, Republic of Ireland.

8:40am **PS+AS+SE-MoM2 Synthesis of Nitrates by Atmospheric Microplasma Over Water : Effect of the Experimental Parameters and Intermediate Species**, ***Nicolas Maira***, *C. De Vos, F. Reniers*, Université Libre de Bruxelles, Belgium

Nowadays, nitrates are used mainly as fertilizers in agriculture. They are produced by the combination of the Haber-Bosch and Ostwald process. Industry, throughout the years, has increasingly optimized the energetic yield of this synthesis. Nevertheless, this method requires the use of a hydrogen source, essentially extracted from fossil fuel. Moreover, nitrates synthesized in colossal plant factories have to be shipped to the end-user. However, in some applications such as hydroponics or urban agriculture, the local production of pure nitrates fertilizers directly available in the flowing water feeding system would be of great interest.

In this study, the same philosophy as for the ozone process is applied: taking advantage of the composition of natural air in order to synthesize nitrates directly in a solution [1]. The mechanism of formation of nitrates using an atmospheric microplasma discharge operating in air or in argon in an open air environment is investigated. The effect of the treatment time, the discharge current and power, the water surface – capillary distance, and the solution pH on the formation of nitrogen oxides in the gas phase and in solution is studied. The liquid phase is analyzed by Ionic Chromatography (IC), UV-visible spectrometry (UV-vis) and pH-metry, whereas the gas phase is probed by Optical Emission Spectroscopy (OES) and atmospheric Mass Spectrometry (MS).

The total amount of NO_x formed in a solution shows a linear trend with the total charge injected into the plasma with however different slopes for nitrites (NO_2^-) and nitrates (NO_3^-). The reaction mechanism involves the formation of gas phase NO, as evidenced by OES. It is known that the synthesis of nitrates is pH-dependent [2]. In an acidic solution with a pH below 3, the formation of nitrates is favored whereas a higher pH allows the formation of nitrites which are oxidized in nitrates after the treatment. The transformation of nitrites into nitrates after plasma synthesis is monitored by IC during time and seems to follow a logarithmic trend. The performed experiments allow the determination of the amount of energy required to form a mole of nitrate in this set-up.

[1] Fridman A. *Plasma Chemistry*, Cambridge University Press, **2008**, 382-398

[2] Machala Z., Tarabova B., Hensel K., Spetlikova E., Sikurova L., Lukes P. Formation of ROS and RNS in water electro-sprayed through transient spark discharge in air and their bactericidal effects, *Plasma Processes and Polymers*, 10, 649-659, **2013**.

9:00am **PS+AS+SE-MoM3 Plasma Catalysis for CO_2 and CH_4 Conversion at Atmospheric Pressure**, *A. Ozkan, S. Chorfi, L. Brune, T. Visart de Bocarmé*, ***François Reniers***, Université Libre de Bruxelles, Belgium

The field of plasma-catalysis, i.e. combining a plasma process and a catalyst, either inside the plasma or in its post-discharge is gaining importance for the conversion of CO_2 and CH_4 mixtures. Indeed, the combination of plasma and catalysis could not only increase the conversion of these gases, but also orient the reaction(s) towards the synthesis of valuable molecules.

This paper will present first the main factors that influence the conversion and the energy efficiency for the reduction of CO_2 using an atmospheric pressure dielectric barrier discharge. Second, an alumina supported catalyst will be added between the electrodes and its effects on the conversion of pure CO_2, pure CH_4 and CO_2/CH_4 mixtures will be presented. Ni, Co, Cu have been tested, as well as various loadings of Ni.

The conversion is studied by atmospheric mass spectrometry, and the chemical identification of the end products was obtained either by mass spectrometry or gas chromatography.

It is shown that the frequency, the pulse mode, the dielectric nature and thickness strongly influence the conversion and energy efficiency of the reaction, whereas the residence time and the power injected into the discharge modify the conversion[1]. An increase in the Ni loadings leads to an increase in conversion of both CO_2 and CH_4. If CO and H_2, starting molecules for more complex organic chemistry, are always the main products of reaction, C2, C3 and C4 molecules, oxygenated or not are also detected. The effect of the nature of the catalyst on the relative amounts of these molecules is discussed.

[1] : A. Ozkan, A. Bogaerts, F. Reniers, J. Phys. D: Appl. Phys. 50 (2017) 084004, doi:10.1088/1361-6463/aa562c

9:20am **PS+AS+SE-MoM4 Aluminium Surface Plasma Treatment at Atmosphere Pressure**, ***Lucia Bonova***, *I.A. Shchelkanov, C. Ahn, S. Chaudhuri, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Plasma surface treatment at atmosphere pressure is a fast growing industry. Among other applications, surface treatment of metals for adhesion and corrosion resistance improvement has attracted widespread interest. Being operated at atmosphere pressure, various types of plasma discharge devices provide efficient, cheap and large scale processing capabilities. In this area, surface treatment of aluminium for surface properties modification is of great interest as it can decrease steps in process for final coating deposition, reduce usage of harmful chemical reagents, which in their turn require costly dispose procedures, and increase functional coatings performance.

The ECAP experiment (Evaporative Coatings at Atmosphere Pressure) was developed at CPMI (Center for Plasma Materials Interaction at UIUC) as a device and a method for multicomponent metal coatings deposition at atmosphere pressure utilizing a 2.45 GHz microwave plasma torch. The device is capable of coating deposition from a solid metal state and from gas carried precursors as well as composites with processing gas like ZrO. These capabilities make ECAP a very flexible tool for gradient coating deposition for surface functionalization and adhesion improvement. In this gradient coating, the alumina facing materials is gradually replaced with a second layer material with perfect adhesion for final functional coating.

Current work discusses several methods, which were used to improve aluminium surface wettability and adhesion to an epoxy. As a fundamental experiment, we have conducted the simple treatment on aluminium plate by ECAP which operated with feedstock gas of evaporated H_2O and He. It shows remarkable enhanced epoxy adhesion on aluminium sample against the

control condition. System configuration for roll-to-roll applications and broad area coatings/cleaning are also discussed.

9:40am **PS+AS+SE-MoM5 The Role of Bulk Liquid Transport Processes in the Plasma-Liquid Interfacial Chemistry**, ***Selma Mededovic Thagard***, *M. Vasilev, D. Bohl, P. Conlon*, Clarkson University **INVITED**

Plasmas formed directly in and contacting a liquid are powerful sources of reactive radicals, ions and high-energy electrons and have been successfully used to sterilize water and fruit juices, purify water, synthesize materials and nanoparticles, and for applications in plasma medicine, electrical transmission, and polymer surface treatment. Nevertheless, despite the obvious versatility in processing capabilities, the optimization and broader application of electrical discharge plasmas in and contacting a liquid have been limited due to a general lack of understanding of the underlying physical and chemical processes occurring at the plasma-liquid interface. Despite the significant progress that has been made towards understanding interfacial chemistry of plasmas in the last decade or so (especially for air plasmas contacting water), relative contributions of plasma processes such as formation and diffusion of reactive species and bulk liquid processes such as electrohydrodynamic flow to interfacial dynamics have not been yet determined.

This work investigates the extent to which bulk liquid processes, primarily bulk liquid composition and plasma-induced electrohydrodynamic flow control the rates of chemical reactions at a plasma-liquid interface. We have determined the efficacy of the plasma process for treatment of a wide range of different compounds and used the results of this investigation to construct a model to predict the approximate treatability of any compound based on just a few of the compound's physical properties. Experiments with different initial bulk liquid concentrations of non-surfactant and surfactant compounds have also been performed to investigate how interfacial compound concentration affects its removal rate. Particle Image Velocimetry has been used to quantify the surface velocity of a liquid as a function of its chemical composition.

