Plasma Science and Technology Division
Room B131 - Session PS1+SE-MoM

Atmospheric-Pressure Plasmas

Moderators: Michael Gordon, University of California at Santa Barbara, François Reniers, Université Libre de Bruxelles

8:20am **PS1+SE-MoM-1 On the Versatility of Atmospheric Non-equilibrium Plasmas: Material Synthesis, Packaging Sanitation and Oncological Applications**, ***Matteo Gherardi,*** *V Colombo, F Barletta, A Bisag, C Bucci, F Capelli, R Laurita,* Alma Mater Studiorum-University of Bologna, Italy*; E Mezzofanti,* AlmaPlasma srl*; T Gallingani,* Alma Mater Studiorum-University of Bologna, Italy, Italia*; G Girolimetti, S Coluccelli, L Amato, G Gasparre,* S.Orsola-Malpighi Hospital, Bologna, Italy*; M Perrone,* S. Orsola-Malpighi Hospital, Bologna, Italy*; A Porcelli,* Alma Mater Studiorum-University of Bologna, Italy*; P De Iaco,* S. Orsola-Malpighi Hospital, Bologna, Italy **INVITED**

Non-equilibrium atmospheric pressure plasmas (APPs) are an extremely versatile sources of reactive species, UV radiation, radicals and electrons, showing the promise of new medical therapies and offering innovative means to induce chemical reactions and synthesize materials. Trying to capture the versatility of this technology and to depict the current challenges, the presentation will deal with three different technological applications of APPs.

In the first part of the talk, APP biocidal potential is discussed in the industrial perspective of producers of food/beverage packaging and packaging machines. In this field, a fast and economic packaging sanitation is required in order to guarantee a sufficient shelf life to the product. Advantages and limitations of APPs with respect to conventional technologies, as well as the challenges of scaling plasma equipment up to the dimensions required by the industrial production volumes will be discussed.

In the second part of the talk, recent findings on the oncological applications of APPs will be presented. The discussion will focus in particular on Epithelial Ovarian Cancer (EOC), the fifth leading cause of cancer-related death among women and a disease characterised by the diffusion of nodules or plaques from the ovary to the peritoneal surfaces (carcinosis), with a poor prognosis at diagnosis (15-20% within 5 years) in advanced stages (III-IV). Due to the limitations of the currently available therapeutic options, the use of APPs is envisioned to produce plasma activated liquids (PALs) containing reactive oxygen and nitrogen species (RONS) to wash the intraperitoneal cavity with the aim of selectively provoking apoptosis in cancer cells without damaging the healthy ones.

Finally, the use of APPs for the synthesis of materials will be discussed in the frame of the development of an innovative multi-layer coating able to reduce biofilm proliferation onto a biomedical device, while at the same time preserving its bio- and hemo-compatibility, avoiding blood clots formation. An APP assisted process is here used to deposit all the different layers of the coating, composed by silver nanoparticles (AgNPs) embedded in a plasma polymerized HMDSO (ppHMDSO) matrix. The coating characteristics will be discussed in light of the results provided by chemo-morphological analysis and cellular and anti-biofilm assays.

9:00am **PS1+SE-MoM-3 Spectroscopic Characterization of a Multi-pins Plasma System**, *M Gulan, R Muddiman,* ***Vladimir Milosavljevic,*** Technological University Dublin, Ireland

The generation of high-energetic species in plasma in plasma using electrical discharge in ambient air renders possible applications such as material functionalization or water treatment. In atmospheric pressure, to get a stable and reproducible plasma discharge, additional to the electrodes, a dielectric would be required. The function of this dielectric is to spread the electrical charge throughout the entire electrode in order to create multiple conducting paths for the discharges to occur. This is the foundation of the Dielectric-barrier discharge (DBD). One or both electrodes in DBD could be covered by a dielectric material which serves as an electric polarizer, and helps maintain a low gas temperature. Over the course of its life, for any DBD system, the biggest disadvantage is the dielectric contamination. In most cases, this dielectric is a polymer, and polymers are very fragile materials, which cannot be sterilised or cleaned. This work presents research of pulsing plasma systems (PPS) which can run at atmospheric pressure under various external parameters. The system has a planar electrode configuration with a bottom (grounded) flat electrode and a top pin array electrode (high voltage). The design of PPS allows setting several parameters such as: discharge frequency (30-125 kHz), duty cycle (1-100%), pulse frequency (100-3000 Hz), peak-to-peak voltage (up 60 kV), power (up to 700 W), distance between electrodes (up to 55mm), and treatment time (unlimited). The new plasma system allows an increase in the surface-plasma interaction selectivity and reduces plasma induced damages to the surface.

