

Monday Morning, October 28, 2013

Plasma Science and Technology

Room: 102 B - Session PS+AS+BI+SE-MoM

Atmospheric Plasma Processing: Fundamental and Applications

Moderator: M.A. Lieberman, University of California, Berkeley

8:20am **PS+AS+BI+SE-MoM1 Field Emission in Microscale Dimensions: A New Approach to Atmospheric Pressure Gas Discharges**, *Y. Li, P. Rumbach, D.B. Go*, University of Notre Dame
INVITED

Electron field emission is traditionally considered a low-pressure phenomenon and most field emission-based technologies, such as scanning electron microscopes, generate field emission under high vacuum conditions. However, over the course of past decade, advances in microscale devices have led to the field emission devices that operate at high pressures, including at and near to atmospheric pressure. At these pressures, the field-emitted electrons can ionize the interstitial gas between the electrodes, leading to the formation of gas discharges. With emerging applications in gas sensing and gas reforming, this new approach to gas discharges not only introduces new, interesting physics but also offers many new technological opportunities. This work will focus on the theory and generation of stable, field emission-driven Townsend discharges. The physical concepts underpinning these discharges will be discussed as theoretical and modeling efforts have highlighted many significant features of this discharge mode – including very high electron densities ($\sim 10^{14} \text{ cm}^{-3}$) and highly non-Maxwellian electron densities. Experimental studies and the role of the cathode material will also be discussed as evidence of pressure scaling for field emission will be presented. Finally, new applications and future opportunities for discovery will be covered.

9:00am **PS+AS+BI+SE-MoM3 Simulation of Microplasma Based Pressure Sensors**, *J.-C. Wang, Z. Xiong, C. Eun, X. Luo, Y. Gianchandani, M.J. Kushner*, University of Michigan

Pressure monitors in hostile environments often use piezoresistive and capacitive based sensors. The smallest dimension of this class of sensors is about 1 mm. Recently, a microplasma-based pressure sensor has been developed which is capable of dimensions at least an order of magnitude smaller. In these sensors, a plasma is initiated between an anode and two competing cathodes in a sealed chamber having a diaphragm as one surface. External pressure deflects the diaphragm which changes the inter-electrode spacing for one of the anode-cathode pairs, thereby redistributing the current collected by the two competing cathodes. Pressure is then proportional to the relative difference in current collected by the two cathodes.

In this presentation, we will discuss the properties of microplasma-based pressure sensors using results from a two-dimensional simulation. The model, *nonPDPSIM*, solves Poisson's equation, transport equations for charged and neutral species, and the electron energy conservation equation for electron temperature. Radiation transport is addressed using a Green's function approach, and sheath accelerated electrons are addressed using Monte Carlo methods. The microplasma is sustained between an anode (A) biased with hundreds of volts and two grounded cathodes (K_1 , K_2) in a sealed chamber filled with 1 atm of Ar or rare gas mixtures. The reference cathode (K_1) is located adjacent to the anode while the sensing cathode (K_2) is mounted on the diaphragm separated by a gap of 10 to 100 μm . We find that following a small amount of electric field emission of electrons from the edges of K_1 and K_2 , the electrons rapidly avalanche in the geometrically enhanced electric field at the edge of the anode and creates a conductive plasma within tens of ns. The current distribution on K_1 and K_2 varies with inter-electrode spacing (AK_2) which is changed by deflection of the diaphragm due to the external pressure. The current distribution can also be optimized by adjusting the impedance connected to electrodes.

*Work was supported by the Advanced Energy Consortium.

