Plasma Science and Technology
Room: 210A - Session PS+SE-MoM

Atmospheric Pressure Plasma Processing I
Moderator: François Reniers, Université Libre de Bruxelles

9:00am **PS+SE-MoM3 Modeling Non-Equilibrium Plasma Jets at Atmospheric Pressure**, ***Leanne Pitchford***, CNRS and University of Toulouse 3, France **INVITED**

The considerable recent interest in 'microdischarges' (discharges in small, spatially-confined geometries) is largely due to their remarkable stability. That is, stable, non-thermal, atmospheric-pressure plasmas can be generated and maintained in electric discharges in small geometries. Further interest in microdischarges is due to the fact that 'plasma jets', initiated from microdischarges operating with pulsed or RF excitation and with an axial helium flow, can propagate in the helium jet which extends some distance (cm's) into the open air past the exit of the microdischarge, while causing little or no increase in the gas temperature. Fast imaging shows that most of the light emitted by the plasma jet is produced in a small 'plasma bullet' that propagates in the helium jet at speeds of some tens of kilometers per second. The possibility to generate non-thermal plasmas in ambient air has incited considerable interest for applications in the biomedical field, among others.

Modeling is an important tool for developing an understanding of microdischarges. It has been shown that the plasma jet is very similar to a cathode streamer (ionization wave) guided by air surrounding the more easily-ionized helium jet. This talk will focus on results from two-dimensional fluid modeling. The properties of the streamer in helium and of the plasma channel behind the streamer head as a function of parameters such as the electrode geometry and voltage pulse waveform will be discussed. We will focus in particular on the the configuration developed by the team of Vincent Puech at the Laboratoire de Physique des Gaz et des Plasmas at the Université Paris Sud in Orsay. This configuration consists of a dielectric tube, some mm in diameter, with an inner, hollow electrode (high voltage) and an outer ring electrode (ground). A discharge is initiated inside the dielectric tube by applying high voltage pulse (some kV's with 100 ns risetime) to the inner electrode. Models reproduce the main features of plasma jets observed experimentally, and quantities such as energy deposition in the plasma jet itself can be obtained from modeling, whereas it is much more difficult to extract such information from experiments. More work is needed to quantify the plasma chemistry triggered by the plasma jet and in particular of the influence of the remnant excitation and ionization on the properties of the subsequent plasma jets.

9:40am **PS+SE-MoM5 Vacuum Ultraviolet Polymer Etching and Modification by a Remote Atmospheric Pressure Plasma Jet**, ***Andrew Knoll***, *P. Luan, E.A.J. Bartis, G.S. Oehrlein*, University of Maryland, College Park

In this study, we investigate the etching mechanism of atmospheric pressure plasma jet (APPJ) treated poly(methyl methacrylate)-based 193 nm photoresist polymer and polystyrene-based 248 nm photoresist polymer using *in situ* ellipsometry to monitor film thickness and refractive index in real time. The kHz-driven, two-ring electrode APPJ used in this work operated with low admixtures of O_2 and N_2 to Ar feed gas flowed at 2 slm. Additionally, we used attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and x-ray photoelectron spectroscopy to characterize the surface modifications post treatment. With pure argon feed gas, we observed etching of the photoresist polymers even when the visible plume is not in direct contact with the polymer surface. This etching rate is sensitive to the Ar gas flow rate and local gas environment. APPJ treatments were compared to a surface microdischarge source with a O_2/ N_2 gas flow added but no etching was seen for that source. Furthermore, the etching was shown to be directional by placing a grounded mesh directly over the sample during treatment. No etching was seen without direct line of sight from source to sample. Optical filters were used to investigate the effect of high energy photons on polymer etching and modification. When a MgF_2 filter with a 114 nm cutoff wavelegth is placed directly over the sample, etching still occurs. When a sapphire filter with cutoff wavelength of 142 nm is used, no etching is seen. Ar_2* excimer species are known to be created in atmospheric pressure plasma and emit photons at 128 nm. Vacuum-ultraviolet (VUV)-induced etching is further supported by experiments that show that etching increases in nitrogen environments compared to oxygen environments as oxygen more effectively absorbs VUV radiation. ATR-FTIR of treated samples shows comparable bulk modifications with or without MgF_2 filter over the sample. These results are consistent with photoresists treated with VUV from low pressure plasma. APPJs are sources of a variety of reactive chemical species which can be used for numerous industrial and medical applications. While the VUV effect of APPJ sources on biodeactivation has been investgiated[1,2], polymer etching has not been seen prior to this work. The authors gratefully acknowledge financial support by US Department of Energy (DE-SC0001939) and National Science Foundation (PHY-1415353).

