

Wednesday Morning, November 2, 2011

Plasma Science and Technology Division

Room: 201 - Session PS+SE-WeM

Atmospheric Plasma Processing and Micro Plasmas

Moderator: P.L.S. Thamban, University of Texas at Dallas

8:00am **PS+SE-WeM1 2011 AVS Peter Mark Award Lecture - Microscale, Atmospheric-Pressure Plasmas: A Platform for Nanomaterials Synthesis at Different Length Scales, M. Sankaran***, Case Western Reserve University **INVITED**

Large-scale, low-pressure plasmas play an essential role in the processing of materials for a wide-range of applications including integrated-circuit (IC) manufacturing. In recent years, new challenges have arisen for these top-down approaches to materials processing. Advanced electronic devices will be comprised of nanomaterials such as nanoparticles and carbon nanotubes that cannot be fabricated by current plasma technology because of limitations associated with photolithography. In addition, emerging applications in sensors, energy, and medicine require nanomaterials that must be prepared from the "bottom-up" and assembled into macroscale structures. The aim of our research is to develop a new class of plasmas, termed microplasmas, for nanomaterials synthesis and assembly.

Microplasmas are electrical discharges formed in geometries where at least one dimension is less than 1 mm. As a result of their pD scaling (p is the gas pressure and D is the smallest dimension), microplasmas operate stably at atmospheric pressure. These properties open up unique opportunities for nanomaterials synthesis and assembly. For example, vapor-phase metal-organic precursors can be dissociated near ambient conditions to homogeneously nucleate metal [1] and alloyed [2] nanoparticles. The formation of well-defined metal nanoparticles in the gas phase allows direct introduction of these materials as catalysts for chiral-enriched carbon nanotube growth [3]. Recently, we have also coupled microplasmas with liquids to electrochemically synthesize nanoparticles from aqueous metal salts [4]. By extending this strategy to thin films, microscale patterns of nanoparticles are fabricated in a single step [5]. In this talk, I will discuss these topics in detail, highlighting the advantages of microplasma-based systems for the synthesis of well-defined nanomaterials at various length scales.

1. W-H. Chiang and R. M. Sankaran, *Appl. Phys. Lett.* **91**, 121503 (2007).

2. P. A. Lin and R. M. Sankaran, in review.

3. W-H. Chiang and R. M. Sankaran, *Nat. Mater.* , 882 (2009) .

4. C. Richmonds and R. M. Sankaran, *Appl. Phys. Lett.* , 131501 (2008).

S. W. Lee, D. Liang, X. P. A. Gao, and R. M. Sankaran, *Adv. Func. Mater.*, available online: doi: 10.1002/adfm.201100093.

8:40am **PS+SE-WeM3 Surface and In-Depth Modification of LDPE using an Atmospheric Plasma Torch, S. Abou Rich, P. Leroy**, Universite Libre de Bruxelles, Belgium, *N. Wehbe*, University of Namur, Belgium, *N. Avril, L. Houssiau*, University of Namur, Belgium, *F. Reniers*, Universite Libre de Bruxelles, Belgium

In order to improve the adherence of a coating onto a polymer, the substrate surface must be properly functionalized. Plasma techniques are more and more used for that purpose. However, plasma treatments do not only modify the polymer surface, as active species can penetrate into its bulk.

In the present study, polyethylene samples are surface-functionalized by an atmospheric plasma torch, using argon and a mixture of argon-oxygen. The surface is characterized by dynamic water contact angle, atomic force microscopy and X-ray photoelectron spectroscopy. The changes in the bulk of the polymer have been characterized using infrared spectrometry, angle-resolved X-ray photoelectron spectroscopy (ARXPS), and secondary ion mass spectrometry (SIMS).

It is shown that both plasma treatments (argon or argon-oxygen) lead to an increase in the hydrophilicity of the surface by the grafting of oxygen-containing polar functions. AFM reveals also a change in surface roughness induced by the plasma treatment, depending on the operational conditions. FTIR, ARXPS and SIMS evidenced that the plasma treatment also modifies a significant zone under the surface. The diffusion depth of oxygen as a function of the plasma parameters (power, treatment time, oxygen ratio in the gas phase) is determined.

