Plasma Science and Technology
Room: 24 - Session PS+TC-WeM

Atmospheric Plasma Processing for PV, Flexible Electronics (incl. R2R)

Moderator: S.A. Vitale, MIT Lincoln Laboratory

8:00am **PS+TC-WeM1 Formation Dynamics and Characterization of Organosilicon Powders in Microwave-Sustained Plasmas at Atmospheric-Pressure**, *V. Roy-Garofano,* ***A. Kilicaslan****, O. Levasseur, L. Stafford, M. Moisan,* Universite de Montreal, Canada*, C. Côté, A. Sarkissian*, Plasmionique, Canada

An atmospheric-pressure plasma sustained by a propagating electromagnetic surface wave in the microwave regime combined with a bubbler/flash evaporator developed by Plasmionique for the injection of liquid precursors was used to generate organosilicon powders. Analysis of the plasma emission revealed the apparition of strong C_2 (Swan system) and CN emission bands along with Si emission lines following the addition of the hexamethyldisiloxane (HMDSO) precursors in the nominally pure argon plasma. Such features were not observed in atmospheric-pressure Ar/HMDSO discharges controlled dielectric barriers, indicating that microwave-sustained plasmas are characterized by much higher precursor fragmentation levels due to their much higher electron density. The emission spectra further showed a high-intensity continuum, the intensity of which decreased with time as powders started to form on the discharge tube walls. Analysis of the powder chemical composition by Fourier-Transform Infrared Spectroscopy showed very strong Si-$(CH_3)_x$ and O-Si-$(CH_3)_x$ bands, consistent with the formation of a silicon carbide. On the other hand, introduction of trace amount of O_2 in Ar/HMDSO produced white powders with strong Si-O-Si bands and no trace of carbon, consistent with the formation of SiO_x.

8:20am **PS+TC-WeM2 Infrared Gas Phase Studies in High-Current Dielectric Barrier Discharges Applied in Roll-to-Roll Deposition of Silica-Like Layers at Atmospheric Pressure**, ***S. Welzel,*** Eindhoven University of Technology, Netherlands*, S.A. Starostin, H. de Vries,* FUJIFILM Manufacturing Europe B.V., Netherlands*, M.C.M. van de Sanden, R. Engeln*, Eindhoven University of Technology, Netherlands

Large-area plasma-enhanced roll-to-roll processing of polymeric substrates in diffusive dielectric barrier discharges (DBDs) have been shown to yield high-quality SiO_2-like barrier layers. This has been obtained through chemical vapour deposition at atmospheric pressure using organo-silicon precursors (HMDSO or TEOS) and industrially relevant air-like gas mixtures (N_2/O_2/Ar). Provided an electronic stabilisation circuit is applied, high currents in different diffusive discharge modes can be achieved without admixtures of Helium. Earlier, extensive surface analysis studies of the synthesised layers revealed a competion between deposition and etching regimes throughout the active plasma zone and led to the development of a deposition model.

This contribution is concerned with complementary studies of the gas phase composition using infrared absorption techniques. Given the challenging optical access to DBDs with gap distances smaller than 1 mm in industrial-like roll-to-roll configuration a gas sampling system was implemented to collect a fraction of the effluent into a multiple pass absorption cell. Main stable products were identified under various discharge conditions such as different O_2 admixtures and (average) power densities. Broadly speaking, a typical H-N-O chemistry in the presence of traces of hydrocarbons is observed for such high-current DBDs. To establish a link to earlier model assumptions both dominant etching and deposition conditions were studied separately (i.e. precursor absent and added, respectively). Formic acid (HCOOH) was found to be a good marker molecule in the gas phase for strong etching of the polymeric substrate or incomplete precursor dissociation. Particularly, the appearance of precursor fragments in the infrared gas phase spectra can be correlated to the injected power and growth rate. Under conditions of complete precursor depletion the effluent zone of the reactor resembles an air-like plasma where NO_2, NO, N_2O and HNO_2 are observed whilst hydrocarbons or alcohols are absent.