[1] Lackmann, J. W., et al. (2013). Journal of the Royal Society Interface 10(89).

[2] Schneider, S., et al. (2011). Journal of Physics D-Applied Physics 44(29).

10:00am **PS+SE-MoM6 Recent Development and Application of Low Cost and Portable Atmospheric Pressure Microplasma Generation Devices**, ***Cheng-Che Hsu***, *P.K. Kao, Y.J. Yang, Y.H. Huang*, National Taiwan University, Taiwan, Republic of China

Low cost and portable atmospheric pressure microplasma generation devices (MGD) offer great opportunities in several applications when plasmas in-situ, on-demand and/or in-field are desired. This study presents the development of simple and economical MGD made on copper clad laminate. This MGD can be sustained using a portable power supply (less than two pounds) that can be powered by 12V-batteries. Matching of the device capacitance with power arrangement is extremely important for this power to properly function. The use of such devices for gas conversion, selective area treatment, and fabrication microfluidic paper-based analytical device (μPAD) on demand will be presented. Such a MGD can be used to perform surface patterning of hydrophobic/hydrophilic contrasts with sub-mm spatial resolution and to effectively decompose CO2 into CO. In addition, using this MGD to fabricate μPADs is demonstrated. With a proper design of the MGD electrode geometry, μPADs with 500 μm-wide flow channels can be fabricated within 1 min and with a cost of less than $USD 0.1/device. We then test the μPADs by performing quantitative colorimetric assays and establish calibration charts for detection of glucose and nitrite. The results show a linear response to glucose assay for 1 -50 mM and nitrite assay for 0.1 -5 mM . This low cost and portable MGD can be used for in-field diagnostic tests, and is believed to bring impact to the field of biomedical analysis, environmental monitoring, and food safety survey.

10:40am **PS+SE-MoM8 Experimental Study of Micron-Scale, Field Emission-Driven Microplasmas**, ***Mihai Bilici***, *C.R. Boyle*, Case Western Reserve University, *D.B. Go*, University of Notre Dame, *R.M. Sankaran*, Case Western Reserve University

Microplasmas are miniaturized versions of low-pressure, direct-current glow discharges that can be stabilized at high pressures, up to and exceeding atmospheric pressure. In particular, atmospheric-operation has resulted in interest in their applications in materials processing, environmental remediation, and ionization sources for mass spectrometry. At these small electrode dimensions, new properties emerge that may also be important for fundamental study. For example, as the electrode gap is reduced to less than ~10 μm, gas breakdown has been found to deviate from Paschen's law due to an additional contribution to electron emission from field emission. In addition, field emission leads to a "pre-breakdown" regime where gas-phase electrons can interact with the background gas and even ionize the gas before complete breakdown occurs. However, to date there is little experimental evidence of these field-emission driven microplasmas to support theoretical predictions.

Here, we present a study of field-emission driven microplasmas using a custom-built tip-to-plane microplasma setup with environmental control and nanometer-resolution stepper motor control. The tip electrode is mounted on a micro-positioning system (Model Newport SMC100CC) and approaches a planar substrate in precise increments of ~20 nm. The entire setup is housed in an acrylic glove box that can be pumped to ~100 Torr and backfilled with a desired gas such as argon. The gap between the electrodes and subsequent breakdown of the gas is imaged by a camera system (Model Dino-Lite AM4115ZTL). Current-voltage (I-V) measurements are obtained at each gap by a programmable voltage supply and a current monitoring system.

