

# Tuesday Afternoon, October 30, 2012

**Advanced Surface Engineering**  
**Room: 22 - Session SE+PS-TuA**

## Atmospheric Pressure Plasmas

**Moderator:** H. Barankova, Uppsala University, Sweden,  
P.H. Mayrhofer, Montanuniversität Leoben, Austria

2:00pm **SE+PS-TuA1 Plasma Medicine: The Journey of a New Field of Research, from Killing of Bacteria to Killing of Cancer Cells.** *M. Laroussi*, Old Dominion University **INVITED**

Research on the biomedical applications of low temperature plasmas started with few limited experiments mainly concerned with the ability of plasma to kill harmful microorganisms, especially bacteria as it relates to sterilization of abiotic and/or biotic surfaces (such as tissues). Low temperature plasmas produce a potent cocktail of highly reactive chemical species including reactive oxygen species (ROS) such as O, O<sub>2</sub>, and OH and reactive nitrogen species (RNS) such as NO and NO<sub>2</sub>. These species are known to exhibit strong oxidative properties and can trigger signaling pathways in biological cells. For example oxidation of the lipids and proteins that constitute the membrane of biological cells leads to the loss of their functions. In such environment bacterial cells were found to die in minutes or even seconds, depending on the strain. Plasmas were also found to be an effective method to control the proliferation of biofilms. Biofilms are very resistant to chemicals found in detergents and even to antibiotics. Therefore, if not controlled, biofilms (including dental plaque, for example) could represent serious health hazards.

Experiments on eukaryotic cells demonstrated that under some conditions, low temperature plasmas appear to cause little damage to living animal and plant tissues. For example, skin fibroblast cells are found to remain viable under plasma conditions that can be lethal to bacterial cells. The proliferation of fibroblasts is an important step in the wound healing process. The ability of plasma to kill bacteria and to accelerate the proliferation of specific tissue cells opened up the possibility to use plasma for the healing of chronic wounds such as diabetic ulcers. Tens of thousands of amputations occur every year in the US alone because of the inability of present medical methods to heal chronic wounds.

Low temperature plasmas have been found to be able to trigger apoptosis in cancer cells. Apoptosis is a natural process of "programmed" cell death. Cancerous cells lose the ability to initiate such a killing process. However, mediated through its specific chemical species, plasmas can trigger the signaling pathway that can start the cascade of events that result in apoptosis. This unique plasma capability opened up the possibility to use plasma for cancer treatment.

Low temperature plasmas therefore constitute a new transformational approach to healthcare referred to as Plasma Medicine [1]. In this paper background work as well as new results both in fundamental understanding and applications will be discussed.

### References

[1] M. Laroussi, "Low Temperature Plasmas for Medicine?", *IEEE Trans. Plasma Sci.* **37**, 714 (2009).

2:40pm **SE+PS-TuA3 VHF Atmospheric Glow Discharge: Electrical and Optical Characterization for Multiple Gases.** *B. Byrns, A. Lindsay, S. Shannon, A. McWilliams, S. Hudak, J. Cuomo*, North Carolina State University

Atmospheric plasmas have the potential to increase the efficiency of many processes involving interactions between materials and plasma due to the increased reactive species densities in the plasma. One challenge in the integration of these sources into high volume applications is the difficulty of producing large area, high density atmospheric plasmas without reaching thermal equilibrium or relying on the formation of arcs; a secondary challenge is the formation of these discharges without helium or other rare gas species that are typically used to sustain atmospheric glows. In this work a large area atmospheric pressure glow discharge operating at 162MHz has been created utilizing a VHF ballasting effect [1]. An electrical model paired with a simple global plasma model is used to characterize the electrical properties of the plasma. Several different feed gases including air, CO<sub>2</sub>, nitrogen, and argon are used to validate the model and study the production of reactive species in the plasma volume; both of these endeavors also enable intelligent process setpoint design to achieve the necessary operating conditions for various gases. These measurements are made using various electrical and optical diagnostics including OES, B-loop probe measurements, and in-line RF metrology. The effects of increasing the pressure, through the use of nozzles, are examined and used

to further refine and validate the system model. This greater understanding of the plasma allows for the potential to increase the size of the plasma, allowing for an increase in the number of reactive species and thus an increase in the efficiency for the treatment of surfaces. Currently the plasma is being studied for use in the removal of HDPE from surfaces as well as for the treatment of water. Preliminary results for both of these applications will be presented.

