## Plasma Science and Technology Division
## Room 104C - Session PS+PB+SE-TuA

### Atmospheric Pressure Plasmas

**Moderators:** Francois Reniers, Université Libre de Bruxelles, Steven Vitale, MIT Lincoln Laboratory

2:20pm **PS+PB+SE-TuA1 Compact, Low Cost Atmospheric Pressure Plasma Jets Driven by Piezoelectric Transformers**, ***Michael Johnson***, National Research Council; *D.R. Boris, L. Petrova, S.G. Walton,* Naval Research Laboratory

In order for non-thermal atmospheric pressure plasma technology to be used for applications outside of the laboratory, there is a need to develop low-cost, portable devices that can be used for applications in the field. Constructing portable power supplies that can produce stable, non-thermal plasmas in full density air can be challenging as large electric fields are required to generate breakdown. Piezoelectric transformers are solid state transformers that can produce large gains in voltage, which makes them attractive candidates for plasma production. In this work, a piezoelectric transformer is used to amplify a low voltage AC signal in order to produce an atmospheric pressure plasma jet. Using this approach, plasma jets were generated with input voltages as low as 10 V when the piezoelectric transformer was operated at its resonance frequency (≈ 88 kHz). The electrical and optical characteristics of the piezoelectric driven plasma jet was compared to a plasma jet produced using a conventional high voltage sinewave of comparable operating frequency. Both jets were examined in helium and argon for a variety of different flow rates and operating voltages. The length of the jets were measured to determine if the piezoelectric transformer limited the potential size of the plasma jet. The current carried by the plasma jets were measured along with optical emission spectroscopy to examine the relative characteristics of the jets. Together, the results suggest the piezoelectric material may have influence beyond simple voltage amplification.

This work was supported by the Naval Research Laboratory Base Program. This research was performed while Michael Johnson held an NRC Research Associateship award at the U.S. Naval Research Laboratory.

2:40pm **PS+PB+SE-TuA2 Process Regimes of Atmospheric Pressure Plasma-enhanced Chemical Vapor Deposition with Source Materials Highly Diluted in Inert Gases**, ***SeungJae Baik***, *J. Jang,* Hankyong National University, Republic of Korea; *H.-J. Oh,* Yonsei University, Republic of Korea

Plasma-enhanced chemical vapor deposition (CVD) is appropriate for fast deposition with moderate film quality, but to form high quality materials such as epitaxial thin films, thermal processes at higher temperature are more favorable. High energy particles that are statistically produced in plasma processes are sources of film quality degradation. It has been previously reported that the plasma process at high working pressure, e.g., atmospheric pressure is feasible for epitaxial Si growth; where source gas species are highly diluted in inert gas. Employing a large dilution of source materials opens a new process regime in plasma-enhanced CVD: (1) low damage plasma processing (2) high deposition rate process with controlled powder generation (3) efficient usage of source materials.

We have performed Si thin film deposition processes with silane and hydrogen as source materials highly diluted in He or Ar gases under working pressure close to the atmospheric pressure (up to 700 torr). The new process regimes showing low damage plasma processing, high deposition rate with controlled powder generation, and efficient usage of source materials are experimentally demonstrated in various process conditions. In addition, the impurity incorporation into the film during deposition processes degrades the crytalline quality of the deposited Si thin films, which can be improved by employing plasma electrode pre-coating or pre-deposition cleaning process. Furthermore, the trade-off relation of plasma power and gas flow velocity revealed the process window of polycrystalline thin film deposition, and even epitaxial growth.

Atmospheric plasma-enhanced CVD tool is promising for fast deposition and low damage processing, and moreover, cheaper setup may also be viable via pre-deposition cleaning processes instead of utilizing expensive vacuum facilities.

3:00pm **PS+PB+SE-TuA3 Plasma-enhanced Chemical Film Conversion (PECFC): Direct, Low-temperature Growth of Solution-processible and Printable Layered Thin Films**, *T. Liu,* ***R. Mohan Sankaran***, Case Western Reserve University

In plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PEALD), the addition of a plasma to dissociate or excite the gas molecules and create active chemical and energetic species can lower the thermal energy required at the substrate to drive thin film nucleation and growth. Here, we show that a similar approach can be used to lower the temperature required to convert molecular precursors deposited from solution onto a substrate to a functional, crystalline thin film which we term plasma-enhanced chemical film conversion (PECFC). We apply this method to layered materials such as hexagonal boron nitride (h-BN) and molybdenum disulfide ($MoS_2$) whose applications are currently limited by the lack of large-area, low-temperature, direct (substrate independent) growth processes.