9:20am **PS+AS+BI+SE-MoM4 A Flexible Paper-based Microdischarge Array Device for Maskless Patterning on Nonflat Surfaces**, *Y.J. Yang*, M.Y. Tsai, W.C. Liang, H.Y. Chen, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This study presents a simple and economical paper-based microdischarge array for maskless surface patterning under atmospheric pressure condition. This paper-based system is a dielectric-barrier-discharge (DBD)-type device and stable plasmas can be sustained in an array of cavities. Due to its flexible feature, this paper-based device allows for performing non-flat surface patterning processes with a feature size down to 500 μm . When a flat or a curved glass surface with 6 mm in its curvature is directly treated by the Ar plasma generated by this device, hydrophilic spots can be generated on the flat or curved surface, respectively. While using tetraglyme as the precursor in Ar atmosphere, this paper-based device is able to perform plasma polymerization and to pattern polyethylene oxide (PEO)-like array of patterns on glass surfaces. Under this arrangement, the optical emission spectrum emanating from the plasma show CO emissions at 561 nm during the deposition process, suggesting that the participation of precursor molecules in the process. The FTIR spectra of deposited films show absorption of C-O-C bonding at 1100 cm^{-1} , indicating retaining of ether groups. To test the anti-fouling property of this film, Alexa Fluor 546-conjugated fibrinogen was utilized as a model reporter molecule for protein absorption test. The fluorescence image shows clear contrast between the coated and non-coated area. The PEO-pattered regions appear to be dark since no protein absorption occurs. This work demonstrates a flexible and cost-effective approach to pattern flat and non-flat surfaces with a maskless process. This work was supported by National Science Council of Taiwan, the Republic of China (101-2221-E-002-163-MY2)

9:40am **PS+AS+BI+SE-MoM5 Hydrophobic Fluorocarbon Films Synthesized from Liquid Monomers by Atmospheric Pressure Plasma**, *J. Hubert, N. Vandecasteele, T. Dufour*, Univ. Libre de Bruxelles, Belgium, *C. Poleunis*, Univ. catholique de Louvain, Belgium, *P. Laha*, Vrije Univ. Brussel, Belgium, *P. Viville*, Materia Nova, Belgium, *A. Delcorte, P. Bertrand*, Univ. catholique de Louvain, Belgium, *H.A. Terry*, Vrije Univ. Brussel, Belgium, *R. Lazzaroni*, Materia Nova, Belgium, *F.A.B. Reniers*, Univ. Libre de Bruxelles, Belgium

The exceptionally low surface energy of polytetrafluoroethylene (PTFE), due to the CF_2 functional groups present on its surface gives the polymer advantageous properties such as hydrophobicity. In order to create PTFE-like films, low pressure plasma deposition of fluorocarbon films has been extensively studied in the last decade. These works focus however on the use of gaseous precursors such as CF_4 , C_2F_6 or C_4F_8 .

In the present study, hydrophobic fluorocarbon coatings have been synthesized from two different precursors, which are liquid at room temperature. Perfluorohexane (C_6F_{14}), a fully saturated monomer and perfluoro(2-methylpent-2-ene) (C_6F_{12}) containing one unsaturated bond are injected in a dielectric barrier discharge (DBD) by a continuous argon or helium flow. In order to characterize the plasma polymer films and the texturization process, both, analysis of the surface and the gas phase have been performed.

Secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) measurements have been performed to highlight the structure and composition of the C_xF_y films depending on the Yasuda factor (W/FM), throughout the influence of the power and the monomer flow rate. Water contact angle (WCA) measurements have shown that the hydrophobicity properties of the fluorocarbon films were similar to that of PTFE as WCA of 110° have been obtained. However, the structure also depends on the nature of the carrier gas (argon or helium) and in some cases, WCA as high as 140° were achieved. Atomic force microscopy (AFM) measurements are used to correlate the increase in hydrophobicity with the increase in roughness, which could be linked to the film thickness.

In order to complete the analysis of the polymerization process, mass spectrometry (MS) and optical emission spectroscopy (OES) have been performed. Fluorocarbon compounds such as CF, CF_2 , CF_3 , or higher mass fragments such as C_3F_3 or C_2F_4 have clearly been identified. Their detection combined to the SIMS analysis could help us to understand the polymerization mechanism/reaction of the two precursors.

