Plasma Science and Technology
Room: B2 - Session PS2-TuM

Atmospheric Plasma Processing and Microplasmas

Moderator: Y. Sakiyama, UC Berkeley

8:00am **PS2-TuM1 Microplasma Synthesis of Dimensionally- and Compositionally-Controlled Metal Nanoparticles for Catalytic Growth of Carbon Nanotubes**, *W.-H. Chiang,* ***R.M. Sankaran***, Case Western Reserve University

Microplasmas operated at atmospheric pressure in a continuous-flow geometry have tremendous potential for gas-phase nanoparticle synthesis. The non-thermal decomposition of vapor precursors in combination with the limited reaction volume afforded by microplasmas allows the fabrication of narrow dispersions of nanometer-sized particles (< 5 nm) *in a single step*. We have recently applied this technique to the synthesis of mono- and bimetallic nanoparticles for catalytic carbon nanotube (CNT) growth [1-3]. Dimensionally- and compositionally-controlled nanoparticles are initially prepared in a microplasma from metal-organic precursors such as ferrocene and nickelocene. To catalyze CNTs, acetylene and hydrogen gases are added to the particle flow exiting the microplasma reactor and heated in a tube furnace. Here, we show that the structure of as-grown CNTs is intimately related to the size and composition of the nanocatalysts. Reducing the mean diameter of the nanocatalysts to ~2 nm results in a high-purity of single-walled CNTs in the reactor product (>75 %). At a constant mean particle diameter, compositional tuning of bimetallic nanocatalysts is found to significantly alter the chirality distributions of the collected single-walled CNTs. In this talk, we will present the synthesis methodology, as well as detailed materials characterization of both the nanocatalysts and the CNTs.

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, "In-flight dimensional tuning of metal nanoparticles by microplasma synthesis for selective production of diameter-controlled carbon nanotubes," J. Phys. Chem. C, Vol. 112, 17920 (2008).

8:20am **PS2-TuM2 Argon-Methyldisiloxane-Oxygen Fed Atmospheric Pressure DBDs for SiO_2-like Thin Film Deposition**, ***F. Fanelli,*** *S. Lovascio, R. d'Agostino, F. Fracassi*, University of Bari, Italy

Organosilicon compounds, such as for instance hexamethyldisiloxane (HMDSO), mixed with oxidants (i.e. O_2 or N_2O) and noble gases (i.e. Ar, He), are widely used both in low pressure and atmospheric pressure plasma enhanced chemical vapour deposition (PE-CVD) of SiO_2-like coatings. In particular very recently atmospheric pressure dielectric barrier discharges (DBDs) fed with organosilicon monomers have been addressed as an attractive route towards the deposition of thin films. Since the deposition mechanism is not definitively known intense research efforts should be directed to the identification of the main reaction steps and to the correlation of the plasma chemistry with the coatings properties. For this reason in this work we report our recent results on the deposition of SiO_x thin films with atmospheric pressure DBDs fed by argon (Ar) in mixture with oxygen (O_2) and different methyldisiloxanes, i.e. hexamethyldisiloxane, pentamethyldisiloxane and tetramethyldisiloxane. The characterization of the deposited films was carried out by XPS, FTIR and SEM. The quali-quantitative determination of stable by-products contained in the exhaust gas, and formed by plasma activation, was performed by gas chromatography coupled with mass spectrometry (GC-MS). The influence of feed composition, in terms of chemical structure of the organosilicon compound and of the oxygen-to-monomer feed ratio, on the properties of the films as well as on monomer depletion and by-products concentration, was investigated.