10:40am **PS+AS+SE-MoM8 Efficiency of Electrolytic Reduction of Aqueous Metal Salts to Metal Nanoparticles at a Plasma-Liquid Interface**, *S. Ghosh*, ***Ryan Hawtof***, Case Western Reserve University, *P. Rumbach, D.B. Go*, University of Notre Dame, *R. Akolkar, R.M. Sankaran*, Case Western Reserve University

Electrolytic cells with a plasma serving as one or both of the electrodes eliminate the solid metal and allow electrochemical reactions to be carried out at a gas-liquid interface. This is particularly beneficial for the synthesis of metal nanoparticles from metal salts since the deposition of a thin film onto the electrode is avoided. However, because of the complexity of the plasma and the resulting interfacial reactions, the mechanism for metal nanoparticle formation remains unknown.

Here, we designed experiments to understand the mechanism of the reduction of silver nitrate ($AgNO_3$) to silver (Ag) nanoparticles by a previously reported atmospheric-pressure, direct current microplasma operated as the cathode. We applied a well-known methodology in electrodeposition to assess the faradaic efficiency whereby the mass of the synthesized material is compared with the theoretical amount of mass estimated from the charge injected into solution. A faradaic efficiency of 100% would indicate that all the charge is going towards the desired reduction of Ag cations to solid Ag, $Ag^+ + e^-$ --> Ag^0, whereas an efficiency less than 100% would suggest that there are side reactions, most probable of which is the second order recombination of (solvated) electrons to form hydrogen gas and hydroxide ions, $e^-_{(aq)} + e^-_{(aq)} + 2H_2O_{(l)}$ --> $H_{2(g)} + 2OH^-_{(aq)}$.

We find that at a relatively high $AgNO_3$ concentration in the bath, the faradaic efficiency depends weakly on the current, reaching values of 100% at 2 mA and decreasing to slightly less than 100% at 6 mA. To corroborate these measurements, the mass change of a Ag foil anode which oxidizes in solution by the reverse of the cathode reaction, Ag^0 --> $Ag^+ + e^-$, was compared and found to yield slightly lower efficiencies, but with the same overall trend. At constant current and varying $AgNO_3$ concentration in the bath, the faradaic efficiency was found to drastically decrease to less than 100%. We interpret these results as follows. The kinetics of the primary reactions, Ag^+ reduction and second order recombination, depend on the respective rate constants which are similar (3.7×10^{10} M/s and 5.5×10^9 M/s) and the reactant concentrations. At low current or high $AgNO_3$ concentration, the rate of Ag^+ reduction is higher than second order recombination and the faradaic efficiency approaches 100%. Conversely, the rate of second order recombination is higher than Ag^+ reduction at high current or low $AgNO_3$ concentration, lowering the faradaic efficiency. A reaction model was developed to support these interpretations.

11:20am **PS+AS+SE-MoM10 Amorphous Indium Zinc Oxide (IZO) Semiconductor Films Grown by Atmospheric Plasma-Enhanced Spatial ALD for Application as High-Mobility Channel in Thin Film Transistors**, *A. Illiberi, I. Katsouras, S. Gazibegović, B. Cobb, E. Nekovic*, TNO-Holst Centre, Netherlands, *W. van Boekel, C. Frijters*, TNO-Solliance, Netherlands, *J. Maas*, TNO-Holst Centre, Netherlands, ***Fred Roozeboom***, TNO-Holst Centre & Eindhoven University of Technology, Netherlands, *Y.L.M. Creyghton*, TNO-Solliance, Netherlands, *P. Poodt*, TNO-Holst Centre, Netherlands, *G. Gelinck*, TNO-Holst Centre & Eindhoven University of Technology, Netherlands **INVITED**

Less than a decade ago, InGaZnO has been reported as a new Amorphous Oxide Semiconductor (AOS) channel material replacing conventional amorphous silicon (a-Si:H) for application in thin-film transistor (TFT) circuits in display back panels [1]. Among these, indium zinc oxide (IZO) is emerging as the most promising AOS candidate for next-generation displays based on oxide TFTs because it combines a very high electron mobility with excellent optical transmission and thermal stability [2,3].

We have grown InZnO thin films by plasma-enhanced spatial atomic layer deposition (s-ALD) [4,5] and these layers have been manufactured into oxide TFT and ring oscillator devices which outperform the state-of-the-art. We will describe the growth of InZnO at atmospheric pressure and high deposition rates (~ nm/sec) starting with a short explanation of the basics and the advantages of this novel deposition technique including the use of a special atmospheric plasma source design of the so-called Surface Dielectric Barrier Discharge (SDBD) type [6]. Next, we will show that by varying the ratio of the trimethyl indium and diethyl zinc chemical precursor vapors, the In/(In+Zn) ratio of the film can be accurately tuned over the entire composition range from zinc oxide to indium oxide. TFT test devices with an In/Zn ratio of 2:1 show very high field-effect mobility exceeding 30 cm^2/V.s (Fig. 1), excellent thermal (Fig. 2) and bias stress stability. We will further demonstrate the scalability of the IZO TFTs by fabricating 19-stage ring oscillators operating at 200 kHz which outperform the state-of-the-art.

This superior electrical performance, in combination with the intrinsic advantages of spatial ALD demonstrate the great potential of this atmospheric plasma concept for application in commercial manufacturing of low-cost and large-area AOS-based electronics.

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6. Y. Creyghton, A. Illiberi, M. Mione, W. van Boekel, N. Debernardi, M. Seitz, F. van den Bruele, P. Poodt, F. Roozeboom, Proc. Int. Conf. on Coatings on Glass and Plastics (ICCG 2016), Braunschweig, Germany, June 12-16, 2016, pp. 93-97

Advanced Surface Engineering Division
Room: 11 - Session SE+2D+NS+SS+TF-WeA

Nanostructured Thin Films and Coatings
Moderators: Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

2:20pm **SE+2D+NS+SS+TF-WeA1 Plasma Process Development and Optimized Synthesis of TiB_2 Coatings from DC Magnetron Sputtering, High Power Impulse Magnetron Sputtering, and DC Vacuum Arc**, ***Johanna Rosen***, Linköping University, Sweden **INVITED**

The use of high power impulse magnetron sputtering (HiPIMS) or cathodic arc for the synthesis of TiB_2 coatings will drastically increase the amount of ionized species impinging on the substrate compared to regular DC magnetron sputtering. In particular for HiPIMS, it is possible to control the flux of ionized species by varying the pulse frequency, which allows exploration of the effect of ion to neutral flux ratio on the coating microstructure while keeping the substrate bias potential constant.

We show that the additional energy supplied during film growth in the HiPIMS process, compared to regular DC sputtering, results in a change from a randomly oriented polycrystalline microstructure to a 001-textured nanocolumnar structure. The change in preferred orientation also influence the hardness, which is enhanced from 36 GPa to ≥ 42 GPa. A further increase in the ion flux to the substrate leads to denser coatings with a higher residual compressive stress. Furthermore, we show that the energy supplied to the film surface is influenced by when the bias is applied relative to the HiPIMS pulse. Based on charge-state-resolved plasma analysis it is found that by applying the bias in synchronous with the HiPIMS pulse, a higher fraction of B^+ ions will constitute the total flux of bombarding ions. This results in a lower residual stress compared to coatings deposited under bombardment of mainly Ar^+ ions.

Finally, we also present results from TiB2 synthesis based on DC vacuum arc, and a route for attaining a stable, reproducible, and close to fully ionized plasma flux of Ti and B by removal of the external magnetic field. Plasma analysis shows increased ion charge states as well as ion energies compared to HiPIMS. Furthermore, while regular DC magnetron sputtering and HiPIMS typically give a B to Ti ratio above 2, the arc deposited coatings have a stoichiometry close to 2. Despite observations of macroparticle generation during synthesis, the film surface is very smooth with a negligible amount of particles.

