# Wednesday Afternoon, November 9, 2022

#### Plasma Science and Technology Division Room 315 - Session PS2+SE-WeA

#### **Atmospheric Pressure Plasmas and their Applications**

Moderators: Adam Pranda, TEL Technology Center, America, LLC, François Reniers, Université Libre de Bruxelles, Belgium

#### 2:20pm PS2+SE-WeA-1 Organized DBD Streamers for Maskless Chemical and Topographic Patterning of Surfaces, *O. Polonskyi, T. Hartig,* UCSB Chemical Engineering; *J. Uzarski,* U.S. Army Combat Capabilities Development Command Soldier Center; *Michael Gordon,* UCSB Chemical Engineering

Current methods for plasma-based modification of material surfaces (e.g., etching; modifying adhesion, surface chemistry, or wettability; and deposition) cannot often deliver precise control over the location of treatment without extensive use of complex lithographic or photoresist masks. Dielectric barrier discharge (DBD) plasmas operating at atmospheric pressure can accomplish such surface treatments through the creation of random plasma filaments or 'streamers' where surface treatment preferentially occurs. Unfortunately, spatially random and intermittent formation of plasma streamers usually precludes precise patterning.

In this work, we demonstrate how DBD streamers can be sufficiently controlled, via self-organization (with voltage and frequency) and more specifically with topographically patterned dielectrics and raster-scanning of a single streamer, to accomplish localized and user-defined spatial treatment of various substrates without the use of lithographic masks. Spatially organized DBD steamers were used to locally modify the wettability (hydrophilic vs. phobic character) and chemistry of various material surfaces (PMMA, nylon, Teflon, glass, metals), as well as modify surface roughness and etch. Contact angle, XPS, AFM, IR and Raman mapping before and after treatment reveal that surface chemical changes occur preferentially where streamers form, and moreover, that streamer exposure can be tailored to achieve different kinds of multifunctional surfaces. Examples to be highlighted include (i) maskless etching of PMMA on Si at specific locations, (ii) creating bio-inspired chemical patterns on glass to mimic insect carapaces with differential wetting, (iii) rendering Teflon hydrophilic at precise locations, and (iv) creating surfaces with orthogonal wetting characteristics (e.g., simultaneously hydrophilic and phobic over different length scales).

#### 3:00pm PS2+SE-WeA-3 An Atmospheric-Pressure Microwave Plasma Source for "Chemical Waste-Free" Surface Cleaning and Anti-Corrosion Coatings, D. Ellis, University of Illinois at Urbana-Champaign; D. Krogstad, Applied Research Institute, University of Illinois at Urbana-Champaign; M. Sankaran, David Ruzic, University of Illinois at Urbana-Champaign

Metals such as steel are widely used in infrastructure, transportation, and manufacturing where they are exposed to corrosive environments. While higher grade metal alloys can have lower corrosivity, they have significantly higher cost. A potentially more cost-effective approach is to protect metals from corrosion by protective coatings. Currently, many of the best protective coatings require application through expensive dip tank processes that result in a high amount of chemical waste that can be potentially hazardous and result in significant waste remediation costs. For this reason, there is a need to develop a low-cost, low-chemical waste process to apply protective coatings to a variety of metals, including mild steel.

We have developed an atmospheric-pressure microwave plasma for the cleaning and coating of metal surfaces. By relying predominantly on gases, such as air or nitrogen, with aerosolized precursors instead of wet chemicals, chemical waste is greatly reduced. Here, we present a study of 1008/1010 mild steel. Cleaning of surfaces was demonstrated by purposefully contaminating with oil or sodium chloride. Following plasma treatment, the surfaces were characterized by Fourier transform infrared spectroscopy (FTIR) and Rutherford backscattering spectroscopy (RBS). In the case of salt, a Bresle test was also employed. We find that the plasma is very effective in removing oil, with no hydrocarbons being detected on the treated surface through FTIR measurements. Plasma treatment is also found to be capable of removing thin layers of salt, including residual salt left after rinsing surfaces with water. We have also shown that the atmospheric pressure plasma can be used to deposit nanoscale silica coatings onto the steel substrates to promote corrosion protection and paint adhesion. Films were deposited by introducing tetraethylorthosilicate

(TEOS) vapor in the plasma. The film properties, including composition and thickness, were characterized by scanning electron microscopy, FTIR, and RBS. Electrochemical testing was used to determine the corrosion protection properties of the films, while accelerated corrosion testing using salt fog was used to determine the corrosion prevention capability of the film under a compromised paint barrier. Plasma-deposited silicon oxide films were found to substantially decrease corrosion.