Our experimental setup consists of an atmospheric-pressure, planar, dielectric barrier discharge and a cold wall substrate heater. Single molecular precursors for h-BN, ammonia borane, or $MoS_2$, ammonia tetrathiomolybdate were dissolved in solution and deposited by a variety of methods including dropcasting, airbrush spraying, spin coating, and inkjet printing on different substrates such as silicon (Si), silicon dioxide ($SiO_2$), and copper. The area of the film was only limited by the current size of our plasma source which is ~2 $in^2$. After conversion, the films were characterized by X-ray diffraction, micro Raman spectroscopy, atomic force microscopy, scanning electron microscopy, and transmission electron microscopy. We systematically compared thermal and plasma-assisted conversion at the same temperatures, background gas environments, and substrates. For h-BN, our results show that thermal conversion requires a minimum of 800 $^oC$ to nucleate on $SiO_2$, but only 650 $^oC$ with the addition of a plasma. Adding 20% $H_2$ enables a further 150 $^oC$ reduction for plasma conversion. For $MoS_2$, our results show that nucleation is enhanced in the presence of a plasma at the same growth temperature of 500 $^oC$ and a subsequent annealing step leads to a smooth (<0.2 nm RMS surface roughness) and highly crystalline film. We suggest that plasma species, especially atomic hydrogen (H), are involved in several important surface reaction mechanisms including abstraction of hydrogen, insertion in strained bonds, and radical formation, to enhance grain growth that overall enhance nucleation and growth of crystalline domains. We will also discuss the performance of the PECFC materials in electronic and energy devices.

3:20pm **PS+PB+SE-TuA4 Plasma-based Remediation of Nanoscale Particulate Matter in Charbroiler Smoke Emissions**, ***Sisi Yang***, *S. Subramanian,* University of Southern California, Los Angeles; *D. Singleton,* Transient Plasma Systems; *C. Schroeder, W. Schroeder, M. Gundersen, S.B. Cronin,* University of Southern California, Los Angeles

Recent studies have shown ultrafine particulate matter (UFPM) produced in commercial charbroiling processes represents a serious health hazard and has been linked to various forms of cancer. In this study, we demonstrate a highly effective method for treating restaurant smoke emissions using a transient pulsed plasma reactor based on a nanosecond high voltage pulse generator. We measure the size and relative mass distribution of particulate matter produced in commercial charbroiling processes (e.g., cooking of hamburger meat) both with and without the plasma treatment. Here, the plasma discharge is produced in a 3" diameter cylindrical reactor with a 5-10 nanosecond high voltage (17 kV) pulse generator. The distribution of untreated nanoparticle sizes peaked around 125-150 nm in diameter, as measured using a scanning mobility particle sizer (SMPS) spectrometer. With plasma treatment, we observe up to a 55-fold reduction in total particle mass and a significant reduction in the nanoparticle size distribution using this method. The effectiveness of the UFPM remediation increases with both the pulse repetition rate and pulse voltage, demonstrating the scalability of this approach for treating higher flow rates and larger systems.

4:20pm **PS+PB+SE-TuA7 The Interactions of Atmospheric Pressure Plasma Jets with Surfaces: *In situ* Measurements of Electron Heating in Materials**, ***Scott Walton***, U.S. Naval Research Laboratory; *J. Tomko, B.M. Foley,* University of Virginia; *D.R. Boris,* U.S. Naval Research Laboratory; *M.J. Johnson,* National Research Council; *Tz.B. Petrova,* U.S. Naval Research Laboratory; *A. Giri, P.E. Hopkins,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest since both contribute to the physicochemical changes during plasma-based materials processing. A unique feature of plasmas compared to other methods of materials

synthesis and processing is that the energy flux is delivered and absorbed at or very near the surface over short time scales, and thus requires fast, surface-sensitive techniques to fully appreciate the dynamics of the plasma-surface interface. To achieve this, we employ pump-probe Time-Domain Thermoreflectance (TDTR) to measure electron and phonon excitation and energy transport dynamics in thin metal films during exposure to an atmospheric pressure plasma jet. The results show the energy delivered by the plasma jet causes a localized thermal spike that is dissipated radially from the point of contact. More specifically, energy delivered via the flux of particles and photons causes the kinetic energy of the electrons within the material to increase over an area commensurate with the plasma jet radius. That energy is then dissipated through electron-electron collisions and electron-phonon interactions as the electrons propagate radially from the point of contact. These results, in conjunction with voltage and current measurements, will be discussed in an effort to develop a first order understanding of energy transfer and relevant kinetics during plasma jet–surface interactions. This work is partially supported by the Naval Research Laboratory base program.