3:00pm **SE+2D+NS+SS+TF-WeA3 Multi-technique Approach for Studying Co-sputtered M-Si-O Thin Films**, ***Lirong Sun***, General Dynamics Information Technology, *N.R. Murphy,* Air Force Research Laboratory, *J.T. Grant*, Azimuth Corporation

In this work, the M-Si-O thin films (M: Al and Ta) were prepared through reactive pulsed DC magnetron co-sputtering of M and Si targets in an O_2/Ar mixture. The M fraction [M/(M+Si)] of different chemical compositions ($M_xSi_yO_z$), as determined through X-ray photoelectron spectroscopy (XPS), was varied between 0 and 100% by changing sputtering power applied to the M targets. The film thickness, refractive index (n) and extinction coefficient (k) were determined by *in situ* spectroscopic ellipsometry (*i*SE). Concurrent with ellipsometry measurements, the *in situ* stress evolution of the films, as correlated to the M fraction, was investigated using a multi-beam optical sensor (MOS) system. The MOS system was used to measure both intrinsic stress resulting from the deposition process as well as thermal stress evolved during heating/cooling process. Data obtained through stress monitoring during heating and cooling was used to calculate the coefficient of thermal expansion (CTE). The density and crystallinity of the films were measured by X-ray diffraction and X-ray reflectivity, respectively. Transmission and reflectance of the films were carried out by UV-Vis-NIR spectroscopy. Finally, this study derives a process-property-microstructure relationship correlating the optical constants, CTE, intrinsic stress, and M fraction.

3:20pm **SE+2D+NS+SS+TF-WeA4 Ultra-high Vacuum Magnetron Sputter-deposition of $Zr/Al_2O_3(0001)$: Effect of Substrate Temperature on Zr Thin Film Microstructure and Thermal Stability of $Zr-Al_2O_3$ Interfaces**, *K. Tanaka, J. Fankhauser,* University of California at Los Angeles, *M. Sato,* Nagoya University, Japan, *D. Yu, A. Aleman, A. Ebnonnasir, C. Li,* University of California at Los Angeles, *M. Kobashi,* Nagoya University, Japan, *M.S. Goorsky*, ***Suneel Kodambaka***, University of California at Los Angeles

Zr thin films are grown on $Al_2O_3(0001)$ substrates in an ultra-high vacuum deposition system via dc magnetron sputtering of Zr target in Ar atmosphere at temperatures T_s between 600 ºC and 900 ºC. The as-deposited layer surface structure and composition are determined *in situ* using low-energy electron diffraction and Auger electron spectroscopy, respectively. Bulk crystallinity and microstructures of the samples are determined using x-ray diffraction, cross-sectional transmission electron microscopy along with energy dispersive spectroscopy. At 600 ºC $\leq T_s <$ 750 ºC, we obtain fully dense, hexagonal close-packed structured Zr(0001) thin films with smooth surfaces. At $T_s \geq$ 750 ºC, the Zr layers are porous, exhibit {0001} texture, and with rough surfaces. Energy dispersive x-ray spectra obtained from the Zr/Al_2O_3 interfaces reveal the formation of Zr-Al intermetallic compounds, whose thickness increases exponentially with increasing T_s. We attribute the formation of this interfacial layers to fast diffusion of Zr and reaction with the Al_2O_3 substrate.}

4:20pm **SE+2D+NS+SS+TF-WeA7 Structural, Mechanical, Optical Properties of Molybdenum Incorporated β-Ga_2O_3 Nanocrystalline Films for Extreme Environment Applications**, ***Anil Battu***, *S. Manandhar, C.V. Ramana*, University of Texas at El Paso

Recently, gallium oxide (Ga_2O_3) has been attracting the attention of researchers as a suitable material for different extreme environment applications, such as high power electronics, optoelectronics, ultraviolet transparent conductive oxides, and gas sensors. β-Ga_2O_3 exhibits the highest thermal and chemical stability, which makes the material interesting for high-temperature oxygen sensor applications. However, the response time and sensitivity must be improved. In recent years, doping Ga_2O_3 with the suitable metal ions has been considered to alter the electronic properties and to improve sensor performance. In this context, the present work was performed on using a mechanically resilient metal (Mo) to incorporate into Ga-oxide (GMO) to provide excellent physical and thermo-mechanical characteristics. The GMO nanocomposite films with variable Mo contents (0-11.23 at%) were sputter-deposited onto Si(100) by varying the sputtering power in the range of 0-100 W. The effect of Mo on the crystal structure, mechanical properties and optical properties of GMO nanocomposite films is significant. While Mo content ≤ 4 at% reatins the β-Ga_2O_3 phase, higher Mo content induces amorphization. Molybdenum incorporation into β-Ga_2O_3, reduces the grain-size leading to amorphous nature of the entire film as well as surfaces. The nanoindentation studies indicate the remarkable effect of structural evolution and Mo content on the mechanical properties of the deposited GMO thin films. While Mo incorporation increases the hardness from 25 to 36 GPa, elesatic modulus decreases. Mo-induced red-shift in the band gap is significant in GMO films. Based on the results, a structure-property relationship in established in Mo incorporated Ga_2O_3 films.

4:40pm **SE+2D+NS+SS+TF-WeA8 Investigating Mass Transport and other Events underlying Rapid, Propagating Formation Reactions in Pt/Al Multilayer Films**, ***David Adams***, *M.J. Abere, C. Sobczak, D.E. Kittell, C.D. Yarrington, C.B. Saltonstall, T.E. Beechem*, Sandia National Laboratories

Metallic thin film multilayers that undergo rapid, self-propagating exothermic reactions are of interest for several applications including advanced joining technology. Reactive multilayers, such as commercially available Ni-Al, have been developed as a heat source to locally solder or braze dissimilar materials. A local heating approach is of great benefit for joining temperature-sensitive components and metastable structures. The development of new materials for reactive joining requires an improved, detailed understanding of mass transport, chemical reactions, heat release and thermal transport processes. With this presentation, we describe recent studies of a more highly exothermic reactive multilayer system (Pt/Al). Thin Pt/Al multilayers exhibit rapid propagating reactions with flame speeds as high as 100 m/s and internal heating rates > $1x10^7$ K/s. Equimolar designs are characterized by a substantial heat of formation, ~100 kJ/mol. at., which is approximately twice that of Ni/Al. Our discussion of equimolar Pt/Al multilayers will focus on the thermal and mass transport characteristics which underly their self-propagating reactions. We have utilized advanced thin film characterization techniques to probe the thermal conductivity of different Pt/Al multilayers having various periodicities. This acquired information is used within the framework of an analytical method developed by Mann et al. (J. Appl. Phys. 1997) to estimate the mass transport properties of Pt/Al multilayers subjected to high heating rates. The analytical model accounts for layer thicknesses, compositional profiles near interfaces, flame temperatures, heats of reaction, and adiabatic temperatures in order to predict reaction wavefront velocity and its variation with multilayer design.

This work was supported by a Sandia Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

5:00pm **SE+2D+NS+SS+TF-WeA9 Adaptive Ceramic Coatings for Extreme Environments**, ***Samir Aouadi***, University of North Texas, *C. Muratore,* University of Dayton, *A.A. Voevodin*, University of North Texas **INVITED**

This talk will provide an overview of the latest research developments in the design and exploration of hard coatings with high temperature adaptive behavior in tribological contacts. The initial focus of the talk will be on understanding the major mechanisms that lead to a reduction in friction and/or wear in high temperature lubricious oxides. Adaptive mechanisms will also be discussed and will include metal diffusion and formation of lubricant phases at worn surfaces, thermally- and mechanically-induced phase transitions in hexagonal solids, contact surface tribo-chemical evolutions to form phases with low melting point, and formation of easy to shear solid oxides. All of these adaptive mechanisms are combined in nanocomposite coatings with synergistic self-adaptation of surface structure and chemistry to lubricate from ambient temperatures to 1000 °C and provide surface chemical and structural reversibility during temperature cycling to maintain low friction coefficients. Changes in the structural and chemical properties of these materials as a function of temperature will be correlated to their mechanical and tribological performance using a range of experimental tools in addition to simulations based on *ab initio* calculations and molecular dynamics simulation methods. This review also includes a discussion of the industrial applications of these coatings as well as of potential improvements to the coating design and other anticipated future developments.