8:40am **PS+TC-WeM3 Atmospheric Pressure Plasma Processes for Preparation of Si-Based Thin Films**, ***K. Yasutake****, H. Ohmi, T. Yamada, H. Kakiuchi*, Osaka University, Japan **INVITED**

Thin-film deposition processes using atmospheric-pressure (AP) plasmas have attracted considerable attention as the low-cost deposition methods, because they can realize low-temperature and high-rate deposition without the necessity for ultrahigh vacuum. Recently, we have demonstrated that good-quality Si films with almost no ion damage can be prepared by using a 150-MHz very high-frequency AP plasma. Based on this result, we are studying applications of AP plasmas in semiconductor processing, e. g., i) atmospheric-pressure plasma chemical vapor deposition (AP-PCVD) of semiconductor and insulator thin films, ii) AP plasma oxidation of Si and Al, and iii) atmospheric-pressure plasma enhanced chemical transport (APECT) processes for Si purification and deposition. In this work, we will report the experimental results on the formation and characterization of Si-based thin films prepared by these AP plasma processes.

Firstly, we have studied the epitaxial Si growth by AP-PCVD. The purpose of the study is to develop a totally low-temperature semiconductor device fabrication process. Epitaxial Si films have been prepared on 4-inch-(001) Si wafers by AP-PCVD using a porous-carbon electrode. Defect-free growth of epitaxial Si is confirmed in the temperature range of 470–570°C by transmission electron microscopy and a selective etching method. A high carrier generation lifetime (≈ 2.0 ms) is observed in the Si film grown at 570°C with a reasonably high growth rate (≈ 0.4 μm/min). *In situ* H_2 plasma cleaning of the substrate surface is effective for eliminating O and C concentration peaks at the film/substrate interface. Heavy B doping with a carrier concentration of about 10^{20} cm^{-3} is achieved using B_2H_6 as a doping gas at 570°C. The relation between the mobility and carrier concentration in p- and n-doped Si films can be well fitted by the reported curves for bulk Si single crystals. These results demonstrate that the electrical quality of Si epitaxial films grown by AP-PCVD is sufficiently good for semiconductor device applications.

One of the other topics is on the AP plasma oxidation of Si. AP plasma oxidation is supposed to be most compatible for a chamber-less and open-air process, which is attractive as a high-throughput oxidation process for photovoltaic applications. SiO_2/Si structures have been prepared by AP plasma oxidation at 400°C using gas mixtures of O_2 and He. Various characterization results reveal that the properties of AP plasma oxides are similar to those of high-temperature thermal oxides, and that the SiO_2/Si structure has a low interface state density of the order of 10^{10} $cm^{-2}eV^{-1}$.

9:20am **PS+TC-WeM5 Deposition of Organic-Inorganic Nanocomposite Coatings by Aerosol-Assisted Atmospheric Pressure DBDs**, ***F. Fanelli,*** Institute of Inorganic Methodologies and Plasmas (IMIP) - CNR, Bari, Italy*, A.M. Mastrangelo, F. Fracassi*, University of Bari Aldo Moro - IMIP CNR, Bari, Italy

Aerosol-assisted atmospheric pressure cold plasma processes have been recently addressed as an attractive route towards the deposition of multifunctional coatings. This approach seems to be particularly convenient, and can even offer the only possible solution, when non-volatile precursors, solutions or dispersions need to be injected directly in the atmospheric plasma. The aerosol of a dispersion of nanoparticles (NPs) in a liquid precursor can lead to the deposition of nanocomposite coatings in which the NPs are embedded in the matrix formed by the plasma polymerization of the precursor.

This contribution is focused on the study of the growth and structure of plasma-deposited polyethylene/zinc oxide (PE/ZnO) nanocomposite coatings with several potential applications due for instance to the UV-protection and photocatalitic properties of ZnO.

