**Advanced Surface Engineering**
**Room: 302 - Session SE+EM+EN+PS+TF-MoM**

**New Developments in Atmospheric Pressure Plasma Deposition and Thin Films for Energy Applications**
**Moderator:** Hana Barankova, Uppsala University, Sweden, Michael Stueber, Karlsruhe Institute of Technology

8:40am **SE+EM+EN+PS+TF-MoM2 Real Time Characterization of Polymer Surface Modification by an Atmospheric Pressure Plasma Jet**, ***Andrew Knoll***, *P. Luan, E.A.J. Bartis, C. Hart*, University of Maryland, College Park, *Y. Raitses*, Princeton Plasma Physics Laboratory, *G.S. Oehrlein*, University of Maryland, College Park

Atmospheric pressure plasma jets (APPJ) have been shown to modify surfaces, leading to a variety of potential industrial and medical applications. APPJ treated surfaces are typically evaluated post treatment, but few studies exist showing surface changes in real time. In this study, we characterized both closely-coupled and remote APPJ treatments of a PMMA-based 193 nm photoresist polymer (PR193) using *in situ* ellipsometry to monitor film thickness and refractive index in real time. The kilohertz-driven, two-ring electrode APPJ was fed with low admixtures of $O_2$ and $N_2$ to Ar. Voltage and current waveforms were collected to electrically characterize the APPJ and measure power dissipation. In addition, high speed photography of the APPJ was conducted in order to characterize plasma interaction with various controlled environments and with PR193. Ellipsometry shows that PR193 etch rates depend on the feed gas chemistry and treatment time. Etch rates are reduced for $Ar/O_2$ compared with pure Ar and $Ar/N_2$. This reduction is correlated to a decrease in plasma density with $O_2$ addition. It is also shown that the etch rate changes over time initially during APPJ heating and reaches steady state as the temperature stabilizes. When the plasma is brought close enough to the sample, the discharge couples with the surface and arcing to the film occurs. This interaction greatly increases the etch rate and introduces major damage to the polymer, which can be observed by the naked eye. From electrical data and high speed photography we see that the pure Ar discharge exhibits filamentary behavior that is enhanced by $O_2$ addition and rendered more diffuse by $N_2$ addition. High speed photography shows that the coupling of the plasma and the environment increases when the environment matches the feed gas chemistry, which causes the plume to extend farther than in open air. While the Ar plume is confined to a single plasma channel, $N_2$ admixture to Ar branches out into many smaller discharges, similar to a Lichtenberg figure. We also correlate damage seen on the polymer surface with observed arcing. The authors gratefully acknowledge financial support by US Department of Energy (DE-SC0001939).

9:00am **SE+EM+EN+PS+TF-MoM3 Gas-Liquid Mixed Phase Plasma at Atmospheric Pressure**, ***Akira Ando***, *G. Tang, R. Ohno, A. Komuro, K. Takahashi*, Tohoku University, Japan **INVITED**

A gas-liquid mixed phase plasma discharge is investigated using nanosecond high-voltage pulse generator. Non-thermal atmospheric pressure plasmas have recently attracted significant attention due to their good energy efficiency in production of reactive species. Plasma in water can generate many reactive species, such as ozone, hydroxyl radicals and oxygen radicals. These products have strong oxidizing power and is applicable for many applications without any thermal stress.

We have utilized a nanosecond high-voltage pulse to produce a discharge within bubbles introduced into water, where semiconductor opening switching (SOS) diodes are used in the pulse generator.

The reactor for the gas-liquid hybrid plasma consists of two regions, gas and liquid regions, separated by a thin plate with a small holes (1mm in diameter). Several working gases are fed into the reactor from the gas region and bubbles are formed via the separator holes in the water. High-voltage pulse with 10-15kV are applied to a wire electrode situated in the gas phase. A grounded electrode is set into the water. When the high voltage pulse with the duration of 40ns is applied, a streamer-like discharge occurs within the bubbles and the streamer extends along the surface of gas-liquid interface.