In this work, the study and diagnostics of plasma includes: optical emission spectroscopy (OES), optical absorption spectroscopy (OAS), and phase resolved optical emission spectroscopy (PROES). These optical diagnostic methods are applied to study the temporal and spatial characteristics of the reactive species produced. Due to its simplicity, optical spectroscopy is commonly used for the measurement and real time monitoring of plasma radicals and plasma kinetic processes. For comparison purposes, the absolute spectral intensity measurement of the atomic lines and molecular bands associated with helium, argon, oxygen, and nitrogen are included.

9:20am **PS1+SE-MoM-4 Breaching Debye Law by Coupling of Y2O3 Vapor Carrying Focused Atmospheric ICP Beam Penetrating Showernead's Holes with Opposite CCP Discharge during Chemical Corrosion Barrier Coating in Open Air**, ***Yuri Glukhoy,*** Nanocoating Plasma Systems Inc

Debye screening is considering as a dielectric phenomenon associated with plasma-solid state interaction and redistribution of space charge in the front of the wall. It prevents penetration into the plasma bulk by an external electric field. On the other hand, Debye screening characterized by the Debye length prevents penetration of plasma inside the holes with the size that is less than this length. This is the main obstacle in plasma chemical corrosion protective coating of the inner walls of the gas holes of showerheads used in the wafer etching processors. Such holes having diameter 0.5 mm and 10 mm depth believed to be not penetrable using the conventional PVD and CVD methods of deposition of the corrosion-resistant films. However, breaching the Debye Law was achieved in our open-air nanocoating process with a focused Atmospheric Pressure Inductively Coupled Plasma (AP-ICP) beam. Such beam having 0.1 mm crossover could deliver inside the holes chemicals for cleaning the inner surface and YSZ vapor droplets created by preliminary melting and vaporization of commercial nanoparticles in the high-temperature atmospheric plasma discharge, from which such beam was originated. As a focused heat source, this beam can provide inside the hole three consecutive processes like chemical cleaning, Y2O3 deposition and final annealing for the transition of deposited amorphous nanolayer to nanocrystalline. However, the Debye layer in the entrance of the gas hole may obstruct such penetration in this case, also. In order to neutralize this layer, the vacuum chuck holding the showerhead was supplied by the means for the generation of CCP discharge in the vicinity of the outlets of the holes in the backside of the showerhead. Due to a small number of neutrals of the beam breaking-through the Debye layer and penetrate the hole, as well as the bottom CCP discharge, this discharge ionizing such neutrals established capacitive coupling with this layer in spite of its remoteness. Finally, the Debye layer is neutralized by displacement current from the RF generator sustaining the CCP discharge. The released AP-ICP beam. receiving access to the inlet and propagating along the hole this beam beside delivering the Y2O3 vapor for deposition and heat for annealing has the ability to neutralize the Debye layer without the additional help of the auxiliary CCP discharge investing own positive plasma species. Uniformity of thickness the Y2O3 layers inside the holes can be achieved by deposition from both sides of the showerhead. Cross-sectional SEM images recording interface morphology and thickness of the nanolayer deposited on the inner walls of the hole will be demonstrated.

9:40am **PS1+SE-MoM-5 Streamers Effects in Cold Atmospheric Plasma Applications: Coatings, Gas Conversion, Surface Chemistries**, *A Ozkan, J Mertens,* ***François Reniers,*** Université Libre de Bruxelles, Belgium

For a long time, research in atmospheric plasma dielectric barrier discharges (DBDs) focused on homogeneous discharges. However, most of the DBDs present inhomogeneities in the form of streamers.

In this presentation, we aim at showing the drastic effect of these streamers on the chemical reactivity of the discharges. Consequences can be found for instance on the chemistry and on the roughness of plasma deposited coatings, on the deposition rates, or on the conversion of gases inside the discharge. These streamers can be studied through a high speed/high sensitivity camera, and by recording the current – voltage curves with a Rogowski coil on an oscilloscope. The chemistry in the plasma phase is studied using mass spectrometry, optical emission spectroscopy and gas chromatography. Roughness can be measured using profilometry or AFM, and the surface chemistry is analyzed by XPS.

