Advanced Surface Engineering
Room: Cimmaron - Session SE+PS-MoM

Atmospheric Pressure Plasmas
Moderator: H. Barankova, Uppsala University, Sweden

8:20am **SE+PS-MoM1 Plasmajet Atmospheric Pressure Plasma: Effects of H2 Addition in N2 Main Plasma Gas on the Optical and Electrical Plasma Characteristics and on Si-based Film Composition**, ***D. Debrabandere***, *X. Vanden Eynde,* CRM (Centre for Research in Metallurgy), Belgium, *F. Reniers*, Université Libre de Bruxelles, Belgium

Si-based coatings were deposited with a cold plasma jet (Plasmabrush® PB1 from Reinhausen Plasma) at atmospheric pressure with nitrogen as main plasma gas and hexamethyldisilazane (HMDSN) as precursor. Effects of hydrogen addition on the plasma characteristics and the coating composition have been evidenced with optical emission spectroscopy (OES), power measurements and XPS in-depth analyses of deposited coatings. The evolution of the nitrogen line (at 315.9 nm) intensity with the applied voltage (ranging from 3.0 kV to 4.5 kV) has a sigmoid shape for the pure nitrogen plasma but it is quite linear with hydrogen addition (up to 3%). Based on OES spectra, the presence of the NH specie in the nitrogen-hydrogen plasmas has been evidenced (around 336.0 nm) but not in the pure nitrogen plasma. The power measured showed the same evolution with the applied voltage as the nitrogen line optical emission intensity: sigmoid shape for the pure nitrogen plasma and straight line for the nitrogen-hydrogen mixture. Although the plasma power is in similar range for both gases (except for applied voltages from 3.2 to 3.6 kV), the nitrogen concentrations in the films as evidenced by XPS were lower with the nitrogen-hydrogen plasma than with the pure nitrogen plasma indicating a chemical effect of the presence of hydrogen in the plasma.

Acknowledgements

The authors would like to thank the Walloon Region (Belgian authorities) for financial support in the framework of a FIRST DOCA program.

8:40am **SE+PS-MoM2 Plasma Polymerization at Atmospheric Pressure: an Environmental Friendly Approach to Synthesize (ultra)hydrophobic, Biocompatible, Hybrid, Barrier or Ion – Exchange Coatings**, *D. Merche, J. Hubert, F. Dabeux, B. Nisol, A. Batan, N. Vandencasteele,* ***F. Reniers***, Université Libre de Bruxelles, Belgium

Plasma treatments are widely used in various applications, such as surface modification (etching, grafting, cross-linking…), cleaning, pollutant removal, and thin films deposition. They are advantageous since they have a low energy cost, they do not release toxic organic solvents into the environment, they are easy to control (the main parameters to control the plasma are the current, voltage, frequency and the gas pressure and composition) and they can be run at room temperature. The plasma polymerization technologies at atmospheric pressure were developed more recently. They allow avoiding expensive vacuum set up, and can be easily implemented in a continuous production line. Two major configurations were used for the deposits: direct (in a DBD system) and remote mode (atmospheric torch). The synthesis conditions (in one step, starting from a liquid precursor, and using an atmospheric pressure plasma) of various types of coatings will be presented and discussed :PEG[1] and PTFE-like coatings [2] (for biocompatible coatings), multifunctional hybrid coatings for barrier properties [3] ; sulfonated polystyrene membranes for fuel cell applications [4,5] . The chemical structures of the various coatings were studied by XPS, FTIR and SIMS spectrometry. Correlations between the chemical structure and composition of the coatings and the plasma parameters were established.

[1] B. Nisol, C. Poleunis, P. Bertrand, F. Reniers, “Poly(ethylene glycol) Films Deposited by Atmospheric Pressure Plasma Liquid Deposition and Atmospheric Pressure Plasma-Enhanced Chemical Vapour Deposition : Process, Chemical Composition Analysis and Biocompatibility”, Plasma processes and polymers, (2010) under press

[2] N. Vandencasteele, O. Bury, F. Reniers "Process to deposit a fluorinated layer on a support", WO/2009/030763

[3] A. Batan, F. Brusciotti, I. De Graeve, J. Vereecken, M. Wenkin, M. Piens, J.J. Pireaux, F. Reniers and H. Terryn, "Comparison between wet deposition and plasma deposition of silane coatings on aluminium", Progress in Organic Coatings , (2010) under press

[4] D. Merche, C. Poleunis, P. Bertrand, M. Sferrazza, F. Reniers, “Synthesis of PS thin films by means of an atmospheric pressure plasma torch and a dielectric barrier discharge”, IEEE trans. on plasma science, 37 (2009), 951-960.

[5] Delphine Merche, Julie Hubert, Claude Poleunis, Patrick Bertrand, Philippe De Keyzer, François Reniers "Synthesis of sulfonated PS films using a Dielectric Barrier Discharge high pressure plasma" plasma processes and polymers, submitted

9:00am **SE+PS-MoM3 Surface Treatment of Energy Conversion Device Components by Cold Atmospheric Plasma**, ***L. Bardos***, *H. Barankova*, Uppsala University, Sweden

Advantage of virtually unlimited substrate sizes makes the cold atmospheric plasma very attractive for treatments of surfaces e.g., for improving the lifetime and performances of renewable energy conversion systems. Samples of fiberglass-reinforced vinylester with a vinylester based gelcoat from windmill turbine blades and steel sheets used for ocean buoys in the linear wave energy converters have been treated by the Fused Hollow Cathode (FHC) and Hybrid Hollow Electrode Activated Discharge (H-HEAD) atmospheric plasma, generated in Ar, Ne and a mixture of air with water. The resulting surface energy has been examined by contact angle measurements. Turbine blade surface becomes hydrophilic after the treatment, sticking of the water droplets is reduced and the surface dries fast after rain, snow or icing. An increased surface tension after plasma treatment of steel relaxes within about 60 min. However, the SEM observations of paint-steel interfaces after an immediate application of the protective paint on treated surfaces have confirmed a considerable improvement of the paint adhesion that can provide better corrosion resistance and lifetime of buoys. Results of tests under different plasma parameters are presented and discussed.