The ageing of the plasma-modified polymers during storage in air is also studied

* Peter Mark Memorial Award Winner

9:00am **PS+SE-WeM4 Surface Analysis of Polymers Treated by Remote Atmospheric Pressure Plasma, R.F. Hicks**, University of California Los Angeles, *E. Gonzalez*, Intel Corporation, *T.S. Williams*, University of California Los Angeles

Atmospheric plasma treatment is a key process for improving the adhesive bond strength of polymers in many products, such as thermoplastic composites on jet aircraft and helicopters, molded plastic parts in automobiles, and plastic tubing and stents in implantable medical devices. In this study, the surfaces of high-density polyethylene (HDPE), poly(methyl methacrylate) (PMMA), and polyethersulfone (PES) were treated with a low-temperature, atmospheric pressure oxygen and helium plasma. The polymers were exposed to the downstream afterglow of the plasma, which contained primarily oxygen atoms and metastable oxygen molecules ($^1\Delta_g \text{O}_2$), and no ions or electrons. X-ray photoelectron spectroscopy of HDPE revealed that 20% of the carbon atoms were converted into oxidized functional groups, with about half of these being carboxylic acids. Attenuated total reflection infrared spectroscopy of all three polymers was obtained in order to determine the types of functional groups formed by atmospheric plasma exposure. It was found that the polymers were rapidly oxidized with addition of alcohols, ketones, and carboxylic acids to the carbon backbone. Chain scission occurred on HDPE and PMMA, while on PES the aromatic groups underwent ring-opening and insertion of carboxylic acid. The implications of this work for forming strong adhesive bonds to these polymers will be discussed at the meeting.

9:20am **PS+SE-WeM5 Deposition of SiO_x Films by Means of Atmospheric Pressure Microplasma Jets: Study of Deposition Mechanism, J. Benedikt, R. Reuter, D. Ellerweg, K. Ruegner, T. de los Arcos, A. von Keudell**, Ruhr-University Bochum, Germany **INVITED**

Deposition of thin films with plasmas at atmospheric pressure is always a challenging task because of high collision rates, absence of ion bombardment, filamentary behavior of the plasma and limited knowledge of plasma chemistry. The preparation of high quality thin films is therefore still the main domain of low pressure plasmas. One of films, which can be prepared at atmospheric pressure, is SiO_2 . Hexamethyldisiloxane (HMDSO) and O_2 (or N_2O) are usually used as precursors fed into the plasma.

We have shown in the past that a good quality SiO_2 films can be prepared by means of microplasma jets driven by RF voltage and operated in Ar or He as plasma forming gas. Here we concentrate on the study of plasma chemistry and surface reactions leading to the film growth. The geometry of the microplasma jet and the localization of the plasma treatment allow studying of gas phase reactions and plasma-surface interaction separately. Molecular beam mass-spectrometry is used to measure HMDSO depletion and stable products in the gas phase. Depletion below 15% and limited fragmentation is observed even under conditions with high O_2 density, which leads to formation of carbon free SiO_2 films. The plasma-surface interaction is studied by application of several jets with different gas mixtures (He/HMDSO, He/ O_2 , He/ H_2 ...) to the same trace on the rotating substrate in controlled helium atmosphere. It is shown that surface reactions are responsible for the carbon removal from the grown film. Infrared spectroscopy, spectroscopic ellipsometry and X-ray photoelectron spectroscopy measurements are performed to analyze film properties and compare them with plasma measurements. A fluid model of gas flow and reaction kinetics in the effluent of the plasma is used to reproduce observed trends and measured deposition rates. Good agreement is achieved with relatively simple model of plasma chemistry and surface reactions.

11:00am **PS+SE-WeM10 Synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Nanoparticles Using an Atmospheric Pressure Plasma Jet, S.M. Chang, E.F. Rodriguez, H.C. Li, Y.J. Yang, N.L. Wu, C.C. Hsu**, National Taiwan University, Taiwan, Republic of China

Nanocrystalline spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is a promising anode material for Li-ion batteries due to its zero-strain during intercalation/deintercalation and the 1.5 V (vs. Li+/Li) potential plateau. Development of a process that allows for rapid synthesis with controllable microstructure has been challenging. In this work, LTO nanocrystalline particles synthesized by an atmospheric pressure plasma jet (APPJ) will be presented. The APPJ is sustained using a repetitive pulsed power source with N_2 gas. Ti and Li ions-containing solution of specific formula is used as the precursor solution. The precursor is ultrasonically nebulized and is then carried into the downstream of the APPJ using a carrier gas. With this process, nanocrystalline LTO can be fabricated in one step with a short contact time (a few ms) between the precursor and the plasma jet without an additional annealing process. The LTO particle size can be effectively controlled using the precursor solution concentration and the carrier gas flow rate. 100-300 nm dense spherical particles can be fabricated under an optimized

condition. The microstructure and porosity of the particles is strongly influenced by the pre-heat process for the nebulized precursor droplets prior to entering the jet downstream. Dense spherical and porous particles are fabricated under conditions with and without preheating, respectively. Finally, full battery performance test will be presented and key factors that dominate the fabricated nanoparticle characteristics will be discussed.