* Coburn & Winters Student Award Finalist

10:00am **PS+AS+BI+SE-MoM6 Deciphering Gas-Phase and Solution-Phase Reactions Initiated by Plasmas at the Surface of Aqueous Solutions**, *P. Rumbach*, University of Notre Dame, *R.M. Sankaran*, Case Western Reserve University, *D.B. Go*, University of Notre Dame

Recent advancements in atmospheric-pressure plasma technology have enabled applications in polymer processing, plasma medicine, and water treatment. Many of these applications rely heavily on physical and chemical interactions between plasmas and aqueous solutions. We have recently shown that plasma electrons are involved in electrolytic reactions such as the reduction of aqueous hydrogen ions (H⁺) to hydrogen gas[1]. In this work, we show that the reactions are more complex and involve a competition between plasma chemistry and solution chemistry.

To study interactions between a plasma and liquid, saline solutions were exposed to an argon (Ar) DC microplasma jet, and the effects of various reactions occurring in the plasma and solution phase were characterized. When the plasma jet was run in a background of argon or oxygen gas, traditional electrolytic reactions yielding sodium hydroxide (NaOH) were found to be dominant, making the solution more basic (pH ~ 8). Running the plasma jet in a background of atmospheric air produced significant amounts of nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) in solution. Production of HNO₃ in air typically occurs at a rate two orders of magnitude higher than NaOH, making the solution more acidic (pH ~ 3). In a background of nitrogen gas, HNO₃ was also produced, but at a rate that is limited by oxygen gas evolution from water electrolysis. Overall, the chemical composition of the solution is affected by both electrolytic reactions at the plasma-liquid interface as well as reactions occurring in the bulk plasma.

[1] M. Witzke, P. Rumbach, D. B. Go, and R. M. Sankaran, *J. Phys. D: Appl. Phys.* **45**, 442001 (2012).

10:40am **PS+AS+BI+SE-MoM8 Prostate Cancer Treatment using Low-Temperature Atmospheric Pressure Plasmas: Advanced Optical Diagnostics and Multi-scale Numerical Simulations**, *D. O'Connell*, University of York, UK **INVITED**

Non-equilibrium plasmas, operated at ambient atmospheric pressure and temperature, are very efficient sources for highly reactive neutral particles e.g. reactive oxygen and nitrogen species (RONS) (such as atomic oxygen, atomic nitrogen, nitrogen oxides), charged particles, UV-radiation, and electro-magnetic fields. Individually many of these components have been implicated in therapeutics. Plasmas have the advantage of delivering these components simultaneously providing potentially superior processes through synergies. This has led to the establishment of low-temperature plasmas with potential in disease therapeutics and plasma pharmacology. The challenges lie in understanding the mechanism of interaction, quantifying and accurately tailoring the plasma and its power dissipation. Suitable optimized plasma sources are currently lacking, and improbable through empirical investigations. Therefore, quantifying the power dissipation and energy transport mechanisms through the different interfaces from the plasma regime to ambient air, towards the liquid interface and associated impact on the biological system through a new regime of liquid chemistry initiated by the synergy of delivering multiple energy carrying species, is crucial.

This presentation will include examining our interaction studies of atmospheric pressure plasma jets with prostate cancer cells and our results of employing advanced diagnostic techniques for direct measurements of reactive plasma species and comparison to chemical kinetics simulations. These include absolute densities of atomic oxygen and atomic nitrogen using non-linear laser spectroscopy and vacuum ultra-violet (VUV) absorption spectroscopy, where the VUV radiation was produced using a synchrotron and detected with a high-resolution Fourier-transform spectrometer.

11:20am **PS+AS+BI+SE-MoM10 Conformal Encapsulation of Three-Dimensional, Bioresorbable Polymeric Scaffolds Using Plasma Enhanced Chemical Vapor Deposition**, *M. Hawker*, *A. Pegalajar-Jurado*, *E.R. Fisher*, Colorado State University