4:40pm **PS+PB+SE-TuA8 Surface Activation by Atmospheric Plasma: the Right Technology for the Right Application**, *A. Ozkan, D. Merche,* ***Francois Reniers,*** Université Libre de Bruxelles, Belgium

Cold atmospheric plasma are widely used for surface activation in many applications. Today, many technologies are available, such as coronas, dielectric barrier discharges (DBDs), remote (or post-discharge) DBDs, torches, operating in the radiofrequency mode, gliding arcs, ……. A wide variety of operating conditions can be found in the literature or on the websites of the manufacturers : AC, DC, kHz range, noble gas or air, high or low power, ….. For the scientist, the lab manager, or the CTO of a company looking for a new, clean, activation technique, the vast list of possibilities, although representing opportunities, may represent a challenge. In this paper, we try to set up a product driven roadmap to help the scientist making the best choice for the plasma technology to implement for his application. Through a few selected examples, all tested in our laboratory equipped with 7 different plasma technologies and 15 reactors, we show which is the best technology for the application of interest. Advantages and drawbacks of each of the tested technologies with respect of the material, the energy consumption, and the time and cost of operation are presented, and discussed in terms of plasma and surface characterization.

The applications chosen addresses a wide range of questions such as:

- which plasma to chose to clean and activate glass substrates (a comparison between torches and in-situ DBDs is proposed)

- atmospheric plasma to grow an oxide layer on aluminium : a comparison between an air operated torch and plasma electrolytic oxidation

- how to activate a macroscopic 3D pre-painted metal piece for further painting using an atmospheric plasma torch. A comparison between 4 torches is presented

- how to activate the surface of selected polymers using DBD, RF torches with different gases

- how to activate surfaces (silicon, polymers, nanotubes) for further grafting of metal nanoparticles

- how to modify PTFE using a torch, what are the side effects, and why.

These examples will be starting points for a more general discussion about methodology, based on the final expectations and the chemistry and physics of each technology.

5:00pm **PS+PB+SE-TuA9 Aluminum Alloy Surface Cleaning by Atmospheric Pressure Microwave Discharge**, ***Lucia Bonova***, *W. Zhu, A. Farrokhpanah, D.V. Krogstad, Z.K. Jeckell, S. Chaudhuri, D.N. Ruzic,* University of Illinois at Urbana-Champaign

Aluminum and its alloys are commonly used as lightweight materials in many industrial sectors including aerospace. During the manufacturing process of aluminum, a series of lubricants and additives are used to avoid sticking of layers and prevent degradation or corrosion. The residual hydrocarbon film is typically removed by a chemical chromate process prior to the deposition of an anticorrosive layer. We present an alternate method to remove the hydrocarbons deposited on the aluminum surface by an atmospheric pressure microwave discharge.

The Center for Plasma Material Interaction (CPMI) at University of Illinois has developed novel patented technologies of Evaporative Coatings at Atmosphere Pressure (ECAP) using a 2.45 GHz microwave power to treat the aluminum surface with an air plasma at atmospheric pressure. The cleaning effect of this microwave plasma was analyzed by contact angle measurements, XPS and ATR-FTIR.

5:20pm **PS+PB+SE-TuA10 Temporal and Spatial Study of a Parallel pin-plate Plasma Reactor**, ***Vladimir Milosavljević,*** *M. Gulan, L. Scally, P.J. Cullen,* BioPlasma Research Group, Dublin Institute of Technology, Dublin, Ireland

Electrical discharges in gases have demonstrated a wide range of effects for material science and energy applications. Under both laboratory and industrial setups, such electrical discharges can produce a stable plasma. From both fundamental and applied purposes, such gaseous plasmas are well studied, the technology has found many applications. Recent interest has turned to operating such plasma under atmospheric conditions. The main advantage of the plasma discharge at atmospheric pressure over low-pressure plasma or high-pressure plasma, is that no reaction vessel is needed. However, with increasing gas pressures, the stability and reproducibility of the plasma discharge are significantly impacted. For atmospheric pressure, in order to obtain a stable plasma discharge in addition to the electrodes a dielectric barrier is 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 generally fragile materials. Therefore, developing a plasma system that does not require a dielectric, and has a reproducible and stable electrical discharge at atmospheric pressure would offer new system designs and applications.

