Plasma Science and Technology
Room: Galisteo - Session PS2-MoA

Atmospheric Plasma Processing and Micro Plasmas

Moderator: A. Rousseau, Ecole Polytechnique, France

2:20pm **PS2-MoA2 High Current Diffuse Dielectric Barrier Discharge in Atmospheric Pressure Air for Thin Silica-Like Film Deposition**, ***S.A. Starostin***, Eindhoven University of Technology, Netherlands, *P. Antony Premkumar*, Materials Innovation Institute (m2i), Netherlands, *M. Creatore*, Eindhoven University of Technology, Netherlands, *H. de Vries*, FUJIFILM Manufacturing Europe BV, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

The dielectric barrier discharge (DBD) is recognized as a promising tool of thin films deposition on various substrates at atmospheric pressure. Emerging applications including encapsulation of flexible solar cells and flexible displays require large scale low costs production of transparent uniform dense layers with low level of surface defects. Unfortunately the common operational mode of the atmospheric pressure DBD is filamentary, resulting in strong spatial non-uniformity of plasma chemistry and affecting the quality of the deposited films. Sustaining of the filament-free non-thermal plasma over the large area substrate at atmospheric pressure remains a challenging task especially considering the discharge in ambient air [1].

In present contribution the diffuse dielectric barrier discharge in atmospheric pressure air was applied for the thin film deposition on polymeric web in industrially relevant roll-to-roll configuration. The silica-like film deposition was performed using the admixture of hexamethyldisiloxane precursor to air flow. Discharge diagnostics was realized by means of fast ICCD imaging; time resolved optical emission spectroscopy and electrical characteristics analysis. ICCD discharge imaging confirms plasma uniformity in a microsecond time scale, while at nanosecond time scale shows fast propagating lateral ionization waves. Morphology and composition analyses, performed by means of AFM, ATR-FTIR and XPS methods, indicate that the process results in ultra-smooth films (roughness comparable to initial substrate roughness) and shows the possibility to synthesize carbon-free layers.

[1] S.A. Starostin, P. Antony Premkumar, H. de Vries, R.M.J. Paffen, M. Creatore, and M.C.M. van de Sanden *Appl. Phys. Lett.* **96**, 061502 (2010)

2:40pm **PS2-MoA3 Microscale, Atmospheric-Pressure Plasmas for Nanomaterials Synthesis**, ***R.M. Sankaran***, Case Western Reserve University **INVITED**

Large-scale, low-pressure plasmas play an essential role in the manufacturing of integrated circuits that are now ubiquitous in consumer electronics. In recent years, new challenges have arisen for these top-down approaches to materials processing. Future electronic devices will incorporate nanoscale materials such as nanoparticles, carbon nanotubes, and silicon nanowires that cannot be fabricated by current plasma technology because of limitations associated with photolithography. In addition, emerging applications in sensors, energy, and medicine require materials that must be prepared from the "bottom-up". The aim of our research is to develop a new class of plasmas, termed "microplasmas", for nanomaterials synthesis.

Microscale plasmas or microplasmas are a special class of electrical discharges formed in geometries where at least one dimension is less than 1 mm. As a result of their unique scaling, microplasmas operate stably at atmospheric pressure and contain large concentrations of energetic electrons (1-10 eV). These properties are attractive for a range of nanomaterials applications. Vapor-phase metal-organic precursors can be dissociated at ambient conditions (i.e. room temperature and atmospheric pressure) to homogeneously nucleate metal[1] and alloyed[2] nanoparticles. The formation of metal nanoparticles in the gas phase allows direct introduction of these materials as catalysts for carbon nanotube and silicon nanowire growth[3]. Recently, we have also coupled microplasmas with liquids or polymeric films to nucleate nanoparticles from metal ions[4]. In this talk, I will discuss these topics in detail, highlighting the advantages of microplasma-based systems for the synthesis of well-defined nanomaterials.

1. W-H. Chiang and R. M. Sankaran, "Microplasma synthesis of metal nanoparticles for gas-phase studies of catalyzed carbon nanotube growth," Appl. Phys. Lett., Vol. 91, 121503 (2007).

2. W-H. Chiang and R. M. Sankaran, "Synergistic effects in bimetallic nanoparticles for low temperature carbon nanotube growth," Adv. Mater., Vol. 20, 4857 (2008).

3. W-H. Chiang and R. M. Sankaran, "Linking catalyst composition to chirality distributions of as-grown single-walled carbon nanotubes by tuning Ni Fe nanoparticles," Nat. Mater., Vol. 8, 882 (2009).

4. C. Richmonds and R. M. Sankaran, "Plasma-liquid electrochemistry: Rapid synthesis of colloidal metal nanoparticles by microplasma reduction of aqueous cations," Appl. Phys. Lett., Vol. 93, 131501 (2008).