5:40pm **SE+2D+NS+SS+TF-WeA11 Ultralow Wear of Stable Nanocrystalline Metals**, ***Nicolas Argibay***, *T.A. Furnish, T.F. Babuska, C.J. O'Brien, J.F. Curry, B.L. Nation, A.B. Kustas, P. Lu, M. Chandross, D.P. Adams, M.A. Rodriguez, M.T. Dugger, B.L. Boyce, B.G. Clark*, Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been recently proposed and supported by demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of mechanical stress on this stability. In this presentation we discuss the results of an investigation on the stress and temperature dependent stability of a nanocrystalline noble-metal alloy (Pt-Au) in the form of sputtered thin films. We show that stabilization of nanocrystalline structure can impart low friction ($\mu \sim 0.2-0.3$) and remarkable wear resistance, 100x lower than any previously reported metal.

6:00pm **SE+2D+NS+SS+TF-WeA12 From Ab-Initio Design to Synthesis of Multifunctional Coatings with Enhanced Hardness and Toughness**, ***Daniel Edström***, *D. Sangiovanni, L. Hultman, I. Petrov, J. Greene, V. Chirita*, Linköping University, University of Illinois at Urbana-Champaign

Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure. Density Functional Theory (DFT) investigations predicted significant improvements in the toughness of several B1 structured transition-metal nitride (TMN) alloys, obtained by alloying TiN or VN with MoN and WN. The calculations reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, which leads to the formation of alternating layers of high/low charge density orthogonal to the applied stress, and allows a selective response to deformations. This effect is observed for ordered and disordered ternary TMN alloys. The essential feature in the disordered alloys, as reported for ordered alloys, is the increased occupancy of electronic $d\text{-}t_{2g}$ metallic states, which allows the selective response to tensile/shearing stresses, and explains the enhanced toughness confirmed experimentally for VMoN films.

Recently, these results have been validated experimentally. Single-crystal VMoN alloys, grown by dual-target reactive magnetron sputtering together with VN and TiN reference samples, exhibit hardness > 50% higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the VMoN films do not crack.

New DFT calculations suggest similar toughness improvements may be obtained in pseudobinary NaCl structured transition-metal carbide (TMC) compounds by alloying TiC or VC with WC and MoC. A comprehensive electronic structure analysis, as well as stress/strain curves DFT-based calculations, carried out for the newly formed ternary TMC alloys, reveal similar trends between shear-stressed TMN and TMC compounds, and predict VMoC as the best candidate alloy with enhanced ductility.

KEYWORDS: nitrides, carbides, toughness, hardness, ductility.

Advanced Surface Engineering Division
Room: 11 - Session SE+PS+SS-ThM

Plasma-assisted Surface Modification and Deposition Processes
Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Suneel Kodambaka, University of California at Los Angeles

8:00am **SE+PS+SS-ThM1 Key Features of Reactive High Power Impulse Magnetron Sputtering**, ***Daniel Lundin***, CNRS/Paris-Sud University, France **INVITED**

For many thin film applications, such as optical coatings, energy-related coatings, hard coatings, etc., the coated layers are not single metal thin films, but rather compound coatings obtained from at least one metal (e.g. Al, Ti) or a non-metal (e.g. C, B) and a reactive gas (e.g. O_2, N_2). This talk will address the challenges and possibilities of depositing compound coatings using a promising thin film deposition technology called high power impulse magnetron sputtering (HiPIMS), and how this method differs from conventional processes. Both nitride and oxide systems will be covered during different modes of operation including pure argon, metallic, transition, and compound modes. Key features in reactive HiPIMS, such as eliminated/reduced hysteresis, stable high-rate deposition in the transition mode, and self-sputter recycling versus working gas recycling, will be addressed by using results from recent plasma process modelling in combination with experimental plasma characterization. Ionization of the material flux will be discussed in detail, since it enables effective surface modification via ion etching and self-ion assistance during film growth, as well as being a key feature in HiPIMS. This includes exploring the temporal evolution of the discharge plasma parameters, such as electron density and temperature, the neutral and ion composition, the ionization fraction of the sputtered vapor as well as of the reactive gas mixture, and the composition of the discharge current. The focus will be on identifying dominating physical and chemical reactions in the plasma and on the surfaces of the reactor affecting the plasma chemistry.

8:40am **SE+PS+SS-ThM3 Depositions of Al_2O_3 Coatings by HiPIMS via Closed-loop Control using a Plasma Emission Monitoring Sensor**, ***Jianliang Lin***, *R. Wei, K. Coulter,* Southwest Research Institute*, F. Papa*, Gencoa Ltd.

Reactive sputtering of insulating oxide coatings, e.g. alumina (Al_2O_3),by high power impulse magnetron sputtering (HiPIMS) is of great interest, as the increased target ionization in HiPIMS can be used for improving the structure and properties of the coatings. Typically there are two challenges for the process including arc suppression and overcoming the decreased deposition rate due to target poisoning. In this paper, Al_2O_3 coatings were reactively sputtered by HiPIMS with deep oscillatory pulses using closed-loop control of oxygen partial pressure to achieve high deposition rates. Stable and Arc-free deposition processes were obtained with a peak target current density up to 1.2 Acm^{-2} by optimizing key pulsing parameters of deep oscillating pulses. The closed-loop control was achieved by controlling oxygen partial pressure from a remote plasma emission monitoring (PEM) sensor which ionizes sample plasma away from the deposition zone. The deposition rate, microstructure and properties of the Al_2O_3 coatings deposited at different oxygen partial pressures and HiPIMS peak target current densities were investigated and compared to those obtained by traditional pulsed dc.

9:00am **SE+PS+SS-ThM4 The Influence of Spokes on Spatial and Energy Distributions of Ions in Magnetron Sputtering Discharges**, ***Matjaz Panjan***, Jozef Stefan Institute, Slovenia*, K. Tanaka, R. Franz, A. Anders*, Lawrence Berkeley National Laboratory

The formation of dense plasma structures, called ionization zones or spokes, is now a well documented phenomenon in magnetron discharges [1,2]. Experiments and models suggest that these structures strongly influence the transport and the energy of electrons and ions [3,4]. Previously, we measured ion energy distribution functions in the plane of the magnetron by moving its target surface sideways with respect to the orifice of a combined mass spectrometer and energy analyzer (EQP300, Hiden Ltd.) [5]. The measurements showed asymmetric flux of ions in the plane of the target, which was attributed to the moving spokes. Here we report on the measurements of ion energy distribution functions for two different magnetron-EQP arrangements. In the first experimental arrangement, the orifice of EQP300 was directed in the plane of the magnetron and the magnetron was moved in the axial direction. In the second arrangement, the magnetron was rotated around its center for different polar angles while the distance between the target and the orifice was fixed. Measurements were performed in direct current magnetron sputtering (DCMS) using a 3” magnetron and niobium target. Ion energy distribution functions were measured for single and double charged argon and niobium ions. The first experiment showed that the largest flux of high-energy ions (i.e. ions above 10 eV) exists around 30 mm above the target. Overall, higher fluxes were observed in the **E**×**B** direction than in the -**E**×**B** direction. Polar measurements showed larger ion fluxes and higher ion energies near the target plane as compared to considerably lower fluxes and energies perpendicular to the target. The results of the measurements are discussed with respect to the plasma potential structure and associated electric field distribution of a rotating spoke, which we recently measured in DCMS discharge [6].