# 3:20pm PS2+SE-WeA-4 Characteristics of Ionization Wave Propagation on Variable Thickness Dielectric Substrate, Joshua Morsell, S. Shannon, North Carolina State University

The interaction of atmospheric pressure plasma jets (APPJ's) with various materials and material topologies can greatly influence an array of existing and new plasma based applications. One area of interest is the ionization waves that are generated by these plasma jets. These ionization waves provide consistent and repeatable application of fields and excited species to the target surface. The focus of this work is to study the effect of dielectric thickness on the propagation of ionization waves as they impinge upon the target surface.

The plasma source in question is an APPJ with helium as the working gas as used in [J. Jiang et al., PSST29(2020), 045023]. The work presented utilizes a nanosecond DC pulse of positive polarity. Pulse width is 500 ns with voltage ranging from 3.5-4.5 kV. Voltage and current data is collected via integrated current probe and a high voltage probe at the source head. The dielectric surfaces consist of two experimental configurations. The first is a 3-D printed stage with a metal foil ground plane. Microscope cover glass 150 micron thick is stacked on this stage to provide a dielectric surface from 0.15 - 3.0 mm thick. The cover glass is 24x24 mm. The second configuration is a 3-D printed stage where the ground plane is a 50 mm square glass plate 1.1 mm thick with conductive ITO deposited on one side. 1 mm thick microscope slides are used to make a dielectric surface of 1.1-10.1 mm thick. Both configurations have a constant gap between the source tip and dielectric surface of 10.5-11mm. A PI-MAX 3 ICCD camera is used to image the ionization wave interaction with the target dielectric. The ICCD is gated to 5 ns and a 5 ns delay time step.

For both experiments, the surface wave velocity has a strong dependence with dielectric thickness, increasing by a factor of three from 0.15mm to 1.65mm.For thicknesses greater than 1.65mm the velocity remains relatively constant for measurements out to 10mm thickness. Surface velocity ranges from  $1.5-4.5*10^4$  m/s. It is noted that the initial conditions for each dataset is kept constant by ensuring that the velocity of the impinging axial ionization wave is constant. Axial velocities for the fine and bulk studies are  $1.88*10^5$  m/s and  $1.81*10^5$  m/s, respectively. These results suggest a transition in electric field structure as the axial component of the impinging wave dissipates into the dielectric bulk more readily than the radial field with a maximum penetration depth that eventually saturates the velocity of the surface wave.

This work is supported as part of the Department of Energy Center for Plasma Interactions with Complex Interfaces (PICI).

#### 5:00pm PS2+SE-WeA-9 Synthesis and Applications of Metal Oxides NPs, Davide Mariotti, University of Ulster, UK INVITED

Metal oxides are an extraordinary class of materials that have found wide applicability for a number of century-defining technologies (e.g. flat-panel display, capacitors and energy storage) mainly due to their dielectric properties and chemical inertness. Doping, defect engineering, quantum confinement and extending to clusters, ternary or high entropy oxides can create disruptive materials with new or improved properties. Atmospheric pressure microplasmas represent a viable synthesis platform to achieve exceptional tuning capability therefore achieving an exquisite control of the size, composition and defects of metal oxide nanoparticles [1-4]. In this contribution we will show how microplasmas can offer a generalized methodology for the synthesis of metal oxide nanoparticles and produce very desirable opto-electronic properties. Therefore we will discuss the formation of metal oxide nanoparticles with gas-phase microplasmas as well as hybrid plasma-liquid systems [5-10]. We will further provide an overview of their application opportunities in energy-related applications as well as other disciplines [8-9]. Examples will include oxides from Ni, Cu, Mn, Sn, Co, Mo and Zn. Finally we will provide future directions at the boundaries between ordered and disordered crystal structures.