The effect of the streamers will be demonstrated using the following examples :

- the plasma polymerization of CFx coatings, in Argon or Helium leads to different coatings chemistriess and roughnesses, induced by the streamers. This leads to coatings with contact angle varying from 110° (PTFE like) to more than 140°.

- the plasma polymerization of anhydrides shows that the number of streamers depends on the nature of the anhydride injected, and more specifically on the presence of double bonds, and their location. This affects the final chemistry of the coatings, but also the deposition rate.

- the conversion of CO_2 by a DBD is a highly filamentary discharge. Although this is due to the electronegative nature of CO_2, we show that, by changing the dielectric, and by playing with the plasma parameters, one can significantly vary the number of streamers. We also show that this number of streamers seems to be a key factor for the gas conversion.

10:00am **PS1+SE-MoM-6 Improved Water Intrusion Resistance on Adhesive Bonded Metals using Atmospheric CVD SiO_2 Barrier Coatings***, **Zachary Jeckell**, D Patel, T Choi, M Schmid, L Bónová, D Barlaz, D Ruzic,* University of Illinois at Urbana-Champaign*; I Shchelkanov, B Jurczyk,* Starfire Industries LLC

Lightweight manufacturing, specifically the bonding of dissimilar metals is gaining traction lately as the automobile industry looks for new ways to reduce the weight of their vehicles without compromising the safety or performance. However, current technologies such as spot welding can either be difficult, as is the case for aluminum and magnesium, or impossible as is the case for carbon fiber reinforced polymers. The Center for Plasma Material Interactions (CPMI) has developed a scalable method for performing atmospheric plasma enhanced chemical vapor deposition (AP-CVD) using a 2.45 GHz microwave power supply and a torch design that allows for inline precursor delivery to the plasma. Atmospheric plasmas offer unique advantages for manufacturing, such as the potential to be directly integrated into an assembly line, as well as the ability to deposit on complex geometries. This research investigates the feasibility of depositing SiO2, using hexamethyldisiloxane (HMDSO) as the chemical precursor, onto materials commonly used in lightweight manufacturing and then applying an automotive adhesive to bond the materials together. The silica layer is intended to function as both an adhesion promoter as well as a water barrier coating. The composition of the film is verified using XPS, and the film morphology and thickness are observed using cross-sectional SEM to verify that the deposited film is dense and in the range of 10-100 nm. The robustness of these films is determined by adhesion testing following deposition of silica, as well as after water soak testing which are used to simulate prolonged exposure to realistic environments. Preliminary water soak testing on aluminum has shown a decrease in max stress of 2.5% after 168 hours of water soak at 55 $^{\circ}$C, which is a significant improvement over the 25% benchmark currently used in the automotive industry.

10:40am **PS1+SE-MoM-8 OES Imaging and Double Langmuir Probe Studies of Flow-through, Supersonic Microplasma Jet Sources***, K Mackie, **Michael Gordon**,* University of California at Santa Barbara

Spatially-resolved OES imaging and double Langmuir probe (DLP) measurements were carried out on flow-through supersonic microplasma jets to highlight how plasma operating conditions (e.g., pressure, current, presence of growth precursors/O_2, distance from the nozzle) affect the local gas (T_{rot} and T_{trans}) and electron (T_e) temperatures in the plasma jet plume. T_{rot} and T_{vib} were estimated using semi-empirical and rigorous quantum mechanical fits to OES spectra of the first positive group of N_2 ($B^3\Pi$ --> $A^3\Sigma_u^+$), and T_e was obtained via fits to DLP IV curves. Experiments on Ar jets with downstream pressures in the 10-200 Torr regime yielded estimates of $T_{rot} = T_g$ and T_{vib} of 500-700 K and 5000-6000 K, respectively, using two independent methods. DLP data gave estimates of T_e in the 1-3 eV range, which depended on the exact location in the expanding jet plume. The transition between a pre-discharge-like operating regime at low plasma currents to true hollow cathode operation at high currents was also observed in the plasma IV characteristic and companion OES measurements. The talk will highlight OES imaging and DLP results, as well as the effect of gas additives, i.e., the presence of film deposition precursors and/or oxidants in the jet feed vs. background gas, on jet operating characteristics (T_e, T_{gas}, etc.).