The formation process of discharge bubbles were observed with a high-speed CCD images of the discharge. The area of discharge extension depends on the gas species and conductivity. Production rate of reactive species, ozone and hydroxyl radicals in a discharge reactor was also depends on the parameters. As the life time of hydroxyl radicals is very short, the amount is estimated from concentration of hydrogen peroxide produced in treated water, which is produced by the recombination process of hydroxyl radicals.

In order to evaluate the oxidation power in the gas-liquid mixed plasma, we applied it to water purification, such as decolorization, sterilization and decomposition of persistent organic pollutants (POPs). The sterilization effect in the water is estimated from the survival ratio of bacillus subtilis and it reaches more than 99.5% after 15min treatment. The survival ratio is large in air discharge and the value of pH in water as well as ultraviolet (UV) ray generated by plasma discharge affects the sterilization. SEM images shows the surface of the bacteria were damaged by the treatment.

9:40am **SE+EM+EN+PS+TF-MoM5 Atmospheric Pressure High Power Impulse Plasma Source (AP-HiPIPS) for Plasma Enhanced Chemical Vapor Deposition of Thin Films**, ***Vasiliki Poenitzsch***, *R. Wei, M.A. Miller, K. Coulter*, Southwest Research Institute

Southwest Research Institute is currently developing a High Power Impulse Plasma Source (HiPIPS) that supplies a high flux of energetic reactants to a surface while maintaining a low processing temperature. HiPIPS is a new plasma enhanced chemical vapor deposition technology that combines variable pressure plasma jets with advanced pulsed power technology. Several complementary techniques, including mass spectroscopy, optical emission spectroscopy (OES) and electrical and thermal probes were employed, for measuring and calculating the plasma characteristics in a wide range of the HiPIPS process parameters and conditions. The preliminary HiPIPS experiments have revealed that high peak power (~40 kW) in the pulses can be achieved resulting in a high peak current (~200 A) and increased plasma density (i.e. n = Ar: $10^{20}$ $cm^{-2}s^{-1}$) while maintaining a low average power (35W) and a low substrate processing temperature (50-150 °C). A prototype atmospheric-pressure HiPIPS (AP-HiPIPS) was successfully developed and proof-of-concept AP-HiPIPS diamond-like carbon (DLC) film deposition was demonstrated. Beyond DLC films, HiPIPS plasmas could be applicable to deposition of many classes of films and many types of surface treatments. In contrast to conventional state-of-the-art non-thermal atmospheric pressure plasma jets, typically driven by RF or AC, the power densities and currents during pulse on-time are 2-3 orders of magnitude higher in HiPIPS. Since plasma is created through inelastic electron collision with precursor gas molecules, the increased power and current directly equates to significantly improved ionization and dissociation of precursor gases in HiPIPS. Thus, distinguishing features of HiPIPS as compared to RF or AC APPJs are increased ionization, enhanced molecular gas dissociation, and higher flux of reactive species while maintaining the same low deposition temperatures. In this presentation, an overview of HiPIPS and AP-HiPIPS will be given with a specific focus on plasma characteristics and areas for further development.

10:00am **SE+EM+EN+PS+TF-MoM6 Importance of Argon's Spectral Emission for Plasma Diagnostics at an Atmospherics Open Air Plasma Discharge**, ***Vladimir Milosavljevic***, *J. Lalor, P. Bourke, P.J. Cullen*, Dublin Institute of Technology, Ireland

In recent years, plasma on atmospheric pressure attracts a lot of attention due to their numerous applications in plasma biology, health care, and medicine, as well as surface and materials processing and nanotechnology. Among several atmospheric pressure plasma devices, a dielectric barrier discharge plasma jet (DBDPJ) is the most used, because of its simplicity and a fact that the generated plasma is in surrounding air and not in a confined space. The dynamics of DBDPJ in noble gases reveal that the plasma plumes propagate at a speed several orders of magnitude higher than the gas flow velocity. This is why it is generally accepted that the propagation of the plasma plumes is driven electrically rather than by the gas flow, which imposes in the first place the importance of the plasma diagnostics. Because of the frequent collisions between electrons and neutrals at high pressure, the electrical probe methods are generally less useful for plasmas produced at atmospheric pressure. Therefore, other diagnostic methods are needed and optical emission spectroscopy (OES) has been used as one of the alternative diagnostics because of its simplicity and non-intrusive nature.

