Plasma Science and Technology
Room: 24 - Session PS+EM-MoM

Atmospheric Plasma Processing and Micro Plasmas

Moderator: S.G. Walton, Naval Research Laboratory

8:20am **PS+EM-MoM1 Plasma Science and Applications in the Spatial Realm Below 1 mm: Recent Advances in Microcavity/Microchannel Plasmas**, ***J.G. Eden***, University of Illinois at Urbana Champaign **INVITED**

The last decade has witnessed the rapid emergence of microcavity plasmas, a new subfield of plasma science and technology that pursues the fundamental physics and applications of low temperature, nonequilibrium plasma confined in at least one dimension to nominally < 1 mm. By melding plasma science with photolithography and other micro/nanofabrication techniques adapted from the integrated circuits and materials science communities, it has become possible to observe plasma behavior and realize electronic/photonic/chemical devices that were inaccessible previously. With all due respect to Captain Kirk, plasmas are now able "to go where no [plasma] has gone before." This presentation will highlight recent advances in microcavity plasma science, such as the realization of plasma confined to < 3 μm. Interfacing a gas phase (e^- – ion) plasma with an e^- – h^+ plasma in a semiconductor to yield an n^+pn plasma bipolar junction transistor will be described. A new form of thin, flat lighting ("lighting tiles") available in sheets as large as 900 cm^2 in area will be demonstrated, and massively-parallel plasmachemical processing of gases/vapors in arrays of microchannel plasmas will be described.

9:00am **PS+EM-MoM3 Development and Limitations of Microplasma Arrays on Silicon Operating in DC**, ***R. Dussart***, *M. Kulsreshath, L. Schwaederle, V. Felix, P. Lefaucheux, O. Aubry, T. Tillocher, S. Sozias*, GREMI - Polytech Orleans/CNRS, France, *L.J. Overzet*, University of Texas at Dallas

Arrays of microreactors built from silicon wafers in clean room facilities were first proposed and developed about ten years ago by G. Eden's team [1]. They consist of Micro Hollow Cathode Discharges (MHCD) operating in parallel in DC or in AC. One of the remarkable properties of these MHCDs relies on the fact that they can operate in DC, in a stable regime at atmospheric pressure, without evolving to an arc regime [2]. Potential applications of these new technological devices are numerous and include different domains such as lighting, detection, local treatments, sensors, lab on chip, treatment and micromachining processing, instrumentation… In this paper, we will focus on DC operation of microdischarges working in helium or in argon. The microreactor geometry was investigated to achieve the best results in terms of life time and ignition. Although we were able to ignite up to 1024 microdischarges (100 μm diameter holes), we observed many spikes on the current waveform, which indicate that microplasmas are not so stable. The quite short life time of our microdevices which varies from few minutes to few hours could be linked to these spikes, which actually cause significant damages. Taking into account our observations by Scanning Electron Microscope, our optical characterization and our electrical measurements, we propose a mechanism explaining the appearance of the damages, which shorten the lifetime of our microdischarges. Finally, we will give some indications to delay the damage mechanisms and to increase the life time of the microplasma arrays.

References

[1] J G Eden, S-J Park, N P Ostrom, S T McCain, C J Wagner, B A Vojak, J Chen, C Liu, P von Allmen, F Zenhausern, D J Sadler, C Jensen, D L Wilcox and J J Ewing, J. Phys. D: Appl. Phys. 36 2869–2877 (2003)

[2] K. H. Schoenbach, R. Verhappen, T. Tessnow, P. F. Peterkin, W. Byszewski, Appl. Phys. Lett. 68, 13 (1996)

9:20am **PS+EM-MoM4 A Foldable Microplasma-Generation Device on a Paper Substrate Operating under Atmospheric Pressure**, ***Y.J. Yang***, *J.H. Tsai, Y.C. Liao, Y.W. Lu, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

The fabrication of plasma generating devices on paper substrates is presented. The device was fabricated using a screen print process. Stable helium plasmas were ignited in two parallel electrodes with a gap of 237 to 710 μm by a DC power source. When the plasma was ignited with a 0.2 μL salt solution droplet with trace amount of metallic elements applied to the discharge gap, clear metallic emission lines emanated from the plasma. The result suggests that this paper-based device can be used in analytical applications. We demonstrate that a stable helium plasma can be sustained when the substrate is flat, rolled, and folded along various orientations. Microarrays were also fabricated on paper substrates. Stable array of discharges can be ignited by an AC power source with a frequency between 50 Hz to 10 kHz. Preliminary results show that a 10*10 discharge array can be ignited under different atmospheres such as argon, helium, and air by properly adjusting the parameters. This work was supported by National Science Council of Taiwan, the Republic of China (100-2628-E-002-012 and 101-3113-E-002-002).