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

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

[3] R. Franz *et al.*, *Plasma Sources Sci. Technol.*, **25** (2016) 015022

[4] A. Anders, *Appl. Phys. Lett.*, **105** (2014) 244104

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

[6] M. Panjan and A. Anders, *J. Appl. Phys.***121** 063302 (2017)

9:20am **SE+PS+SS-ThM5 Silicon Nitride Deposition for Organic Electronics by VHF (162MHz)- PECVD**, *G.Y. Yeom,* ***KiHyun Kim****, K.S. Kim, Y.J. Ji, J.S. Oh*, Sungkyunkwan University, Republic of Korea

Deposition of permeation barrier film for organic-based electronics is one of the most important issues in organic electronic device fabrication process because the permeation of moisture and oxygen into organic materials causes significant degradation of the device performance and stability. In this study, as an effective thin film barrier material for organic electronics, we investigated low-temperature (~ 80 °C) silicon nitride deposited by very high frequency (VHF, 162MHz) PECVD using multi-tile push-pull electrodes with a gas mixture of NH_3/SiH_4. The composition of the silicon nitride film deposited by VHF PECVD was similar to the ideal stoichiometry of silicon nitride (Si : N = 1 : 1.33) and the deposited film exhibited high optical transparency over 90% in the visible region. The deposited silicon nitride also exhibited a high step coverage of 1:1.29. When water vapor transmission rate (WVTR) was measured with single (400 nm thick) SiN_x layer deposited on PET, excellent WVTR of 4.39 x 10^{-4} $g/m^2 \cdot day$ could be obtained. I-V characteristics of organic light emitting diode (OLED) devices were measured before and after the film deposition on the devices, and no noticeable changes of I-V characteristics after the deposition of silicon nitride film on the OLED devices were observed indicating no noticeable electrical damage by the deposition of silicon nitride using VHF PECVD which is ascribed by low electron temperature characteristics of the plasma and the lack of current flow to the substrate for the VHF-PECVD method utilizing multi-tile push-pull-type electrodes.

Keywords : encapsulation, silicon nitride, organic light emitting diode (OLED), very high frequency (VHF), water vapor transmission rate (WVTR), step coverage

9:40am **SE+PS+SS-ThM6 Printed Circuit Board Assembly- an Ensemble of Different Surface Energy Components and their Surface Modification**, ***Shailendra Vikram Singh***, *S. Woollard, G. Aresta, A.S. Brooks, G. Hennighan*, R&D Semblant Limited

Plasma-produced thin film liquid ingress barrier coatings for electronic devices have several advantages over conventional parylene-based coatings. However, issues connected with plasma processing conditions, electronic device casing designs, and manufacturing technicalities and throughput, independently or in combination, may limit appropriate implementation of such coatings. Hence, it is critical to apply such coatings directly on the printed circuit board assembly (PCBA) of a device to achieve excellent protection against liquid ingress damages. Moreover, an additional coating on the device case can provide extra features and advantage. A PCBA is a complicated substrate in terms of conformality and adhesion requirements. It comprises an ensemble of different surfaces of different shapes and sizes and various materials: metals, polymers, polyester (fiber and resins), graphite, solder residue, etc. The surface energies of these components on boards vary from ~10 mN/m to up-to ~70 mN/m. In this study, we have addressed the surface treatment and etch cleaning requirements for better adhesion of a reworkable conformal plasma coating. The main challenge resides in altering the surface energy consistently across all the surfaces present on a PCBA. Furthermore, in a manufacturing situation the chance of surface contamination due to handling is very high. Especially, in our case, where, the manufacturing speed is >700 standard phone PCBAs/hr/coater batch. Surface chemistry, type and amount of such randomly introduced

contaminations cannot be easily predicted. In this regard, we have also studied several hypothetical contamination situations investigating the relationship between etch-clean and surface energy change.

11:00am **SE+PS+SS-ThM10 Plasma Surface Engineering of Biomaterials**, ***Paul K. Chu***, City University of Hong Kong, Hong Kong **INVITED**

The chemical and biological interactions between biomaterials and biological tissues depend on the surface properties of the biomaterials and associated biological responses. However, many types of biomaterials that possess favorable bulk properties such as hardness, strength, robustness may not perform the pre-designed biological functions and so surface modification is frequently performed to enhance the biological and chemical properties. Plasma-based technology offers the unique capability that selected surface properties can be modified to address specific biological requirements while the desirable bulk properties of the materials such as those mentioned above are preserved. In particular, plasma immersion ion implantation and deposition (PIII&D) is one of the widely used plasma-based surface techniques suitable for biomaterials and biomedical devices. Being a non-line-of-sight technique, it is especially suitable for biomedical devices with a complex shape like dental and orthopedic implants, scoliosis correction rods, cardiovascular stents, and artificial heart valves. In this invited presentation, recent research performed in the Plasma Laboratory of City University of Hong Kong related to plasma treatment of biomaterials and biomedical devices will be described. Examples include biocompatibility of nanostructured surfaces and coatings, biocompatibility of biodegradable materials, bacterial resistance, as well as osseointegration and osteogenesis.

12:00pm **SE+PS+SS-ThM13 Tuning the Properties of Plasma Polymer Varying the Substrate Temperature: a Step Toward the Fabrication of Micro/nano Pattern**, ***Damien Thiry***, University of Mons, Belgium, *N. Vinx, F.J. Aparicio,* University of Mons, *T. Godfroid, S. Deprez,* Materia Nova, *R. Snyders*, University of Mons, Belgium

Plasma polymerization is a well-known technique developed during the last decades for the development of solid organic functionalized thin films (100nm - 1µm) from a large range of organic precursors. The retention of the precursor functionalities and the synthesis of soft material has rapidly become a challenge in the field. The usual strategy consists in limiting the fragmentation of the precursor in the plasma by reducing the load of energy in the discharge. In this work, an almost unexplored approach based on varying the substrate temperature for a given set of plasma parameters is studied in order to extend the control that plasma polymerization provides over the cross-linking degree and the chemical composition of the formed layers. As a case study, propanethiol plasma polymer films (Pr-PPF) finding application as support for gold nanoparticles and biomolecules immobilization are investigated.

The deposition rate of Pr-PPF was found to follow an Arrhenius law with the substrate temperature (T_s) varying from -10 °C to 45°C. This behavior is explained through the influence of T_s on the residence time of the film-forming species at the growing film interface. With regard to the chemical composition of the layers, the atomic sulfur content is nearly constant (i.e. ~ 45 at. %) in the range -10 °C < T_s < 23 °C and strongly decreases (i.e. ~ 30 at. %) for T_s > 23 °C. Based on these data, it can be proposed that a critical T_S has to be reached for favouring the desorption of sulfur-based species before their incorporation within nascent plasma polymer. On the other hand, "rough" indentations measurements combined with optical microscopy imaging reveal that for T_s < 10°C, a deformation of the Pr-PPF takes place when applying a force (i.e. 1 mg) on the top of the polymer with the tip of the profilometer. Furthermore, a fast recovery of the plasma polymer layer occurs over a time scale of about 3 min. As an important result, these data disclose the possibility to produce soft and visco-elastic plasma polymer layer. Finally, inspired by the wrinkling phenomenon occurring in a bilayer system exhibiting a high contrast in terms of mechanical properties, a thin aluminium coating is deposited by magnetron sputtering on the top of a low cross-linked Pr-PPF synthesized at T_s = 10°C. The mismatch between the mechanical properties between both layers results in the formation of a wrinkled surface. By tuning the thickness of the aluminium and the Pr-PPF coatings, the height (i.e. from 0.4 to 5.2 µm) and the width (i.e. from 0.6 µm to 6.5 µm) of the nano/micro objects can be easily tailored offering a great flexibility in terms of nano/micro engineering.