Bioresorbable polymers such as poly(ϵ -caprolactone) (PCL) have a multitude of potential biomaterial applications such as controlled-release drug delivery and regenerative tissue engineering. Fabricating these polymers into porous, three-dimensional (3D) materials is critical for such biological applications to maximize their surface-to-volume ratio, mimic the extracellular matrix, and increase drug-loading capacity. Three-dimensional porous PCL scaffold materials have been fabricated via the porogen leaching method. These scaffolds can be plasma-treated to improve or modify their surface properties while maintaining the desirable bulk polymer characteristics. For example, plasma polymerization can be used to encapsulate the polymer scaffold, thereby potentially providing a mechanism for controlled release drug delivery. Here, two different fluorocarbon (FC) precursors, octafluoropropane (C₃F₈) and

hexafluoropropylene oxide (HFPO), were used to deposit FC films on PCL scaffolds using plasma enhanced chemical vapor deposition. X-ray photoelectron spectroscopy (XPS) analysis showed that high-CF₂ content films were deposited on the PCL scaffolds, similar to those previously deposited in our labs on one-dimensional and two-dimensional materials. Cross-sectional XPS data demonstrated that FC film deposition occurred both on the outer scaffold surface and throughout the 3D structure. Scanning electron microscopy data confirmed that FC film deposition yielded conformal rather than blanket coatings as the porous scaffold structure was maintained after plasma treatment. Additional parameter studies suggest that treatment time, substrate location, and precursor gas have significant impact on the nature of the deposited films. This work demonstrates that conformal FC coatings can be deposited on 3D polymeric scaffolds using plasma processing. Results from cell adhesion studies as well as other film deposition systems and alternate bioresorbable scaffold materials will also be presented.

11:40am **PS+AS+BI+SE-MoM11 Deactivation of Lipopolysaccharide by an Atmospheric Pressure Plasma Jet**, *E.J. Bartis*, *C. Hart*, *Q. Yang*, University of Maryland, College Park, *T.-Y. Chung*, *D.B. Graves*, University of California, Berkeley, *J. Seog*, *G.S. Oehrlein*, University of Maryland, College Park

Low temperature plasma treatment of surfaces has been shown to degrade and sterilize bacteria as well as deactivate harmful biomolecules. However, a major knowledge gap exists regarding which plasma species are responsible for the modifications required for deactivation. Lipopolysaccharide (LPS) and lipid A, the toxic element of LPS, are the main components of the outer membrane of Gram-negative bacteria and induce a strong immune response in animals. In this study, LPS-coated silicon substrates were exposed to the effluent of an atmospheric pressure plasma jet (APPJ) under a controlled environment to examine the effect of plasma-generated reactive species on the surface chemistry and biological activity. Additionally, spatially-resolved optical emission spectroscopy, UV absorption spectroscopy, and electrical characterization were performed on the jet to identify and characterize plasma-generated species. Biological activity of LPS was measured using an enzyme-linked immunosorbent assay (ELISA) and correlated with changes in surface chemistry measured by vacuum transfer to x-ray photoelectron spectroscopy (XPS). The kHz-driven atmospheric pressure plasma jet consists of two tubular electrodes surrounding an alumina tube. By flowing Ar with small admixtures of O₂/N₂ through the tube and applying a high voltage across the electrodes, the plasma ignites to form a stable jet. The species that arrive at the sample can be regulated by adjusting the distance from the source to the sample. At longer source-to-sample distances, species with short lifetimes will not reach the sample. Adding oxygen to the gas flow causes the most significant changes. For source-to-sample distances > 10 cm, where radical species dominate, higher levels of deactivation were observed for O₂/Ar plasma than for Ar and N₂/Ar plasmas. O₂/N₂/Ar plasma showed decreased deactivation compared to O₂/Ar plasma with the same O₂ admixture due to creation of NO_x, whose formation consumes reactive oxygen species. With XPS, we observed that O₂-containing discharges remove C-C bonding from the surface while N₂-containing discharges cause minimal changes. XPS studies of APPJ-treated films showed that deactivation depends on C-C bonding measured in the C 1s, which depends on the admixture of O₂ into the APPJ. The decrease in C-C bonding correlates with the loss of lipid A's aliphatic chains, which are partially responsible for its toxicity. The authors gratefully acknowledge financial support from US Department of Energy (DE-SC0005105 and DE-SC0001939) and National Science Foundation (PHY-1004256).

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