[1] Brandon Byrns et al 2012 J. Phys. D: Appl. Phys. 45 195204

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3:00pm **SE+PS-TuA4 Atmospheric Pressure Glow Discharge for Point-of-Use Water Treatment.** *A. Lindsay, B. Byrns, S. Shannon, D. Knappe*, North Carolina State University

Treatment of biological and chemical contaminants is an area of growing global interest where atmospheric pressure plasmas can make a significant contribution. Atmospheric plasmas have demonstrated the potential to reform aqueous chemistry<sup>1</sup> and mitigate water contamination<sup>2</sup>. One of the key challenges is scaling of these systems for volume processing. A large volume VHF coaxial plasma source has been developed that enables scale up of these systems under ambient air conditions, addressing volume processing and operating cost due to the absence of a noble gas carrier to sustain a volume glow.<sup>3</sup> The 162 MHz atmospheric glow discharge presented here offers several features uniquely applicable for disinfection. Because of ballasting effects, attributable to the very high drive frequency, the electric discharge is maintained at a steady glow, allowing formation of critical non-equilibrium chemistry. High densities,  $n_e = 10^{11}$ - $10^{12}$ , have been recorded. The atmospheric nature of the device permits straightforward and efficient treatment of material samples. Using air as a process gas, [H] concentrations in 150 milliliter tap water samples have been shown to drop five orders of magnitude after five minutes of discharge exposure. Recent literature has demonstrated that increasing acidity is strongly correlated with a solution's ability to deactivate microbial contaminants.<sup>1</sup> The work presented here will explore the impact of treatment gas, system configuration, and power density on water treatment including disinfection and PFC abatement. An array of plasma diagnostics including optical emission spectroscopy and electrical measurement of plasma discharge condition are combined with post-process water chemistry analysis including Quanti-Tray analysis of coliform and E.coli bacteria, gas chromatography, and mass spectrometry. Continued development of volume processing atmospheric plasma disinfection technology offers promise for point-of-use treatments in developing areas of the world, potentially supplementing or replacing supply-dependent chemical and weather-dependent solar disinfection methods.

1. Traylor (2011) J. Phys. D: Appl. Phys. 44 (2011) 472001

2. Takeuchi (2011) IEEE Trans. On Plasma Sci. 39(12) 3358-3363

3. Byrns (2012) J. Phys. D: Appl. Phys. 45 (2012) 195204

\* Work supported by generous gift donations from Bird Technologies, Advanced Energy, and Verity Instruments

4:00pm **SE+PS-TuA7 Cold Atmospheric Plasma in Liquids.** *H. Barankova, L. Bardos*, Uppsala University, Sweden

Atmospheric pressure plasmas and their applications, especially those based on non-thermal processes, have been extensively studied in the last decade, with focus on surface treatment, coatings and gas conversion. Individual applications depend on the current status of development in atmospheric pressure plasma sources. The plasma source based on the Fused Hollow Cathode (FHC) geometry was developed for generation of plasma in liquids. Effect of various generation regimes on the performance of plasma and on plasma distribution in water is studied without and with different auxiliary gases. The paper also discusses importance of the plasma source/reactor design for control of plasma chemical kinetics and comments on advantages and limitations of atmospheric plasma.

4:20pm **SE+PS-TuA8 Characterization of Amorphous and Microcrystalline Si Films Grown in Atmospheric-Pressure Very High-Frequency Plasma.** *H. Kakiuchi, H. Ohmi, T. Yamada, A. Hirano, T. Tsushima, K. Yasutake*, Osaka University, Japan

Hydrogenated amorphous silicon (*a*-Si) and microcrystalline silicon (*μ*c-Si) prepared at low temperatures are promising thin film materials for use in large-area electronic devices. The goal of our study is to develop a highly efficient deposition process of good-quality *a*-Si and *μ*c-Si films on polymer substrates using an atmospheric-pressure (AP) plasma technology in which

stable reactive plasma excited by a 150-MHz very high-frequency (VHF) power under AP is effectively used.