Results show that in the absence of O_2 polymer-like coatings are deposited. Oxygen addition to the feed leads to a decrease of the carbon content of the film which is more evident when the number of methyl groups in the monomer is lower. GC-MS analyses allowed to appreciate that many linear and cyclic compounds, containing up to five silicon atoms, are formed in the plasma. As an example, in the case of HMDSO, the presence of species containing the dimethylsiloxane ($-Me_2SiO-$) repeating unit appears to be indicative of oligomerization processes (e.g. chain propagation, ring formation, and expansion reactions) which bring to linear and cyclic compounds with general formulas $Me-(Me_2SiO)_n-SiMe_3$ (n = 1-4) and $(Me_2SiO)_n$ (n = 3 - 4), respectively. The extent of unreacted monomer does not depend significantly on the feed composition even if the O_2-to-HMDSO feed ratio is varied in a wide range (i.e. 0-25). However, O_2 addition influences the quali-quantitative distribution of by-products.

The results allow to support hypotheses on the nature of films precursors as well as to clarify some aspects of the overall deposition mechanism and of plasma-surface interaction.

8:40am **PS2-TuM3 Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition by Homogeneous Dielectric Barrier Discharge**, ***N. Gherardi***, *L. Maechler, I. Enache, C. Sarra-Bournet, N. Naudé, H. Caquineau,* LAPLACE - CNRS - Université de Toulouse, France, *F. Massines*, Promes - CNRS, France **INVITED**

Low pressure plasma enhanced chemical vapor deposition (LP-PECVD) is widely used in the industry since it allows obtaining thin films without any substantial temperature increase. On the other hand, these last years, there has been an increasing interest in atmospheric pressure PECVD (AP-PECVD) since it can lead to an appreciable cost reduction. The potential cost saving is related to the suppression of the vacuum equipment and to the on-line processing capability.

In case of two dimensional materials such as rolls of thin polymer films, metal foils or glass plates, dielectric barrier discharge (DBD) appears as one of the most suitable discharges because it is a cold discharge, which is robust, and not disturbed by the motion of the substrate. DBDs normally operate in the usual filamentary mode, but it is now well-known that depending on the gas, electrical parameters, and electrode configuration, DBDs can also operate in homogeneous modes. Depending on the gas in which they are ignited, these homogeneous DBDs generally present different features. In the rare gases (helium, argon, neon…) they are known as atmospheric pressure glow discharges (APGD) as they are characterized by high current densities and an electric field profile between the electrodes showing a cathode fall, a negative glow, a Faraday dark space, and a positive column. In nitrogen, they are called atmospheric pressure Townsend discharge (APTD) as they show lower current densities and a constant high field in between the electrodes.

If AP-PECVD can be achieved using filamentary discharges, the filamentary and statistical nature of this regime leads most of the time to a lack of control of the thin film quality, deposition rate and coating uniformity on large surface. Hence this paper focuses on an AP-PECVD process using homogeneous DBDs.

More precisely, we report here on the deposition of silicon based thin films using homogeneous DBDs working at atmospheric pressure, from hexamethyldisiloxane (HMDSO) diluted either in N_2 or in He, with or without small admixture of nitrous oxide (N_2O) as the oxidizing gas. Our approach consists in studying the thin film properties as a function of the discharge type (APGD or APTD) and N_2O content in the gas phase, using various surface analysis techniques: ellipsometry, profilometry, scanning electron microscopy, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The gas phase is characterized mainly through optical emission spectroscopy. Results obtained either without motion of the substrate or in a roll-to-roll configuration are discussed, showing the capability of AP-PECVD to realize multilayers.

9:20am **PS2-TuM5 On the Deposition Mechanism of the Silica Like Films in Atmospheric Pressure Glow Discharge**, ***S.A. Starostin***, Eindhoven Univ. of Technology, The Nethelands, The Netherlands, *A.P. Premkumar,* Materials Innovation Institute (M2i), The Netherlands, *M. Creatore,* Eindhoven Univ. of Technology, The Netherlands, *H. de Vries, R.M.J. Paffen,* FUJIFILM Manufacturing Europe BV, The Netherlands, *M.C.M. van de Sanden*, Eindhoven Univ. of Technology, The Netherlands

Atmospheric pressure plasma enhanced thin film deposition (PECVD) is nowadays in focus of increasing scientific and industrial interest. The benefits of this newly emerging technology are in possibilities for cost-efficient in-line roll-to-roll production without expensive and cumbersome vacuum equipment. Yet, comparing to the well studied low pressure PECVD, there is a serious lack of insights on thin film deposition mechanisms on the moving substrates at high pressure.