3:40pm **PS2-MoA6 Micro-discharge Plasma using Silicon Platform**, ***M.K. Kulsreshath***, *T. Dufour, P. Lefaucheux, O. Aubry, S. Dozias, P. Ranson*, CNRS/Université D'Orleans, France, *J.-B. Lee, M.J. Goeckner, L.J. Overzet*, University of Texas, Dallas, *R. Dussart*, CNRS/Université D'Orleans, France

4:00pm **PS2-MoA7 Electron Current Extraction from rf Micro-Dielectric Barrier Discharges**, ***J.-C. Wang***, University of Michigan, Ann Arbor, *N. Leoni, O. Gila*, Hewlett Packard Research Labs, *M.J. Kushner*, University of Michigan, Ann Arbor

Micro dielectric barrier discharges (mDBD's) consist of micro-plasma devices (10-100 μm diameter) in which the electrodes are fully or partially covered by dielectrics, and operate at atmospheric pressure driven with radio frequency (rf) wave forms. After the plasma is generated charging of the dielectric terminates the discharge. At atmospheric pressure, particularly in attaching gases, the plasma formation and decay times can be as short as a few to tens of ns whereas the rf period may be tens to hundreds of ns. So the micro-plasma may need to be re-ignited with each discharge pulse. In certain applications, it may be desirable to extract electron current out of the mDBD plasma, which necessitates a third electrode. As a result, the physical structure of mDBD and the electron emitting properties are important to its operation. In this presentation, we will discuss the properties of mDBD's sustained in atmospheric pressure N2 and air using results from a two-dimensional plasma simulation. The micro-DBD's are sandwich structures with an opening of ten-of-microns excited with rf voltage waveforms of up to 25 MHz up to 0.5 mm away. The model, nonPDPSIM, solves Poisson's equation and transport equations for charge species and electron energy conservation equation for electron temperature. Rate coefficients and transport coefficients are obtained from local solutions of Boltzmann's equation for the electron energy distribution. Radiation transport is addressed using a Green's function approach. We find that following avalanche by electron impact ionization in the mDBD cavity, the plasma can be expelled from the mDBD's cavity towards the collection electrode during the part of the rf cycle when the collection electrode appears anodic. This extraction can be enhanced by biasing the extraction electrode. At lower frequencies, the plasma needs to be reformed every cycle. Long lived neutral species facilitate the generating of plasma by production of UV photons that continuously seed secondary electrons at surfaces until the potential is favorable to re-ignite plasma. The amount of extracted charge per pulse is not a strong function of rf frequency for values up to 25 MHz, but is sensitive to the dielectric constant of the barrier. For applied voltages of up to 2-3 kV, electric field emission appears not to play an important role.

4:20pm **PS2-MoA8 Ignition and Extinction of a Micro Hollow Cathode Discharge Operating in DC Regime**, ***R. Dussart***, *M.K. Kulsreshath, T. Dufour*, CNRS/Université D'Orleans, France, *L.J. Overzet*, University of Texas at Dallas, *P. Lefaucheux, T. Tillocher, O. Aubry, S. Dozias, P. Ranson*, CNRS/Université D'Orleans, France, *M.J. Goeckner*, University of Texas at Dallas, *J.-B. Lee*, University of Texas, Dallas

Microdischarges have gained the interest of the plasma community for the 15 past years. Among them, Micro Hollow cathode Discharges (MHCDs) have the very interesting property to operate at atmospheric pressure in a stable non thermal regime. We have studied the ignition and extinction of such microdischarges. Our samples are made in alumina, covered by a 5 μm thick Nickel layer on both sides and drilled by a laser process. We made experiments in helium and argon at a pressure between 100 and 1000 Torr. To initiate the plasma, we increase the discharge voltage linearly and slowly (20 sec) until the voltage breakdown was reached. During the microplasma ignition, a high current pulse as high as several tens of microamps appeared before a stable and constant lower value was obtained. We will compare these current pulses to those obtained in the so-called self pulsing regime. We will also show electrical and optical measurements carried out to characterize the phenomenon. Finally, we will show the discharge current and voltage temporal evolution at the very last moments of the microplasma, just before its extinction. The physical mechanism of the ignition and extinction will be discussed to explain the measured waveforms.