Thin Films Division
Room: 20 - Session TF+SE-ThM

Control, Characterization, and Modeling of Thin Films I
Moderators: Hilal Cansizoglu, University of California, Davis, Tansel Karabacak, University of Arkansas at Little Rock

8:00am **TF+SE-ThM1 *In Situ* Synchrotron Characterization Techniques Enabled Nanostructured Materials using ALD**, ***Yu Lei***, University of Alabama in Huntsville

To achieve the goal of rational design of next generation of advanced materials, we have been working on developing atomic layer deposition (ALD) as a promising method to tailor size and composition of nanostructured materials for a wide range of applications. Benefiting from self-limiting surface reactions, ALD enables conformal coatings of materials on three-dimensional substrates. The atomic level control of depositions makes it attractive to precisely synthesize the size and composition of nanomaterials. The size and composition of nanomaterials play important roles in achieving high performance in many applications. In this talk, we will discuss nanomaterials synthesized using Pd ALD and their applications in catalysis and energy storage. We will also illustrate that *in situ* characterization techniques such as synchrotron X-ray based X-ray absorption spectroscopy (XAS), X-ray pair distribution function (PDF), and FT-IR significantly advance our understandings of ALD in terms of surface chemistry and surface dynamics.

8:20am **TF+SE-ThM2 Probing the Atomic Scale Structure of Polar Oxide Interfaces**, ***Sanaaz Koohfar***, *D.P. Kumah*, North Carolina State University

Complex oxide heterostructures possess a wide range of functional electronic and magnetic properties including metal-insulator transitions, superconductivity, ferroelectricity and colossal magnetoresistance effects. At epitaxial interfaces formed between atomically thin complex oxide films, electronic, chemical and structural interactions can be used to effectively tune the physical properties of these materials. Using a combination of atomic-scale controlled thin film synthesis and high resolution synchrotron diffraction based imaging, we show that structural distortions at the interfaces between polar $La_{1-x}Sr_xMnO_3$ films and non-polar substrates can be effectively tuned by chemical modifications at these interfaces to control ferromagnetism in [001]-oriented $La_{1-x}Sr_xMnO_3$ films with thickness less than 1 nm. We show that atomic-scale chemical control at polar/non polar oxide interfaces provides a powerful route to engineer novel electronic and magnetic phenomena at complex oxide interfaces.

8:40am **TF+SE-ThM3 CVD Chemistry of Trimethylboron - Gas Phase Reactions and Surface Poisoning Effects**, ***Henrik Pedersen***, *L. Souqui, M. Imam,* Linköping University, Sweden, *R. Tonner,* Philipps Universität Marburg, *H. Högberg*, Linköping University, Sweden

Organoborons with short alkyl groups; trimethylboron (TMB), $B(CH_3)_3$, triethylboron (TEB), $B(C_2H_5)_3$, and tributylboron (TBB), $B(C_4H_9)_3$, were suggested as alternative, highly reactive, less-poisonous, non-explosive B-precursors in the mid 1990's[1].TEB was found to exhibit the best properties for CVD of boron-carbon films, making it a popular CVD precursor[2]. TMB and TBB were deemed not suitable as CVD precursors as no boron was found in the films deposited from these molecules. Consequently, these molecules are less investigated in CVD.

We study the gas phase chemistry of TMB in a thermal CVD process, using a combination of B-C film deposition experiments at several temperatures in both hydrogen and argon atmosphere and quantum chemical calculations for a wide range of possible gas phase reactions. We suggest that without assistance from the carrier gas, i.e. in argon ambient, TMB most likely decomposes by α-H elimination of CH_4 to form H_2CBCH_3. Methane is not highly reactive in CVD at deposition temperatures below 1000 °C, meaning that the H_2CBCH_3 species is the major film forming species. This correlates well with the B/C ratio of about 0.5 observed for films deposited in Ar at 700-900 °C. At higher temperatures, the B/C ratio of films increases as attributed to further decomposition to H_2BCH_3.

With assistance from the hydrogen carrier gas, TMB can also decompose to $HB(CH_3)_2$ that can further decompose to H_2BCH_3 and finally to BH_3, all with negative Gibbs free energies, albeit with some high energy barriers. This in combination with the unimolecular α-H elimination with a somewhat lower energy barrier, can explain the higher B/C ratios of films deposited in H_2.

Furthermore, we note that the onset of film deposition from TMB is 700 °C and at then at a very low deposition rate. Interestingly the film thickness does not increase with longer deposition time at 700 °C, indicating a surface

poisoning effect. As this is seen both in Ar and H_2, we speculate that this is caused by CH_4 or H_2CBCH_3, which is currently the subject of our further investigations.

[1]J. S. Lewis et al. Chemical vapor deposition of boron-carbon films using organometallic reagents. *Mater. Lett.* **1996**, *27*, 327.

[2]M. Imam et al. Gas phase chemical vapor deposition chemistry of triethylboron probed by boron–carbon thin film deposition and quantum chemical calculations. *J. Mater. Chem. C* **2015**, *3*, 10898.

9:20am **TF+SE-ThM5 *In Situ* Synchrotron-based Characterization of Noble Metal ALD Processes**, *J. Dendooven, **Eduardo Solano**, R.K. Ramachandran, M.M. Minjauw,* Ghent University, Belgium*, A. Coati,* Synchrotron SOLEIL, France*, D. Hermida-Merino,* ESRF, France*, C. Detavernier*, Ghent University, Belgium **INVITED**

Supported noble metal nanoparticles (NPs) are widely used in heterogeneous catalysis because of their high resistance against chemical poisoning. Atomic Layer Deposition (ALD) can be used to synthesize noble metal NPs on different high surface area supports, and offers sub-monolayer control over the metal loading (atoms per cm^2 of support) [1]. However, an improved understanding of how the deposition parameters influence the formation and growth of noble metal NPs is required to fully exploit the tuning potential of ALD.

We developed a synchrotron-compatible high-vacuum setup that enables in-situ monitoring during ALD [2]. Using this setup and focusing on ALD of Pt with the $MeCpPtMe_3$ precursor at 300 °C [3], we present an in-situ investigation of Pt NP growth on planar SiO_2 substrates by means of X-ray fluorescence (XRF) and grazing incidence small-angle X-ray scattering (GISAXS). The surface density of Pt atoms was determined by XRF. Analysis of the GISAXS patterns [4] yielded dynamic information on average real space parameters such as Pt cluster shape, size and spacing. The results indicate a diffusion-mediated particle growth regime for the standard O_2-based Pt ALD process, marked by a decreasing average areal density and formation of laterally elongated Pt clusters. Growth of the Pt NPs is thus not only governed by the adsorption of Pt precursor molecules from the gas-phase and subsequent combustion of the ligands, but is largely determined by adsorption of migrating Pt species on the surface and diffusion-driven particle coalescence [5].

Next, we have studied the influence of the reactant type (O_2 gas, O_2 plasma, N_2 plasma, NH_3 plasma [6]) on the Pt NP growth. Surprisingly, a clear difference in island growth behavior was found for the oxygen- vs. nitrogen-based processes. The latter processes were marked by a constant average particle distance during the growth process. Particle dimension analysis furthermore revealed vertically elongated NPs for the N_2 and NH_3 plasma-based Pt ALD processes. Therefore, it is concluded that atom and cluster surface diffusion phenomena are suppressed during the nitrogen-based processes. Finally, this insight provided the ground for the development of a tuning strategy that is based on combining the O_2-based and N_2 plasma-based ALD processes and offers independent control over NP size and coverage.