This work presents a pulsing plasma system (PPS) which can run at atmospheric pressure under various external parameters. The system has a planar configuration with a bottom (grounded) flat electrode and a top multiple pin electrode (high voltage). The design of this PPS allows several parameters to be modified, such as: discharge frequency (30-125 kHz), duty cycle (1-100%), duty cycle 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 to reduce plasma induced damages to surfaces. The electron properties and gas radical density generated for the system under such control parameters are reported.

This work was funded by the Dublin Institute of Technology and PlasmaLeap Technologies, Ireland.

5:40pm **PS+PB+SE-TuA11 Plasma-modulated Metamaterials and Photonic Crystals**, ***Jeffrey Hopwood***, *H. Kim,* Tufts University

Metamaterials are periodic assemblies of man-made structures that can mimic naturally occurring materials. By clever design, electromagnetic transmission through metamaterials may have extraordinary properties such as negative refractive index. In this paper we describe the formation of atmospheric pressure argon microplasmas within metamaterials as well as photonic crystals. Microplasma ignition within these materials is initiated by first creating an implicit microwave or millimeter wave resonance within the structure. For example, a vacancy in the artificial crystalline structure can act as a millimeter wave cavity. Incident EM waves excite this resonance and the strong resonant electric field causes gas breakdown.

In general, metamaterials are pre-configured during the design process and exhibit fixed transmission characteristics. The self-initiated plasma, however, dynamically changes the metamaterial. We show that depending on the gas pressure and electron density, microplasma inclusions may act as dielectrics or conductors. Experimentally one observes that the appearance of microplasma causes a change in the material from transparent to reflective, or vice versa. A metamaterial consisting of an array of copper split-ring resonators (3x3x9) is described in terms of the plasma density and its microwave transmission from 1-3 GHz. The appearance of microplasmas quenches the resonance and decouples the resonators from one another; the transmission spectra are radically changed upon de-coupling. In the millimeter wave band, a photonic crystal consisting of alumina rods is shown to support argon plasma at 43 GHz. The transient response of the photonic crystal during pulsed EM radiation and plasma formation is measured and found to act as a power limiting device.

6:00pm **PS+PB+SE-TuA12 Generation of Large-Volume Transient Glow Discharge Plasma by an External Fast Ionization Wave (FIW) from a Plasma Jet**, ***Hamid Razavi**, M. Laroussi,* Old Dominion University

A non-thermal transient glow discharge can be generated remotely in a nonconductive low–pressure chamber by an external guided fast ionization wave (FIW). We used an atmospheric-pressure LTP jet (APLTPJ) as an external source of FIW to transfer the enhanced electric field at the wavefront to a reduced–pressure Pyrex glass chamber with no electrical connection to the chamber [1]. Here, we study on the interaction of FIW with a dielectric surface which forms the wall of the low-pressure system.

In this study, key characteristics of the transient diffuse plasma are discussed. Plasma parameters were measured by Langmuir probe and APLTPJ electrical measurements were done to elucidate the operational mechanisms of the FIW as an igniter of a reduced pressure glow discharge plasma. It is shown that the transient discharge in the low-pressure chamber generates a bulk plasma with negative potential due to the nonconductive boundary. We also used Optical emission spectroscopy (OES) to show the physical and chemical characteristics of the APLTPJ plasma and the transient glow discharge plasma. It is shown that the glow discharge plasma is capable of producing second and third ionized nitrogen and oxygen atoms (OII, NII, and NIII). Fast images were taken by an intensified CCD to study the launching and propagation phases of both APLTPJ plasma and the transient reduced pressure glow discharge plasma as well as the incidence of the guided FIW on a dielectric surface.

[1] M. Laroussi and H. Razavi, “Indirect Generation of a Large Volume Diffuse Plasma By an Ionization Wave from a Plasma Jet”, *IEEE Trans. Plasma Sci*., Vol. 43, No. 7, pp. 2226-2229, (2015).

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