4:40pm **PS2-MoA9 Characterization and Applications of Three Different Configured Atmospheric Pressure Plasma Sources**, ***Z. Ouyang***, *V. Surla, S. Jung, M.J. Neumann, D.N. Ruzic*, University of Illinois at Urbana-Champaign

The Center for Plasma-Material Interactions (CPMI) at the University of Illinois at Urbana-Champaign has developed large-scale microwave-induced atmospheric plasma sources for use in various manufacturing applications. The microwave source employed has a working frequency at 2.45 GHz, and a maximum input power of 6 kW. Plasma sources of three different configurations have been developed in order to tailor the plasma configuration to various specific applications. A cold plasma torch head has the ability to generate an atmospheric plasma with a temperature range from room temperature (20°C) to more than 1,000 °C. A thermal plasma torch has been developed such that the temperature range extends to 2,000 °C. A linear line source suitable for production line integration has the ability to sustain a 20-centimeter long atmospheric plasma. Various gas compositions (He, Ar, N_2 and O_2) are used to reveal the functionalizations of different radicals and particles. OES system has been used to analyze critical characteristics such as electron density (n_e~$10^{14}cm^{-3}$) and temperature (T_e~1eV), plasma temperature (T_g~300-2,000K) under different operating conditions and results of material processing correlated to those measurements so that a selectable and repeatable material process can be obtained. Hydrophilicity tests on polymer substrates reveal that the "cold" atmospheric plasma has the ability to modify the surface energy within seconds of exposure at a relatively low flux of incident particles, without deforming bulk material substrates; while the "thermal" atmospheric plasma is used to assist in Nd:YAG laser ablation (f=100Hz, P_{av} = 2.0W at 266 nm, 12.5W at 532nm, and 32.5W at 1064nm) of metal or ceramic materials, to provide a means to deposit high quality contamination free films on substrate with better lamination at a relatively higher deposition rate (~5,000 nm/min) in comparison to traditional PVD methods.

5:00pm **PS2-MoA10 Study of Atmospheric Pressure Plasma Jets: The Influences of Ambient Air and the Application on ZnO Thin Film Deposition**, ***Y.J. Yang***, *Y.W. Hsu, Y. Lin, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This presentation includes the diagnostic studies of an atmospheric pressure plasma jet (APPJ) and the use of this plasma jet to perform ZnO thin film deposition. The APPJ under investigation is sustained by a pulsed power supply with a repetitive power frequency up to 25 kHz using N_2 or O_2 as the plasma gas. The assessment of how the ambient air influences the plasma characteristics and how it can effectively be minimized are the focus of the diagnostic work. To minimize the ambient air influence, the exit of the jet is shielded with a glass tube with the inside diameter ranging from 3 to 5 cm . The exit of the tube is covered by a metal plate and leaving a gap of 0.5 to 3 mm. When the N_2 plasma is used, the visible jet length is much longer with such an arrangement. The effective area within which the jet is treated increases by more than a factor of two, as confirmed by the contact angle measurement made on the treated glass surface. In O_2 plasmas, the intensity of atomic oxygen emission (777.4 nm) increases by more than one order of magnitude with the presence of the glass tube. When photoresist is etched using this oxygen plasma jet, the jet with the presence of the glass tube shows a increase in the etching rate by more than 50 % than the case without the presence of glass tube.

The use of this APPJ to perform ZnO thin film deposition is studied as the second part of this presentation. ZnO thin films are deposited on a silicon wafer by spraying nebulized zinc-containing salt solutions, namely $ZnCl_2$ and $Zn(NO_3)_2$, into the downstream of the plasma jet. Preliminary studies show that by using N_2 plasmas, a better quality film can be obtained comparing with using O_2 plasmas. The film quality is found to be sensitive to the plasma conditions. With properly adjusted process parameters, dense and smooth films can be deposited with a rate higher than 75 nm/min. Improvement of the electrical conductivity and the study of the photoluminescence properties of the film are currently underway.

5:20pm **PS2-MoA11 Atmospheric-Pressure Microplasma-Jet Modified Polystyrene Surfaces as Substrates for Epithelial Cell Growth**, ***J.-S. Oh***, *J.W. Bradley, K.G. Doherty, C.M. Sheridan, R.L. Williams, A. Bowfield, P. Unsworth, P. Weightman*, The University of Liverpool, UK

Non-thermal atmospheric pressure plasma jets (APPJs) have recently been the subject of much interest as an alternative to low-pressure plasma treatment since they are relatively simple to construct, and have the advantages that expensive vacuum equipment and high grade gases are not needed. APPJs have potentially numerous applications such areas such as deposition, surface modification and particularly, in biomedicine, sterilization and wound treatment. Here we focus on developing micro-plasma jet technology based on capillary dielectric barrier (DBD) discharges for the localized surface modification of polystyrene (PS) as a substrate for biomaterial processing. The micro-capillaries have an internal diameter of 280 μm and an outer diameter of 330 μm. The surface modification is spatially investigated by dynamic water contact angle (WCA) measurement with about ~0.2 μL water droplets. The results show that the WCA of untreated PS is 90° reducing to angles between 30° and 20° for exposure times between a few seconds and several minutes. The treated areas have typically radial extensions of several millimeters varying with discharge voltage, excitation frequency, gas flow rate and capillary-substrate distance. The modified surface properties will be discussed in more detail with focus on X-ray photoelectron spectroscopy measurements of the surface chemistry and the relationship to epithelial cell culture growth and proliferation.

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