[1] Lu et al., Surf. Sci. Rep. 71 (2016) 410. [2] Dendooven et al., Rev. Sci. Instrum. 87 (2016) 113905. [3] Aaltonen et al., Chem. Mater. 15 (2003) 1924. [4] Schwartzkopf et al., Nanoscale 5 (2013) 5053. [5] Mackus et al., Chem. Mater. 25 (2013) 1905. [6] Longrie et al., ECS J. Solid State Sci. Technol. 1 (2012) Q123.

11:00am **TF+SE-ThM10 *In-situ* FTIR Study of the Atomic Layer Deposition of Scandium Oxide Films using Bis(methylcyclopentadienyl)3,5-dimethylpyrazolatoscandium with Ozone and with Water**, ***Rezwanur Rahman**, J.P. Klesko, A. Dangerfield,* University of Texas at Dallas*, J.-S. Lehn, C.L. Dezelah, R. Kanjolia,* EMD Performance Materials*, Y.J. Chabal*, University of Texas at Dallas

Scandium oxide (Sc_2O_3) thin films have been thoroughly studied for their use in microelectronic devices.[1–2] However, processes for the atomic layer deposition (ALD) of Sc_2O_3 films are scarce, and have mostly involved $Sc(thd)_3$,[1] $ScCp_3$,[1] $Sc(MeCp)_3$,[2] and $Sc(amd)_3$[3] precursors. To date, the only mechanistic investigation has focused on the $Sc(MeCp)_3/H_2O$ process using *in-situ* time-resolved quadrupole mass spectrometry to probe the Sc_2O_3 ALD chemistry.[2]

Herein, we have explored the Sc_2O_3 ALD using bis(methylcyclopentadienyl)3,5-dimethyl pyrazolatoscandium ($Sc(MeCp)_2(Me_2pz)$) with ozone and with D_2O. This precursor reacts with hydroxyl-terminated silicon, Si(111)– SiO_2–OH, at 150 °C and appears to remain thermally stable to 450 °C. Between 225 and 275 °C, there is a clear ligand exchange with ozone observed in the differential IR absorption spectra involving the formation of intermediate formate and carbonate species (1400–1600 cm^{-1}) after each ozone pulse. A short incubation period (≤ 5 ALD cycles) is observed at 225 °C prior to the onset of steady-state ligand exchange. The signature for the formation of Si–O–Sc bonds (1240 cm^{-1}) is clearly present after cycles 1–2 for the ozone process at 275 °C. The Sc_2O_3 growth is quantified by X-ray photoelectron spectroscopy (XPS) and by spectroscopic ellipsometry (SE), from which a growth rate of ~0.3–0.9 Å/cycle is extracted over the 225–275 °C temperature range.

In contrast, there is no ligand exchange observed for the D_2O process within the same temperature range, although some deposition occurs. The deposition rate for the D_2O process calculated by XPS and SE, is ~1.3 Å/cycle within the 225–275 °C window, which is higher than the non-uniform growth rate measured for the ozone process within that temperature range. The higher growth rate and lack of ligand exchange observed with D_2O is tentatively attributed to a CVD component that dominates the film growth process.

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11:20am **TF+SE-ThM11 Ultra Fast Compositional Depth Profile Analysis for Microelectronics Applications**, ***Agnès Tempez**,* Horiba France S.a.s., France*, Y. Mazel, J.-P. Barnes, E. Nolot,* CEA/LETI-University Grenoble Alpes, France*, S. Legendre,* Horiba France S.a.s., France*, M. Chausseau*, HORIBA Instruments Incorporated

Wouldn't it be a considerable gain of time to be able to check the stoichiometry of just deposited thin films in a few minutes? A recently commercially available sputter-based technique called plasma profiling time-of-flight mass spectrometry (PP-TOFMS) is capable to produce, in a few minutes, nm-scale depth resolved profiles of all elements (including light elements) of the periodic table, over a wide dynamic range (from 100% down to ppm)[1]. A simple ratio of the amount of ions detected from a given layer provides a calibration free semi-quantification.

For such fast feedback purposes a PP-TOFMS instrument (Horiba Scientific, Horiba FRANCE SAS, France) has been installed in the clean room of the CEA-LETI in close proximity to process tools.

In this paper we will present data obtained from microelectronics and nanotechnology thin films to demonstrate the performance of the technique. It will be shown that PP-TOFMS can be used for determining composition, detecting contamination, measuring doping level, and characterizing diffusion mechanisms.

For example we will show the ease of detecting, identifying, and locating in depth the presence of unexpected contamination in magnetic Iron Cobalt Boron multi-layers. Another example will show the depth profile of a Germanium Antimony Tellurium alloy deposited on silicon oxide used for phase change memories, a type of non-volatile random access memory. PP-TOFMS depth profiles agree with TOF-SIMS and STEM-EDX analyses for both the first nanometers and the in-depth composition.

[1] A. Tempez et al., J. Vac. Sci. Technol. B (2016) 34

11:40am **TF+SE-ThM12 Surface Termination of Fe_3O_4(111) Films Studied by CO Adsorption**, ***Francesca Mirabella**, E. Zaki, F. Ivars, S. Shaikhutdinov, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*, X. Li, J. Paier, J. Sauer*, Humboldt Universität zu Berlin, Germany

Although the (111) surface of Fe3O4 (magnetite) has been investigated for more than twenty years, substantial controversy remains in the literature regarding the surface termination [1, 2]. To shed more light on this issue, we performed CO adsorption studies on (111) and (001) oriented thin films, using in-situ infrared reflection absorption spectroscopy, temperature programmed desorption, and scanning tunneling microscopy. The experimental results were rationalized on the basis of theoretical calculations, thus leading to a unified picture in which the Fe_3O_4(111) surface is terminated by 1/4 monolayer of tetrahedrally coordinated Fe^{3+} ions on top of a close-packed oxygen layer as previously determined by low energy electron diffraction. However, surface defects play a crucial role in adsorption properties and most likely dominate chemical reactions on Fe_3O_4(111) when exposed to the ambient.

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Advanced Surface Engineering Division
Room: Central Hall - Session SE-ThP

Advanced Surface Engineering Poster Session

SE-ThP1 Surface Passivation of Energetic Particles Via Atomic Layer Deposition, ***Kai Qu***, Huazhong University of Science an Technology, PR China, *C.L. Duan, P.H. Zhu, J.M. Cai, R. Chen*, Huazhong University of Science and Technology, PR China

Energetic particles, such as aluminum hydride (AlH_3) and aluminum (Al) nanoparticles, have shown great potentials for military and astronautic uses. Due to their high reactivity, the practical implementations of these materials rely on their safe storage, handling, transportation, etc. For example, during the storage of AlH_3, hydrogen could be slowly released through reaction with moisture and oxygen. When mixing AlH_3 with other fuels or transportation, the heat generated from inter-particle friction may lead to the temperature rise, resulting in rapid hydrogen release and may trigger explosion. When fabricate explosive in water at 60-70°C, aluminum nanoparticles will react with water molecules. Thus it is imperative to passivate the AlH_3 and Al particles to improve their stabilities. In this talk, both α-AlH_3 and Al particles were passivated *via* atomic layer deposition to improve their storage, transportation, and mixture stabilities. The transmission electron microscopy showed conformal amorphous Al_2O_3 shells around the crystalline AlH_3 cores. The hydrogen capacity was well retained after hydrothermal aging test. The friction sensitivity got reduced, while the overall hydrogen capacity and dehydrogenation speed are kept about the same. For Al nanoparticles, a few cycles of compact ALD coating could completely isolated the water bath at 60°C-80°C. The minimum thickness of coating layers ensured that high energy of the Al nanoparticles were well retained.