Nitrogen dominates the ionic composition of atmospheric discharge and has an impact on the breakdown voltage. Nitrogen acts as a 'sensor gas' and OES diagnostics are applied in assumption that most nitrogen molecular emissions are excited during electron impact of ground state N2(X). When nitrogen is added/mixed with argon plasma discharges, the argon emission lines are significantly quenched and the resulting plasma spectral emission is changed. Measurements and analysis of neutral argon spectral emission lines give very important information about the plasma properties. In this work the absolute spectral emissions of the atomic and molecular lines associated with argon, oxygen, nitrogen and hydrogen are presented. Wavelength resolved optical emission profiles of argon's spectral lines

shows that the change in electron energy distribution functions (EEDF) has taken place for a low gas flow rate only. After the gas flow rate goes above a certain limit, the EEDF remains constant. At the same time the density of argon metastable atoms are changed with the gas flow rate. Overall, analysis of the spectral intensities assist in the development of optimised plasma processing parameters for treatments such as surface activation or removal of contaminates.

The research leading to these results has received funding from the European Union´s Seventh Framework Programme managed by REA Research Executive Agency (FP7/2007-2013) under Grant Agreement number 605125

10:40am **SE+EM+EN+PS+TF-MoM8 Hot 'n Flaky: Thermal Properties of Layered Atomic Structures**, ***Christopher Muratore***, University of Dayton, *V. Varshney*, Air Force Research Laboratory/UTC, *J.J. Hu*, Air Force Research Laboratory/UDRI, *A.A. Voevodin*, Air Force Research Laboratory **INVITED**

Synthesis capability for uniform growth of 2D materials over large areas at lower temperatures without sacrificing their unique properties is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into novel devices. We have demonstrated, for the first time, vapor phase growth techniques for precisely controlled synthesis of continuous, uniform molecular layers of all $MoX_2$ and $WX_2$ transition metal dichalcogenide (TMD) compounds on diverse substrates, including graphene, hexagonal boron nitride, highly oriented pyrolitic graphite (HOPG), $SiO_2$, and metal substrates over several square centimeters. Preliminary results show $MoX_2$ and $WX_2$ transition metal dichalcogenide materials grown in a novel ultra-high vacuum (UHV) physical vapor deposition (PVD) process demonstrate properties identical or even superior (e.g., electron mobilities >500 $cm^2 V^{-1} s^{-1}$) to exfoliated layers. Growth of bi-layer $MoS_2$ on few-layer graphene with a 30% lattice mismatch and TMD/TMD heterostructures are shown to demonstrate how natural accommodation of stresses at 2D van der Waals interfaces has the remarkable potential to transform the way materials selection is considered for synthetic heterostructures, as concerns regarding lattice constant matching can be abandoned with preference given to desired properties and performance. Investigations relating to application of these materials in thermoelectric device applications are presented. Thermal conductivity values of TMD thin films were compared to bulk crystals, revealing expected trends with mass, but a >10 fold reduction in thin film thermal conductivity. Phonon scattering lengths at domain boundaries based on computationally derived group velocities were consistent with the observed film microstructure, accounting for the reduction. We also explore thermal anisotropy in $MoS_2$ films. Measurement results are correlated with MD simulations of thermal transport for perfect and defective $MoS_2$ crystals, demonstrating the importance of thermal boundary scattering.

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