Our results show that at small gaps of less than ~10 μm, the I-V curves exhibit a turn-on voltage, defined as the voltage where a current above the noise of ~100 nA is measured, followed by a non-linear, approximately exponential increase in current with applied voltage. The turn-on voltage is found to increase with gap from ~1-10 μm. Above ~10 μm, the non-linear regime is not observed and the I-V curve abruptly increases as a result of complete gas breakdown. To analyze the results, we have fitted the I-V curves at small gaps to Fowler-Nordheim theory, confirming that the current is produced from field emission. However, a major challenge is

reproducibility of the data because of tip and substrate damage which continually affect field-emission behavior. We will discuss these issues and show our efforts to connect the experimental data to existing theory.

Keywords: microplasmas, field emission

11:00am **PS+SE-MoM9 Precise Energy and Temperature Measurements in Dielectric Barrier Discharges (DBD) at Atmospheric Pressure.**, *B. Nisol*, Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal, Canada, *M. Archambault-Caron*, *H. Gagnon*, Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal, *S. Lerouge*, Department of Mechanical Engineering, École de Technologie Supérieure (ETS), and Centre de Recherche du CHUM (CRCHUM), ***Michael Wertheimer***, Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal, Canada

A specially designed dielectric barrier discharge (DBD) cell and associated equipment has been used to carry out precise measurements of electrical energy, E_g, dissipated per discharge cycle of the applied a.c. voltage, V_a, over the frequency range $5 \leq f \leq 50$ kHz. Twin pairs of several different dielectric materials (2.54 cm diameter discs, thicknesses = 2.0 or ca. 0.1 mm) with relative permittivities between $2.1 \leq K' \leq 9.5$ were used as dielectric barriers in DBDs of four different gases: He, Ne, Ar and N_2. Much of the work relates to the study of atmospheric pressure glow discharge (APGD) plasma in flowing He gas; five separate thermometers (including fiber-optic probes immune to high voltage and high-frequency electromagnetic fields) have enabled us to perform a detailed calorimetric (heat balance) investigation in He APGD, believed to be the first of its kind. Fair agreement in the overall energy balance, which includes vacuum ultraviolet (VUV) light emission, lends strong support to the validity of both measurements and methodology. The latter includes refined algorithms that permit rapid data acquisition and processing. The present results are compared with literature, allowing several important conclusions / recommendations to emerge.

Next, we turn to the particular case of DBD in Ar in a pilot-scale reactor dedicated to deposition of thin organic films (PECVD) for biomedical applications. We have found that transfer of data from the small to the large (near 50-fold greater surface area) apparatus has been very successful, and that we can now precisely measure the amount of energy (ΔE_g) consumed in a particular PECVD process. We finish by presenting specific example reactions and link energy measurements with physico-chemical characteristics of deposits.

11:20am **PS+SE-MoM10 Plasma-Induced Conductivity in Dielectrics: A Study of Dielectric Barrier Discharges**, ***Floran Peeters****, FOM Institute DIFFER, Netherlands, *R.F. Rumphorst*, Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, FOM Institute DIFFER, Netherlands

In plasma devices, the surfaces bounding the plasma form an integral part of the system. Despite this, surfaces are generally described as perfect absorbers for electrons and ions, without any further consideration of potentially relevant processes taking place within the material. Dielectric surfaces, for instance, are treated as single capacitive elements, providing a wall potential. For most discharges this model is sufficiently accurate, but if the characteristic dimensions of dielectric and plasma are very dissimilar, such as in etched micro- and nanostructures or if the discharge itself is non-uniform, understanding the build-up of surface charges and their subsequent behavior becomes of paramount importance.