11:00am **PS1+SE-MoM-9 Time-resolved Optical Emission Spectroscopy of an Atmospheric Pressure Plasma Jet – Surface Interaction***, **Michael Johnson**, D Boris, T Petrova, S Walton,* U.S. Naval Research Laboratory

Atmospheric pressure plasma jets (APPJs) have become a valuable tool for the modification of surfaces. One of the large benefits of APPJs is their ability to generate a chemically-rich environment in open air, allowing for the modification of a board range of surfaces including metals, polymers, ceramics, and biological materials. However, when an APPJ interacts with a surface, the surface will influence the structure of the plasma jet and thereby alter the chemistry of the jet. This is particularly vital because different chemical species important for surface modification will form in different quantities depending on the surface. Because of this, two different surfaces treated by the same plasma jet will undergo exposure to slightly different conditions. In this work, time-resolved measurements of the optical emission of a pulsed-DC plasma jet impinging on different surface is measured to investigate how the structure and chemistry of the plasma on the surface evolve in time. Initially, the plasma source emits a streamer which propagates out from the jet nozzle into the open air and eventually collides the surface. With a metal surface, a 'secondary stroke' forms on the surface and extends back towards the jet outlet. The formation, extension, and duration of the stroke are functions of the pulse width and frequency of the voltage waveform used to generate the plasma jet. The metal surface allows for the formation of a long-lived, surface plasma that exists for the duration of the pulse. If a dielectric surface is impinged with the APPJ, the streamer will strike the surface and produces an ionization wave that extends along the surface. The ionization wave is short-lived and not significantly affected by the length of the pulse. This work is supported by the Naval Research Laboratory base program.

11:20am **PS1+SE-MoM-10 Atmospheric-Pressure Plasmas As Ionization Sources For Atomic, Molecular, And Biological Mass Spectrometry***, **Jacob Shelley**, S Badal, C Walton, G MacLean,* Rensselaer Polytechnic Institute*; I Ayodeji,* University of South Florida*; G Chan,* Lawrence Berkeley National Laboratory*; T Evans-Nguyen,* University of South Florida **INVITED**

Analytical plasmas that operate at ambient pressures and mass spectrometry (MS) have been in a symbiotic relationship since the near-coincident advent of the inductively coupled plasma (ICP) ionization source and atmospheric-pressure (AP) inlets for mass spectrometers. Preceding that discovery by only a few years, it was shown that low-power plasmas could be used for soft ionization of intact molecules through chemical ionization pathways. More recently, analytical plasma source development has seen a resurgence with the realization of a variety of low-power AP plasma designs useful as MS ionization sources. AP plasmas are unique in that they have the ability to create a wide-range of energetic species useful for desorption and/or ionization processes.

Plasmas produce highly energetic species (e.g., ions, metastable neutrals, fast electrons, etc.), which can lead to high-energy physical or chemical processes to fragment and ionize molecules. This fragmentation can be so extensive that molecules are broken down into bare elemental constituents. In addition, low-energy ionization reactions can also occur due to the abundance of collisional cooling that can take place at ambient pressures. For instance, the helium-based flowing atmospheric-pressure afterglow (FAPA) source has been shown to produce intact molecular ions of molecular species with quite high ionization efficiencies.

This presentation will demonstrate the broad utility and range of applications of low-power AP glow discharges, specifically the FAPA discharge, and the solution-cathode glow discharge (SCGD). The possibilities of these devices extend well beyond conventional atomic and small molecule detection. By tuning the chemistry of the discharge, we can alter conventional ionization modes to encompass elemental analysis to biomolecular detection to polymer analysis. For instance, our group has developed a method to detect elemental ions with FAPA-MS via online complexation reactions with volatile ligands. But, the open-air nature of FAPA can produce isobaric interferences from ambient species. To overcome this issue, differential mobility spectrometry was used as a post-ionization filter to remove background ions. Ultimately, FAPA-DMS may dramatically improve selectivity and sensitivity in fieldable MS applications. Meanwhile, it was found that SCGD-MS could be used for the detection of atomic, molecular, and biological species directly from solutions. Furthermore, it was found that peptides could be tunably fragmented at atmospheric pressure, which led to 100% sequence coverage for many of the peptides examined.

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