The experiments were conducted in an AP plasma CVD system that had a parallel-plate-type electrode ( $2 \times 8 \text{ cm}^2$ ), whose surface was coated by alumina of  $\sim 0.1 \text{ mm}$  thickness. By supplying a VHF power through an impedance matching unit, AP  $\text{He}/\text{H}_2/\text{SiH}_4$  plasma was stably confined in the narrow gap region ( $0.3\text{--}0.7 \text{ mm}$ ) between the electrode and a substrate. Under a constant process pressure of  $1 \times 10^5 \text{ Pa}$ , VHF power density ( $P_{\text{VHF}}$ ),  $\text{H}_2$  and  $\text{SiH}_4$  flow rates, plasma gap and substrate heating temperature ( $T_{\text{sub}}$ ) were varied as principal parameters. Si dusty particles formed by gas-phase condensation in the outside of the plasma region were completely removed by sucking the gas flow before their adhering to the substrate surface.

By examining the influence of gas residence time in the plasma on the film growth behavior, it was shown that the source  $\text{SiH}_4$  gas was immediately decomposed after being introduced into the plasma region and contributed to the film growth. Under the condition of  $P_{\text{VHF}} = 14 \text{ W/cm}^2$ ,  $\text{H}_2$  and  $\text{SiH}_4$  flow rates of 500 and 50 SCCM, respectively ( $\text{H}_2/\text{SiH}_4 = 10$ ), and  $T_{\text{sub}} = 220 \text{ }^\circ\text{C}$ , the film started to crystallize in only 0.3 msec. Both increasing  $P_{\text{VHF}}$  and  $\text{H}_2/\text{SiH}_4$  ratio caused the decrease in gas residence time necessary for the phase transition of the resultant Si films. On the other hand, an excessively long gas residence time ( $> 1 \text{ msec}$ ) led to the formation of highly crystallized  $\mu\text{c-Si}$  films even if  $\text{H}_2$  was not added to the process gas mixture. However, such  $\mu\text{c-Si}$  films showed poor electrical properties, which resulted from the sparse film structure without enough passivation of the grain boundaries with amorphous Si tissues. These suggest that the precise control of gas residence time is primarily important for the formation of good-quality *a-Si* and  $\mu\text{c-Si}$  films using AP-VHF plasma, together with the optimization of  $P_{\text{VHF}}$  and  $\text{H}_2/\text{SiH}_4$  ratio.

The *a-Si* and  $\mu\text{c-Si}$  films deposited with high rates ( $> 10 \text{ nm/s}$ ) in AP  $\text{He}/\text{H}_2/\text{SiH}_4$  plasma were used as the channel layers of bottom-gate thin film transistors (TFTs). The performance of the TFTs will be presented in the conference.

4:40pm **SE+PS-TuA9 Atmospheric Plasma Polymerization of Esters: Tuning the Coating Chemistry by Tuning the Precursor Chemistry**, *B. Nisol, A. Batan*, Université Libre de Bruxelles, Belgium, *A. Kakaroglou, M. Wadkar, G. Scheltjens, G. Van Assche, B. Van Mele, I. De Graeve, H. Terryn*, Vrije Universiteit Brussel, Belgium, **F. Reniers**, Université Libre de Bruxelles, Belgium

The influence of the chemical environment of an ester function on the plasma polymerization process and on the chemical structure of the deposited coating is investigated, and the consequences on the coatings properties (barrier and adhesion) are discussed. Allyl methacrylate (AMA), n-propyl methacrylate (nPMA) and propyl isobutyrate (PIB) containing respectively two, one and no double bonds were injected in a home made dielectric barrier discharge reactor. Argon was used as the main plasma gas, and the power of the discharge was varied from 30 to 80 W. The thickness of the deposited coating was determined by visible spectroscopic ellipsometry and allowed to calculate the deposition rate. The surface chemistry was investigated by X-ray photoelectron spectroscopy (XPS) and the bulk structure was analyzed by reflection – absorption infrared spectrometry (IRRAS). Differential scanning calorimetry was used to probe the remaining unreacted groups in the coating. The results evidence a great change in the polymerization rate that depends on the presence of the double bonds. Moreover, the concentration of ester groups at the surface of the coatings also depends on the surrounding double bonds present in the precursor. Indeed, whereas the relative amount of ester groups in poly-AMA remains stable when increasing the plasma power, it drops drastically for poly-PIB. A stabilization of the ester groups by the double bonds is suggested.

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