9:40am **PS+EM-MoM5 Cold Atmospheric Microplasma Arrays for Processing of Flexible Materials**, ***J. Hopwood***, *A. Hoskinson, C. Wu, N. Miura*, Tufts University **INVITED**

Microplasmas offer a pathway to atmospheric pressure plasma processing using low-temperature, low-cost substrates. Unlike arc and torch technologies, the atmospheric microplasma typically operates near room temperature. Corona discharges share this distinction, but modern microplasma devices produce electron densities that are several orders of magnitude greater than the corona. The combination of low gas temperature and high electron density suggests that a unique process window exists for deposition, etching, and surface modification of flexible materials at atmospheric pressure. In this lecture, we describe the plasma physics of a steady-state microplasma excited by 1 GHz microwave power. Spatially resolved laser diode absorption, imaging spectroscopy, and electrical probe measurements show that the individual microdischarge has an intense inner core surrounded by a cooler region that is rich in metastable atoms. These physical insights are combined with data from deposition experiments using acetylene mixed with a helium gas flow. High densities of electrons and energetic species produced by steady-state microplasmas are believed to be crucial to quality film formation at one atmosphere. Finally, we explore scaling the microplasma toward roll coating geometries. Linear arrays of microplasmas are excited from a single microwave power source through the use of resonant energy sharing. This technique allows over 100 microplasmas to operate in parallel without the usual problem of instabilities induced by ionization overheating and negative differential discharge resistance. This work was supported in part by the U.S. Department of Energy under award No. DE-SC0001923 and by the National Science Foundation under Grant No. CBET-0755761.

10:40am **PS+EM-MoM8 Nucleation of Nanodiamond Clusters at Ambient Pressure via Microplasma Synthesis**, ***A. Kumar***, *P.A. Lin, A. Xue, R.M. Sankaran*, Case Western Reserve University

Since their discovery, nanodiamonds have been an active area of research due to their unique size, chemical stability, high thermal conductivity, and biocompatibility.[1] Nanodiamonds have been detected in outer space (meteorites, interstellar dust) and synthetically produced by high pressure/high temperature (HPHT) and detonation processes. In addition to their potential technological use, the formation of nanodiamond is of great scientific interest. While bulk graphite is more stable than bulk diamond at lower pressures and temperatures (e.g. ambient conditions), recent modeling has suggested that nanometer-sized particles of diamond-phase carbon could be thermodynamically favored at these same conditions as a result of surface energy considerations.[2]

Previously, microplasmas have been shown to be capable of nucleating high-purity nanometer-sized metal nanoparticles from vapor precursors.[3] Here, we present a study of nanodiamond synthesis at atmospheric pressure using a similar microplasma process. Ethanol vapor was used as a carbon precursor for the nucleation of carbon clusters. Aerosol measurements confirm that carbon clusters less than 6 nm in mean diameter are nucleated in the microplasma. *In situ* optical emission spectroscopy (OES) indicates the presence of C_2 dimers and atomic H species which have been linked to diamond nucleation. The collected product is characterized by several techniques including micro Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM). Results confirm the presence of nanodiamond with uniform sizes of *ca.* 3 nm in diameter and crystal structures corresponding to known phases of diamond. The synthesis of nanodiamond at low pressure may allow new technologies to be realized, and help explain their formation in extraterrestrial material.

1. V. N. Mochalin *et al.*,"The properties and applications of nanodiamonds", *Nat. Nanotech.* **7**, 11 (2012).

2. P. Badziag *et al.*, " Nanometre-sized diamonds are more stable than graphite", *Nature* **343**, 244 (1990).

3. A. Kumar *et al.*, "New insights into plasma-assisted dissociation of organometallic vapors for gas-phase synthesis of metal nanoparticles", *Plasma Proc. Polym.*, in review.

11:00am **PS+EM-MoM9 Atmospheric Pressure Plasma Effects on the Adhesive Bonding Properties of Stainless Steel and Epoxy Composites**, ***T.S. Williams***, *H. Yu, P. Yeh, J. Yang, R.F. Hicks*, University of California, Los Angeles

An atmospheric pressure helium and oxygen plasma has been used for the surface preparation of 410 stainless steel and carbon-fiber epoxy laminates prior to bonding them together. Lap shear results for stainless steel coupons and carbon-fiber epoxy laminates demonstrated an 80% and a 150% increase in bond strength, respectively, after plasma activation. Following 7 days of aging, wedge crack extension tests revealed a crack extension length of 7.0 mm and 2.5 mm for the untreated and plasma activated steel. The untreated stainless steel had 30% cohesive failure compared to 97% for steel activated with the plasma. Surface analysis by X-ray photoelectron spectroscopy showed that carbonaceous contamination was removed by plasma treatment, and specific functional groups, e.g. carboxylic acids, were formed on the surface. These functional groups promoted strong chemical bonding to the epoxy film adhesive. Atmospheric pressure plasmas are an attractive alternative to abrasion techniques for surface preparation prior to bonding. The process is easily automated, does not damage the materials, and has no environmental, health and safety concerns.