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Dendooven, J.: TF+SE-ThM5, 7
Deprez, S.: SE+PS+SS-ThM13, 6
Detavernier, C.: TF+SE-ThM5, 7
Dezelah, C.L.: TF+SE-ThM10, 7
Duan, C.L.: SE-ThP1, 8
Dugger, M.T.: SE+2D+NS+SS+TF-WeA11, 4

— E —

Ebnonnasir, A.: SE+2D+NS+SS+TF-WeA4, 3
Edström, D.: SE+2D+NS+SS+TF-WeA12, **4**

— F —

Fankhauser, J.: SE+2D+NS+SS+TF-WeA4, 3
Franz, R.: SE+PS+SS-ThM4, 5
Freund, H.-J.: TF+SE-ThM12, 7
Frijters, C.: PS+AS+SE-MoM10, 2
Furnish, T.A.: SE+2D+NS+SS+TF-WeA11, 4

— G —

Gazibegović, S.: PS+AS+SE-MoM10, 2
Gelinck, G.: PS+AS+SE-MoM10, 2
Ghosh, S.: PS+AS+SE-MoM8, 2
Go, D.B.: PS+AS+SE-MoM8, 2
Godfroid, T.: SE+PS+SS-ThM13, 6
Goorsky, M.S.: SE+2D+NS+SS+TF-WeA4, 3
Grant, J.T.: SE+2D+NS+SS+TF-WeA3, 3
Greene, J.: SE+2D+NS+SS+TF-WeA12, 4

— H —

Hawtof, R.: PS+AS+SE-MoM8, **2**
Hennighan, G.: SE+PS+SS-ThM6, 5
Hermida-Merino, D.: TF+SE-ThM5, 7
Högberg, H.: TF+SE-ThM3, 6
Hultman, L.: SE+2D+NS+SS+TF-WeA12, 4

— I —

Illiberi, A.: PS+AS+SE-MoM10, 2
Imam, M.: TF+SE-ThM3, 6
Ivars, F.: TF+SE-ThM12, 7

— J —

Ji, Y.J.: SE+PS+SS-ThM5, 5

— K —

Kanjolia, R.: TF+SE-ThM10, 7
Katsouras, I.: PS+AS+SE-MoM10, 2
Kim, K.H.: SE+PS+SS-ThM5, **5**
Kim, K.S.: SE+PS+SS-ThM5, 5
Kittell, D.E.: SE+2D+NS+SS+TF-WeA8, 3
Klesko, J.P.: TF+SE-ThM10, 7
Kobashi, M.: SE+2D+NS+SS+TF-WeA4, 3
Kodambaka, S.: SE+2D+NS+SS+TF-WeA4, **3**
Koohfar, S.: TF+SE-ThM2, **6**
Kumah, D.P.: TF+SE-ThM2, 6
Kustas, A.B.: SE+2D+NS+SS+TF-WeA11, 4

— L —

Lalor, J.: PS+AS+SE-MoM1, 1
Legendre, S.: TF+SE-ThM11, 7
Lehn, J.-S.: TF+SE-ThM10, 7
Lei, Y.: TF+SE-ThM1, **6**
Li, C.: SE+2D+NS+SS+TF-WeA4, 3
Li, X.: TF+SE-ThM12, 7
Lin, J.: SE+PS+SS-ThM3, **5**
Lu, P.: SE+2D+NS+SS+TF-WeA11, 4
Lundin, D.: SE+PS+SS-ThM1, **5**

— M —

Maas, J.: PS+AS+SE-MoM10, 2
Maira, N.: PS+AS+SE-MoM2, **1**
Manandhar, S.: SE+2D+NS+SS+TF-WeA7, 3
Mazel, Y.: TF+SE-ThM11, 7
Mededovic Thagard, S.: PS+AS+SE-MoM5, **2**
Milosavljevic, V.: PS+AS+SE-MoM1, **1**
Minjauw, M.M.: TF+SE-ThM5, 7
Mirabella, F.: TF+SE-ThM12, **7**
Muratore, C.: SE+2D+NS+SS+TF-WeA9, 4
Murphy, N.R.: SE+2D+NS+SS+TF-WeA3, 3

— N —

Nation, B.L.: SE+2D+NS+SS+TF-WeA11, 4
Nekovic, E.: PS+AS+SE-MoM10, 2
Nolot, E.: TF+SE-ThM11, 7

— O —

O'Brien, C.J.: SE+2D+NS+SS+TF-WeA11, 4
Oh, J.S.: SE+PS+SS-ThM5, 5
Ozkan, A.: PS+AS+SE-MoM3, 1

— P —

Paier, J.: TF+SE-ThM12, 7
Panjan, M.: SE+PS+SS-ThM4, **5**
Papa, F.: SE+PS+SS-ThM3, 5
Pedersen, H.: TF+SE-ThM3, **6**
Petrov, I.: SE+2D+NS+SS+TF-WeA12, 4
Poodt, P.: PS+AS+SE-MoM10, 2

— Q —

Qu, K.: SE-ThP1, **8**

— R —

Rahman, R.: TF+SE-ThM10, **7**
Ramachandran, R.K.: TF+SE-ThM5, 7
Ramana, C.V.: SE+2D+NS+SS+TF-WeA7, 3
Reniers, F.: PS+AS+SE-MoM2, 1; PS+AS+SE-MoM3, **1**
Rodriguez, M.A.: SE+2D+NS+SS+TF-WeA11, 4
Roozeboom, F.: PS+AS+SE-MoM10, **2**
Rosen, J.: SE+2D+NS+SS+TF-WeA1, **3**
Rumbach, P.: PS+AS+SE-MoM8, 2
Ruzic, D.N.: PS+AS+SE-MoM4, 1

— S —

Saltonstall, C.B.: SE+2D+NS+SS+TF-WeA8, 3
Sangiovanni, D.: SE+2D+NS+SS+TF-WeA12, 4
Sankaran, R.M.: PS+AS+SE-MoM8, 2
Sato, M.: SE+2D+NS+SS+TF-WeA4, 3
Sauer, J.: TF+SE-ThM12, 7
Scally, L.: PS+AS+SE-MoM1, 1
Shaikhutdinov, S.: TF+SE-ThM12, 7
Shchelkanov, I.A.: PS+AS+SE-MoM4, 1
Singh, S.V.: SE+PS+SS-ThM6, **5**
Snyders, R.: SE+PS+SS-ThM13, 6
Sobczak, C.: SE+2D+NS+SS+TF-WeA8, 3
Solano, E.: TF+SE-ThM5, **7**
Souqui, L.: TF+SE-ThM3, 6
Sun, L.: SE+2D+NS+SS+TF-WeA3, **3**

— T —

Tanaka, K.: SE+2D+NS+SS+TF-WeA4, 3; SE+PS+SS-ThM4, 5
Tempez, A.L.: TF+SE-ThM11, **7**
Thiry, D.: SE+PS+SS-ThM13, **6**
Tonner, R.: TF+SE-ThM3, 6

— V —

van Boekel, W.: PS+AS+SE-MoM10, 2
Vasilev, M.: PS+AS+SE-MoM5, 2
Vinx, N.: SE+PS+SS-ThM13, 6
Visart de Bocarmé, T.: PS+AS+SE-MoM3, 1
Voevodin, A.A.: SE+2D+NS+SS+TF-WeA9, 4

— W —

Wei, R.: SE+PS+SS-ThM3, 5
Woollard, S.: SE+PS+SS-ThM6, 5

— Y —

Yarrington, C.D.: SE+2D+NS+SS+TF-WeA8, 3
Yeom, G.Y.: SE+PS+SS-ThM5, 5
Yu, D.: SE+2D+NS+SS+TF-WeA4, 3

— Z —

Zaki, E.: TF+SE-ThM12, 7
Zhu, P.H.: SE-ThP1, 8