## 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.

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