The coatings are deposited in a parallel plate dielectric barrier discharge (DBD) fed with He and the aerosol of a dispersion of oleate-stabilized ZnO NPs in octane or octane/1,7-octadiene mixtures. The characterization of the coatings is performed using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), water contact angle (WCA) goniometry.

A comprehensive study on the effect of different process parameters (e.g., atomization conditions, dispersion composition in terms of liquid precursor and ZnO NPs concentration, deposition time) on the chemical composition and structure of the film will be presented.

Preliminary results show that, as expected, with increasing the concentration of ZnO NPs in the starting dispersion from 0.5 to 5% p/p, the ZnO content in the coating increases. Surprisingly, the addition of a small amount of 1,7-octadiene to octane (0.5% v/v) favors the inclusion of the NPs and hence results in an increase of the ZnO concentration of the coatings.

Advancing and receding WCAs steeply increase with the NPs content in the film and reach values higher than 165° with low hysteresis indicating the formation of slippery superhydrophobic surfaces. SEM images confirm that this superhydrophobic character is due to the hierarchical micro-/nano-structured surface morphology of the coatings. ZnO NPs generally aggregate in almost spherical clusters that can be incorporated to a different

extent into the polyethylene-like matrix as a function of the deposition process conditions.

10:40am **PS+TC-WeM9 Modified Dielectric Barrier Discharges for Display Materials Processing**, *G.Y. Kim,* Sungkyunkwan University, Korea, *J.B. Park,* SKKU Advanced Institute of Nano Technology (SAINT), Korea, ***G.Y. Yeom***, Sungkyunkwan University & SKKU Advanced Institute of Nano Technology (SAINT), Korea **INVITED**

Atmospheric pressure plasmas have been investigated tens of years for the application to semiconductor and display processing. Especially, due to the uniform discharge characteristics, dielectric barrier discharges (DBDs) composed of electrodes covered with dielectric material have been investigated intensively for those applications. In our study, the conventional DBDs have been modified to enhance the plasma density and also, the different types of DBDs such as remote-type DBD and hybrid-type DBDs (which is composed of direct-type DBD and remote-type DBD) have been used for the surface treatment, growth, deposition, and etching of material applied to flat panel displays and their effects on the material processing have been studied. In this presentation, I will present the plasma characteristics and materials characteristics obtained with those different types of modified DBDs and will suggest possible applications of the DBD-type atmospheric pressure plasmas for the next generation display processing such as in-line/roll-to-roll processing, flexible display substrate processing, inkjet processing, etc.

11:20am **PS+TC-WeM11 Etching of PTFE by Atmospheric Plasmas: Effect of the Gas Composition on the Reactions Processes and Hydrophobicity**, ***J. Hubert****, *T. Dufour, N. Vandencasteele,* Université Libre de Bruxelles, Belgium, *S. Desbief, R. Lazzaroni,* Materia Nova Research Center, Belgium, *F. Reniers*, Université Libre de Bruxelles, Belgium

Poly(tetrafluoroethylene) (PTFE) is a hydrophobic material due to its fully fluorinated backbone (-CF2-CF2-), with properties interesting for practical applications such as self-cleaning surfaces. It has been shown that super-hydrophobic surfaces can be obtained by the treatment of PTFE in a helium-oxygen plasma at atmospheric pressure [1]. Contrary to oxygen-containing plasmas, the modification of PTFE by a pure helium plasma at atmospheric pressure usually leads to a strong decrease in water contact angle, in addition to an oxygen incorporation [2].

The treatment of PTFE by the atmospheric post-discharge of an RF plasma torch supplied in He and He-O2 highlighted two totally different behaviors [3]. For this reason, the effect of the gas composition (ratio He/O2) on the polymer modifications has been investigated. The treated surfaces have been characterized by WCA, XPS and AFM. Moreover, the species responsible for the modifications have been identified by optical spectroscopies (OES/OAS).