11:20am **PS+EM-MoM10 Numerical Simulation of Gas Heating in a Capacitively Coupled Microcell Plasma at Atmospheric Pressure**, ***T. Yagisawa***, *T. Makabe*, Keio University, Japan

A microcell plasma at atmospheric pressure has been widely investigated. One of the biggest advantages is in the capability to produce a small-size and high-density plasma, broadening a range of applications such as nano-material synthesis, light sources, biomaterial processing, green technology and so on. With decreasing the size of the reactor, the ratio of volume to surface area also decreases. Under these circumstances, the contribution of the wall surface to the loss of charged and neutral particles becomes much larger. The energy is accumulated in the plasma in the form of a thermal energy by the interaction between energetic ions and gas molecules and the ion impact on the wall. Therefore, the effects of local heating of gas molecule on the plasma structure is of great inportance particularlly in a microcell plasma at high pressure.

In this study, the two-dimensional (2D) structure of a capacitively coupled microcell plasma (CCP) driven at radio frequency (13.56 MHz) with the power of ~4.7 W cm^{-3} is numerically investigated in a sealed cylindricals chamber at atmospheric pressure. Pure argon is considered as a parent gas molecule, where electron, Ar^+, Ar_2^+ and long-lived metastable atom (Ar^m) are traced in the simulation. In order to discuss the effects of local gas heating, the governing system consisting of a coupled set of models is developed: a neutral transport model including the gas temperature T_g, a conventional plasma model in gas phase, as well as a heat conduction model in solid phase. Large amount of metastable atom ~10^{14} cm^{-3} makes huge influence on the plasma structure via stepwise ionization process caused by low energy electrons (~4.3 eV), as well as metastable pooling. The temperature dependence of the thermal conductivity (~ $T_g^{1/2}$) of argon is considered and the result is compared with that of constant thermal conductivity. The local peak of gas temperature T_g ~ 600 K appears due to the Joule heating by energetic ions in the sheath region in front of the powered electrode, resulting in the local reduction of gas density $N_g(r)$ under the constant gas pressure. Taking the gas heating into account, electron density increases by the enhancement of reduced field $E/N_g(r)$. In addition, electron density distribution slightly expands toward the radial direction.

11:40am **PS+EM-MoM11 Reactions at the Interface of Plasmas and Aqueous Electrodes: Identifying the Role of Electrons**, *M. Witzke*, Case Western Reserve University, *P. Rumbach, D.B. Go*, University of Notre Dame, ***R.M. Sankaran***, Case Western Reserve University

Plasmas formed at the surface of or inside liquids have been of historical interest for the potential to mediate electrochemical reactions with gaseous species.[1] Recently, there has been technological interest in plasma/liquid systems for a wide range of applications including nanomaterials synthesis, water treatment, and medicine. However, the nature of reactions at the plasma/liquid interface remains poorly understood. Specifically, since plasmas are a source of electrons, ions, UV light, and radicals, it has been difficult to isolate and identify the role of the various species on reactions that occur in the liquid phase.

Here, we present evidence of electrolytic reactions at the plasma/liquid interface. Experiments were carried out with a non-thermal, atmospheric-pressure, direct-current microplasma jet formed at the surface of an aqueous electrolyte. The plasma was operated as the cathode with a Pt foil immersed in solution as the anode. To isolate the role of electrons, we selected model electrolytic reactions such as the conversion of ferricyanide [$Fe(CN)_6^{3-}$] to ferrocyanide [$Fe(CN)_6^{4-}$] which can be easily monitored by UV-vis absorbance spectroscopy.[2] Cyclic voltammetry was performed to verify that ferricyanide was not dissociated. Alternatively, using acidic solutions, hydrogen gas was detected by mass spectrometry, indicating that protons (H^+) are electrochemically reduced by the plasma.[3] Overall, these results reveal the significant role electrons can play in plasma/liquid systems.

1. J. Gubkin, *Ann. Phys. Chem. N. F.* **32,** 114 (1887).

2. M. Witzke *et al.*, *J. Am. Chem. Soc.* **133**, 17582 (2011).

3. M. Witzke *et al.*, submitted.

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