In this contribution we present a study of the deposition process of silica-like films in the diffuse high power variety of the dielectric barrier discharge referred as atmospheric pressure glow discharge (APGD) [1, 2]. This process is capable to produce uniform carbon-free silica-like films on the polymeric webs in low cost gas mixtures [2]. Considering deposition mechanisms in a roll-to-roll atmospheric PECVD reactor with a moving polymer substrate and gas flow, three different pathways which are

simultaneously contributing to the film formation can be identified: a) ionic deposition, where ionized products of the decomposed precursor drift in the electric field towards the surface; b) diffusive deposition of neutral radicals produced in plasma and afterglow phases and c) deposition of large particles or dust. Due to the gas flow and depletion of the precursor, each of these mechanisms leads to layers characterized by a specific composition, morphology and location within the discharge area. In this contribution we will address the influence of the different mechanisms on film deposition, supported by space-resolved spectroscopic ellipsometry, XPS, SEM and water contact angle measurements. The experimental profiles of the deposition rate along the gas flow were analyzed with a 2D numerical convection-diffusion deposition model.

[1] S. Okazaki, M. Kogoma, M. Uehara, Y. Kimura, J. Phys. D: Appl.Phys., **26**, 889, (1993)

[2] S.A. Starostin, M.A. ElSabbagh, E. Aldea, H. de Vries M. Creatore, M.C.M. van de Sanden, *IEEE Trans. Plasma Sci*. **36**, 968 (2008)

[3] S. Starostine, E. Aldea, H. de Vries, M. Creatore, M. C.M. van de Sanden, Plasma Process Polym, **4**, S440 (2007)

9:40am **PS2-TuM6 Industrial Scale Pulsed Atmospheric Dielectric Barrier Discharges**, ***B.D. Schultz**, *W.M. Hooke, W.F. Hargrove, A.R. Martin*, International Technology Center

Atmospheric dielectric barrier plasma glow-like discharges over 1 meter in length and 500 square centimeters in area have been generated in air with a custom high voltage driving source. Pulse peak currents well in excess of 1 kiloampere at atmospheric pressure with total charge transfer up to 90 microcoulombs have been repeatedly generated in homogeneous discharges at frequencies up to 100 hertz. A rapid voltage rise time at 20-30kV is readily achieved by the source and is sufficient to produce a voltage across the electrodes in excess of the DC breakdown voltage prior to the onset of breakdown. The overvoltage condition plays an important role in determining the uniformity of the plasma discharge. Electrical modeling of the discharge characteristics show the resistivity of the plasma to change over the course of an individual pulse causing the discharge characteristics to switch from an oscillatory state to a critically damped state. Charge transfer and power densities in dielectric barrier discharges are limited by the electrode size and the intrinsic material properties of the dielectric used to distribute the space charge. It will be shown that the charge transfer of each pulse scales proportionally with the size of the electrodes for a given dielectric as should be expected for a complete homogeneous discharge. This paper will emphasize the correlation between overvoltage conditions, dielectric material properties, and electrode size to the electrical charge transfer of the glow-like discharge. The impact of the charge transfer scaling behavior on the scaling of other critical parameters like current density will also be discussed.