In pure helium plasmas, no significant change of the surfaces regarding chemical composition (XPS), wettability (WCA) and morphology (AFM) has been observed and this, despite an important mass loss measured. According to these observations, we presume a layer-by-layer physical etching without any preferential orientation, where the highly energetic helium metastables should be the main species responsible for the scission of -(CF2)*n*- chains. The XPS analysis of an aluminum foil (known to be an efficient fluorine trap) placed close to the PTFE tends to confirm this assumption as fluorine atom and –CF2 fragments have been detected.

In He-O2 plasmas, the helium metastables species being consumed by oxygen, fewer of them are then available to etch the PTFE, reducing the mass losses and fluorine detection on aluminum for higher O2flow rates. However, as it was previously shown [2], WCA and AFM measurements indicate an increase in hydrophobicity and roughness of the PTFE surface. The alveolar structures observed by AFM are then assumed to come from the anisotropic etching where the atomic oxygen etches mainly the amorphous phase.

[1] T. Dufour, J. Hubert, P. Viville, C.Y. Duluard, S. Desbief, R. Lazzaroni, F. Reniers, PTFE surface etching in the post-discharge of a scanning RF plasma torch: evidence of ejected fluorinated species, *Plasma Process. Polym.*. 2012, DOI. 10.1002 /ppap.201100209.

[2] **N. Zettsu, H. Itoh, K. Yamamura,***Thin Solid Films*, 2008, 516,6683.

[3] J. Hubert, T. Dufour, N. Vandencasteele, S. Desbief, R. Lazzaroni, F. Reniers, Etching processes operating on a PTFE surface exposed to He and He-O2 atmospheric post-discharges. (Accepted : *Langmuir*).

11:40am **PS+TC-WeM12 Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition of Hydrophobic Thin Film Coatings Using Liquid Precursors**, ***J. Yim,*** *V. Rodriguez-Santiago, A. Williams, J. Hirvonen, D. Pappas*, U.S. Army Research Laboratory

Hydrophobic coatings are known to impart self-cleaning, anti-fouling, anti-fog and wicking properties on polymeric substrates and textiles. These coatings are largely derived from either wet chemical methods or low pressure plasma-based chemical vapor deposition techniques using gaseous precursors. In an effort to eliminate the use of large quantities of chemicals and solvents associated with wet chemistries and to deter the use of costly vacuum systems, we explored the practicality of an atmospheric pressure plasma jet (APPJ) as a comparable alternative to low pressure plasma systems. To obtain coatings typically achieved through wet chemistry, and often limited by commonly used fluorocarbon gases such as C_3F_6, liquid fluorinated precursors such as fluoroalkyl silanes (FAS) were explored. FAS with varying fluorocarbon chain lengths were studied and deposition conditions as a function of electrode-substrate gap distance, deposition time and power were investigated. Ultra high molecular weight polyethylene (UHMWPE) films served as the model polymer system in which the coatings were deposited owing to its simple molecular structure consisting of -CH_2-CH_2- chains. The characteristic properties of the coatings on UHMWPE such as hydrophobicity, chemical composition, uniformity and deposition rates were studied to establish a correlation between processing parameters and the coating properties. X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) measurements confirmed the presence of CF, CF_2, and CF_3 functionalities in the coating composition and reveal that there is a strong dependence of these groups on the chain length of fluorocarbon groups in the FAS precursors. Water contact angle (WCA) measurements confirm hydrophobicity of the coating, where angles over 90° were recorded. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) techniques were utilized to probe the morphological profiles of the coatings. Profilometry and ellipsometry show deposition rates of the coating ranging from nanometer to sub-micrometer thick coatings. Results show that the use of APPJ with liquid precursors is promising in achieving hydrophobic coatings under atmosphere without producing large volumes of hazardous waste.

***** Coburn & Winters Student Award Finalist

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