11:20am **PS+SE-WeM11 Laser-Assisted Plasma Coating at Atmospheric Pressure: Production of Yttria-Stabilized Zirconia Thermal Barriers**, *Z. Ouyang, P. Raman, Y.L. Wu, L. Meng, T.S. Cho, D.N. Ruzic*, University of Illinois at Urbana-Champaign

A laser-assisted plasma-coating technique at atmospheric pressure (LAPCAP) for use in thermal-barrier coatings (TBC) deposition has been developed. This technique allows PVD-quality depositions to be done at atmospheric pressure. The microwave source employed has a working frequency at 2.45 GHz, and a maximum input power of 6 kW, and the attached plasma torch head has the ability to generate various types of atmospheric-pressure plasmas at the temperatures of room temperature (20°C) to more than 2,000 °C. Optical emission spectroscopy (OES) technique has been used to spatially analyze some critical characteristics of plasma, such as electron density ($n_e > 10^{14} \text{cm}^{-3}$), electron temperature ($T_e \sim 1 \text{ eV}$), and plasma gas temperature ($T_g \sim 400\text{-}3,000 \text{ K}$), under different operating conditions (gas type, input power and gas flow rate). A helium atmospheric plasma has been used to assist in Nd:YAG laser ablation ($f = 100 \text{ Hz}$, Energy/pulse = 20 mJ at 266 nm; 120 mJ at 532 nm; 325 mJ at 1064 nm) of a 3% yttria-stabilized zirconia (3YSZ) target, to provide a means to deposit high quality, adhesive thin films on René N5 superalloy substrates with better lamination at a relatively higher deposition rate ($\sim 1,000 \text{ nm/min}$), in comparison to traditional PVD methods. The morphology and characteristics of the films have been compared at three laser wavelengths (266 nm, 532 nm and 1064 nm), different laser energy densities ($1\text{-}10 \text{ J/cm}^2$) and substrate temperatures (20-1100 °C), using microanalysis techniques such as scanning electron microscope (SEM), focused ion beam (FIB), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD).

11:40am **PS+SE-WeM12 Investigation on the Discharge Formation Mechanisms and Surface Analysis of SiO₂-like Layers on Polymers Synthesized using High Current Dielectric Barrier Discharge at Atmospheric Pressure**, *M.C.M. van de Sanden*, FOM-Inst. for Plasma Phys. Rijnhuizen & Eindhoven Univ. of Tech., Netherlands, *A. Premkubar*, Eindhoven Univ. of Tech. & M2i, Netherlands, *S. Starostin, H. de Vries*, Fujifilm Tilburg, Netherlands, *M. Creatore*, Eindhoven Univ. of Tech., Netherlands

The dielectric barrier discharge is recognized as a promising tool for PECVD of thin films at atmospheric pressure. Emerging applications including encapsulation of flexible solar cells and flexible displays requires low costs production of transparent uniform and dense layers with low level of coating defects. Among the two discharges Townsend like discharge (TD) and glow like discharge (GD) the latter offers more flexibility for the high growth rates in plasma enhanced deposition. In this investigation we demonstrate the utilization of glow like discharge in, He free, industrially relevant gas mixture comprising Ar/N₂/O₂/HMDSO for the deposition of high quality silica like films on large area polymeric substrates (PET or PEN) in a roll-to-roll configuration. While the discharge physics exhibiting the glow like behaviour is investigated via fast ICCD camera, voltage-current waveforms and optical emission spectroscopy, the deposited silica like films is comprehensively analyzed using AFM, SEM, XPS, SE and FTIR. The time evolution of the diffuse atmospheric discharge showed several phases starting from the initial ignition of the low current Townsend-like mode followed by the transition to glow like discharge which then undergoes lateral expansion providing uniform treatment of the whole substrate width. As a generic characteristic of the developed technology, it is observed that, irrespective of precursors (TEOS or HMDSO) and process gases (Ar, N₂ or air) employed, the films are smooth, both locally and globally, and of near stoichiometric silica with very low carbon content (< 2%). Detailed AFM morphology description and surface statistical analysis on SiO₂ dynamics showed that no film roughening in growth front and lateral directions observed and the synthesized layers ($\sim 350 \text{ nm}$) grow in a self-similar fashion following the topology of the substrate. The films are uniform with no defects or particle being incorporated during the deposition process and exhibit excellent barrier performances towards O₂ and H₂O permeation.

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