10:40am **PS2-TuM9 Optical Emission Spectroscopy of an Argon DC Microdischarge: Electron Density and Gas Temperature Profiles**, ***S.G. Belostotskiy**, *T. Ouk, V.M. Donnelly, D.J. Economou,* University of Houston*, N. Sadeghi*, Université Joseph Fourier de Grenoble, France

Optical Emission Spectroscopy was employed to study a high pressure (100s of Torr) DC microdischarge in argon, with traces of N_2 and H_2 present and acting as optical tracers. Spatially resolved measurements of gas temperature across the 600 μm slot-type discharge were obtained from analysis of the rotational structure of two transitions of the first positive band of N_2: $B^3\Pi_g(v=4) \rightarrow A^3\Sigma_u^+(v=1)$ and $B^3\Pi_g(v=5) \rightarrow A^3\Sigma_u^+(v=2)$. Gas temperature profiles peaked at the cathode side of the discharge and slowly decreased towards the anode. Such behavior is consistent with the physics of DC discharges, where most of the power dissipation occurs in the cathode layer. The gas temperature increased with increasing current, reaching a maximum of T_g = 1200 K at I = 30 mA and P = 600 Torr. Electron densities were extracted from the spectral profile of the H_β line. The profile was fit with a Voigt function, which included Doppler, pressure, instrumental and Stark broadening. The electron density was estimated from the contribution of Stark broadening. The spatial profile of electron density was found to have a maximum in the cathode sheath edge region, followed by a minimum in the bulk plasma, and then a maximum some distance from the anode. This spatial distribution was explained by the non-homogeneous structure of the microdischarge, having a highly contracted positive column. The electron density near the sheath edge increased with both pressure and current reaching $n_e = 1.7 \cdot 10^{14}$ cm^{-3} at I = 30 mA and P = 600 Torr.

11:00am **PS2-TuM10 Argon Microplasma Diagnostics by Diode Laser Absorption**, ***N. Miura**, *J. Xue, J. Hopwood*, Tufts University

Argon gas kinetic temperature and the resonance state ($1s_4$) density in argon microplasma were measured by tunable diode laser absorption[1]. The experimental argon gas pressure was varied from 1 to 760 torr. A 900 MHz microstrip split ring resonator[2,3] was used as the microplasma generator. A single-mode diode laser was tuned to scan through the argon 801.4nm line ($1s_4$-$2p_7$) by modulating the diode's driving current. The output of the diode laser was collimated and passed through the microplasma. The obtained absorption lineshapes were fit by a Voigt profile, which is the convolution of Gaussian and Lorentz profiles. The Gaussian part corresponds to Doppler broadening and the Lorentz part corresponds to collisional and Stark broadening. Under our high-pressure experimental conditions, collisional broadening dominates and Stark broadening are almost negligible. Since the Doppler and collisional broadening can be expressed by a single variable T (gas temperature), the absorption lineshapes were fit with two parameters, amplitude and gas temperature[4]. The line integrated density of the resonance state was estimated from the integral of the absorption profile. The line integrated densities of argon $1s_4$ are 1.7×10^{15} m^{-3} m at 1 torr and 1.4×10^{15} m^{-3} m at 760 torr with 1W of input power. The visually observed length of plasma decreases from 1 cm at 1 torr to a few hundred microns at 760 Torr. The measured gas temperature increases from 350 K at 1 Torr to 750 K at 760 Torr. The microplasma is also simulated using a fluid model, which is compared with experimental measurements.

[1] D. Bear and R. Hanson, J. Quant. Spectrosc. Radiat. Transfer **47**, 455 (1992).

[2] F. Iza and J. Hopwood, Plasma Sources Sci. Technol. **14**, 397 (2005).

[3] F. Iza and J. Hopwood, IEEE Trans. on Plasma Sci. **31**, 782 (2003).

[4] S. Belostotskiy, V. Donnelly, D. Economou, and N. Sadeghi, IEEE Trans. on Plasma Sci., to appear June 2009.