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5:40pm PS2+SE-WeA-11 AVS Graduate Research Awardee Talk: Immobilization of Plasma Filaments in a DBD: Discharge Characterization and Patterned Coating Deposition, Annaëlle Demaude<sup>12</sup>, A. Remy, D. Petitjean, J. Zveny, Université libre de Bruxelles, Belgium; K. Baert, T. Hauffman, Vrije Universiteit Brussel, Belgium; E. Goormaghtigh, Université libre de Bruxelles, Belgium; M. Gordon, University of California Santa Barbara; F. Reniers, Université libre de Bruxelles, Belgium

Dielectric barrier discharges (DBDs) can be ignited in different discharge modes: glow, homogeneous or filamentary. At atmospheric pressure, in most gases, the latter mode is more often obtained than the others. Filamentary DBDs are characterized by the presence of micro-discharge channels (filaments), which are very short-lived (few ns) and ignite randomly in the interelectrode space.<sup>1</sup> This can be seen as a drawback for surface functionalization/thin film deposition by DBDs, as it can lead to inhomogeneous treatments.<sup>2</sup> Instead of avoiding these filaments, their higher density in current and energetic species was recently exploited to locally modify surfaces. This was achieved using auto-organized filamentary DBDs or directly by immobilization of the filaments.<sup>3,4</sup> Using this latter method, our team has extended the concept further to the deposition of patterned thin films.<sup>5</sup>

In this work, control over the ignition location of the filaments has been achieved in Ar and in N<sub>2</sub> by texturizing one of the dielectric surfaces to locally favor the ignition of the micro-discharges. The distribution of the filaments in the discharge gap and their electrical properties were examined by high-speed camera imaging and by electrical measurements, respectively. By injecting different precursors such as propargyl methacrylate (PMA) or vanadium(V) oxide triisopropoxide in the Ar or N<sub>2</sub> immobilized filaments, hydrophilic/phobic patterned surfaces or crystalline vanadium oxide (VO<sub>x</sub>) patterns were obtained, respectively. The spatial differences in chemistry, morphology, wettability (for PMA films) and crystallinity (for VO<sub>x</sub> films) of the deposited films were investigated by micro-XPS and micro-IR analysis, by profilometry, water contact angle measurements and XRD, respectively. The properties of the deposited films and of the corresponding discharges could then be correlated.

This opens a new route for the deposition of patterned coatings in a one step-process at atmospheric pressure and could contribute to a better understanding of chemical reactions occurring in filamentary DBDs.

#### References:

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<sup>5</sup> Demaude, A.; Baert, K.; Petitjean, D.; Zveny, J.; Goormaghtigh, E.; Hauffman, T.; Gordon, M. J.; Reniers, F. *Advanced Science***2022**, 2200237.

## 6:00pm **PS2+SE-WeA-12 Maximizing Photon Flux in a Miniaturized Photoionization Detector**, *Mackenzie Meyer*, *X. Huang*, *A. Sivakumar*, *X. Fan*, *M. Kushner*, University of Michigan

Photoionization detectors (PIDs) use wavelength specific UV and VUV radiation to selectively ionize, for example, volatile organic and inorganic compounds (VOCs and VICs). These compounds are then detected by collecting the resulting ion current. Miniature PIDs are of interest for labon-a-chip applications. A miniature PID has been developed in which VUV photons are produced by a pulsed He atmospheric pressure plasma generated in a double dielectric barrier discharge (DBD). Maximizing the fluence of photons that reach the analyte inlet will increase performance of the PID, lowering the detection limit or increasing speed of operation. The operation and optimization of a DBD-PID with the goal of increasing photon fluence were computationally investigated using the 2-dimensional model nonPDPSIM. Several strategies were identified to increase the photon fluence. For example, making the powered electrode V-shaped instead of flat increased the photon fluence, as the electric field is enhanced at the tip of the powered electrode. Using an array of powered electrodes capable of sustaining multiple streamers also increased the photon fluence, as did positioning the electrodes closer to the analyte inlet. The most substantial increase in photon fluence came from increasing the capacitance of the bounding dielectric by increasing the relative permittivity from 10 (typical of conventional fabrication materials) to 300 (for specialized materials). Increasing the capacitance of the dielectric increased the voltage drop across the plasma and stabilized the plasma filament while increasing current for a given voltage

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