In our work, we use a typical non-uniform discharge to investigate the plasma-dielectric interaction: the dielectric barrier discharge (DBD) in filamentary mode. Filamentary DBDs can be described by an equivalent circuit which assumes discharging occurs uniformly across the surface, i.e. by treating the dielectric as a single continuous capacitive element. This is counter-intuitive, since DBD actually consists of many spatially and temporally separated, transient microdischarges. Studying the electrical characteristics of DBDs more closely, using both conventional *Q-V* diagrams combined with a circuit designed to record the transferred charge per filament, we developed an improved electrical model of the DBD. An extension to the electrical model for DBDs introduced by Manley in 1943, our model explicitly takes into account the localized nature of the discharge. Using this model, we find that individual filaments are always roughly equivalent; irrespective of the phase or amplitude of the applied voltage. We show that this leads to limited control over the chemical processing efficiency of DBD. The fundamental cause of the insensitivity of the discharge to the applied voltage is identified as the constant redistribution of surface charge on the dielectric.

Further investigation reveals that this redistribution of charge does not occur via the gas-phase of the residual plasma, as is often assumed, but is likely the result of excess charge carriers being introduced into the dielectric by the discharge. We provide corroborative evidence that these excess charge carriers, involving free electron and hole densities not normally seen in high-band gap materials, provide a boost to the conductivity of the material in locations affected by the plasma. As shown here for a DBD, this plasma-induced conductivity can have a significant effect on the behavior of the discharge and should be considered in any models of plasma involving dielectric surfaces.

11:40am **PS+SE-MoM11 Fabrication of Flexible, Electrically-Conductive Features by Microplasma Reduction of Cation-Cross-Linked Polyacrylic Acid (CCL-PAA) Films**, ***Souvik Ghosh****, *R. Yang*, *P.X.-L. Feng*, *C.A. Zorman*, *R.M. Sankaran*, Case Western Reserve University

Patterned metal formation on substrates is typically achieved by subtractive methods. Recently, additive manufacturing techniques have emerged that can selectively deposit materials to produce patterned structures. Examples of additive methods include ink-jet, aerosol, and screen printing. A common feature of all of these approaches is the ink, a solution of stabilized colloidal metal nanoparticles that is deposited onto an arbitrary substrate. Removal of the organic stabilizers is often carried out by annealing at high temperatures (>200 ^{o}C) to produce electrically conductive features, limiting what substrates can be used. There are also challenges with deposition of the inks associated with the viscosity and adhesion of the inks to the substrate.

An alternative approach to fabricating patterned metals in polymers is *in situ* reduction of metal containing polymers. Here, we present an atmospheric-pressure microplasma process for the selective reduction of metal ions in polymer films to produce flexible, electrically-conductive metal patterns [1]. The films are made from polyacrylic acid (PAA) which reversibly cross links with metal cations such as silver (Ag^+). The films are subsequently exposed to a microplasma formed in a flowing argon gas on a two-dimensional scanning stage to "write" a desired pattern. Characterization of the films by X-ray diffraction (XRD) confirms that the Ag^+ is reduced to crystalline Ag after exposure to the microplasma. Further materials analysis by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) show that reduction leads to the formation of Ag nanoparticles whose size and morphology depend on the exposure conditions (i.e. plasma current, scanning rate, etc.). Cross-sectional characterization of the films shows that the reduction does not penetrate through the film bulk. We suggest that the Ag^+ diffuses to the film surface during reduction, leading to a near-surface layer of reduced crystalline Ag with bulk resistivity ~1 mΩ-cm. Stretchable films have been produced by casting PAA-Ag^+ films on top of a polydimethylsiloxane (PDMS) substrate, followed by exposure to the microplasma. Dynamic mechanical analysis (DMA) of the multilayer films yield a breaking force value of >3 MPa and the films can be stretched to >100%. Electrical measurements are performed on the films as a function of strain to analyze the change in resistivity with stretching. We will also present our recent efforts to reduce the size of the patterns, which is currently ~100 μm, to approximately 10 μm by incorporating stencil masks.

[1] S. Ghosh *et al.*, ACS Appl. Mater. Interfaces **6**, 3099 (2014).

*** Coburn & Winters Student Award Finalist**

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