11:20am **PS2-TuM11 Experiment and Simulation Results of Limited Cathode Area MHCDs Operating in He**, ***R. Dussart**, Universite d'Orleans - CNRS, France*, T. Dufour,* Universite d'Orleans, France*, L.J. Overzet, M. Mandra, J.B. Lee, M. Goeckner,* University of Texas, Dallas*, L.C. Pitchford,* CNRS - Laplace, France*, N. Sadeghi,* LSP - CNRS, France*, P. Lefaucheux,* CNRS, France*, P. Ranson*, Universite d'Orleans, France

Micro Hollow Cathode Discharges (MHCDs) offer the unique property to create DC micro plasmas in a stable regime at atmospheric pressure [1]. In collaboration with UTDallas (Texas), micro reactors are elaborated by usual microtechnology techniques (sputtering, electrodeposition, lithography, …), usually used in microelectronics and MEMS technology. A first set of microcavities in alumina were prepared and tested in helium. Optical and electrical characterizations were carried out in different cases: single or several cavity devices and for a limited or not cathode area. V- I characteristics were plotted in the different configurations and for different experimental conditions. When the cathode area is limited, an abnormal glow regime can be obtained, which favors the initiation of the plasma in multiple cavities [2]. By adding a small amount of N_2 to the discharge, the gas temperature was determined by fitting the second positive system $C^3\tilde{O}_u$-$B^3\tilde{O}_g$ emission spectra using the software developed at the LSP at Grenoble (France). Simulations of a single MHCD with variable cathode surface area were also carried out using the 2D code developed in Toulouse [3]. Simulation results will be compared to the experimental data. Finally, by applying voltage ramps to the microdischarge, hysteresis effects were observed and will be also discussed.

[1] K. H. Schoenbach, R. Verhappen, T. Tessnow, P. F. Peterkin, W. Byszewski, « Microhollow cathode discharges » Appl. Phys. Lett. 68, 13 (1996)

[2] T. Dufour, R. Dussart, P. Lefaucheux, P. Ranson, L. J. Overzet, M. Mandra, J. B. Lee, M. Goeckner « Effect of limiting the cathode surface on direct current microhollow cathode discharge in helium » Appl. Phys. Lett., 93, 071508 (2008)

[3] J. P. Boeuf and L. C. Pitchford, K. H. Schoenbach, « Predicted properties of microhollow cathode discharges in xenon » Appl. Phys. Lett., 86, 071501 (2005)

11:40am **PS2-TuM12 Linear Microplasma Array using Strongly-Coupled Resonators**, ***J. Hopwood**, *Z. Zhang*, Tufts University

Instabilities in atmospheric pressure plasmas are responsible for the irreversible glow-to-arc transition of cold microplasmas into destructive arcs. DC microplasmas are usually stabilized using a ballast resistor. Alternatively, AC microplasmas are controlled by rapidly extinguishing the discharge through the electrical charging of dielectric barriers surrounding the electrodes (*i.e.*, the DBD). The negative differential resistance of the glow-to-arc region also makes parallel operation of plasmas difficult. Stable arrays of DC and AC microplasmas, however, are possible using distributed ballasting[1]. In this work, we stabilize the individual microplasma using a quarter-wave resonator constructed from a microstrip transmission line. As the microwave input power increases, the microplasma's electrical resistance drops and the resonator is automatically quenched; thus arcing is avoided. Microwave impedance spectroscopy measures the plasma

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resistance as a function of input power and confirms the negative differential resistance of the microplasma. The technical challenge to operate multiple microwave resonators is met by employing coupled-mode theory[2]. An array of high-Q resonators will couple energy efficiently among themselves provided that all resonators share a common resonance frequency. A single microwave power source (400 MHz, 4 watts) drives the first resonator in a linear array and the remaining undriven resonators redistribute the input energy such that multiple microplasmas operate in a stable, parallel manner. Solutions to the classic coupled-mode theory equations are compared with electromagnetic simulations of the resonator array and with the observed excitation of multiple microplasmas. Having confirmed that coupled-mode theory is applicable to microplasma arrays, we then demonstrate the production of stable, high density ($n_e > 10^{14}$ cm^{-3}) cold atmospheric pressure plasma in a linear configuration that is suitable for high-rate material processing.

[1] K. H. Becker, K. H. Schoenbach and J. G. Eden, J. Phys. D: Appl. Phys. **39,** R55 (2006).

[2] H. A. Haus and W. Huang, Proc. IEEE **19**, 1505 (1991).

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