9:20am **SE+PS-MoM4 Smooth and Self-Similar SiO_2-like Layers on Polymers Synthesized using Dielectric Barrier Discharge Assisted CVD at Atmospheric Pressure**, ***P. Antony Premkumar***, *S.A. Starostin,* Eindhoven University of Technology, Netherlands, *H. de Vries,* FUJIFILM Manufacturing Europe BV, Netherlands, *M. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

High quality inorganic oxide thin films applied over polymers are of significant technological interest in the field of optics, vapour barrier coatings, microelectronics, flat panel displays and protective coatings. The layers prepared by PECVD at atmospheric pressure (AP-PECVD) is considered as a promising technology due to its economical and technological advantages. Despite these benefits, the major challenge of this coating technology is the usually reported poor film quality which arises mainly due to the intrinsic instabilities of the plasma as well as from the complex reactions of the deposition process.

In this investigation, we demonstrate the remarkable SiO_x film properties synthesized using AP-PECVD in a roll-to-roll configuration [1]. The depositions were performed, in He free gas mixtures, using uniform glow-like dielectric barrier discharge as the electrical sources to assist CVD at atmospheric pressure. As a generic characteristic of the developed technology, it is observed that, irrespective of precursors (TEOS or HMDSO) and process gases (Ar, N_2 or air) employed, the films are smooth, both in short and long range length scales, and of near stoichiometric silica with very low carbon content (<2%). Detailed AFM morphology description and surface statistical analysis on SiO_2 dynamics showed that no dynamical film roughening in growth front and lateral directions are observed and the synthesized layers (~ 350 nm) follow the topology of the substrate, mimicking its surface texture characteristics. The value of the roughness exponent (α), close to 1, determined from the height-height correlation function analysis, indicates a self-similar scaling of the SiO_2-like film morphology with the polymer substrate. The films are uniform with no defects or particle being incorporated during the deposition process and exhibit excellent barrier performances towards O_2 and H_2O permeation.

[1] P. Antony Premkumar, S.A. Starostin, M. Creatore, H. de Vries, R.M.J. Paffen, P.M. Koenraad, M.C.M. van de Sanden, *Plasma. Proc. Polym*. (2010) In Press

9:40am **SE+PS-MoM5 Atmospheric-pressure Plasma Activation of Silicon and Glass Surfaces for Low-Temperature Direct Bonding**, ***C.-P. Klages***, *M. Eichler,* Fraunhofer Institute for Surface Engineering and Thin Films (IST), Germany, *B. Michel*, Technische Universität Braunschweig / Institut für Oberflächentechnik (IOT), Germany **INVITED**

Low-temperature direct bonding of silicon wafers has been industrially established for several years now. To achieve a lowered annealing temperature required for sufficient bond strength from about 1000 °C to a few 100 °C only, low-pressure plasma treatment came into use more than 20 years ago. As shown at Fraunhofer IST more recently, also plasma activation at 1 bar is capable of reducing required annealing temperatures to around 100 °C while still achieving bond energies 2 to 3 times higher compared to RCA-cleaned reference wafer pairs.

Many questions concerning the key effects, responsible for lowering the required annealing temperature, are still under investigation, especially for the attractive atmospheric-pressure method. At IOT and IST, the effects of dielectric barrier discharge (DBD) treatments performed under a wide range of conditions at 1 bar pressure on the properties of native or thermal SiO_2 layer on silicon wafers and on the achieved bond strength have been investigated in the recent years. The presentation will give an overview of the results from these investigations which were obtained using several surface analytical methods.

Recently, main interest has shifted from silicon to other materials and to alternative atmospheric-pressure plasma processes. With special gases used for the plasma activation, an increased bonding strength is also achievable for borosilicate glass bonding. However, while the mechanism of bonding enhancement in case of native oxide layers on Si can clearly be attributed to a surprisingly rapid growth of a porous oxide film, a convincing explanation for the effects achieved with glasses is still missing.

A common attribute of surface activation by DBD and low-pressure plasmas is a direct access of the plasma to the surface. By contrast, corona discharge makes use of the inhomogeneity of the electric field near a needle tip. Plasma zone and wafer are spatially separated and the electric field stress at the wafer surface is greatly reduced. Promising results of corona discharge treatment as an activation method for low-temperature wafer bonding have been obtained, indicating that relatively stable charged species play an important role. On the other hand, excimer UV radiation was virtually ineffective.

New insights into the kinetics of silanol condensation were also made possible by continuous measurements of the bonding strength *in situ* during annealing. Results of these studies show that the bond strength increase can be attributed to the expansion of bonded micro regions instead of statistical formation of siloxane bridges between the wafers.

10:40am **SE+PS-MoM8 Atmospheric Pressure Microcavity Plasma Arrays for Spatial Surface Modification**, *R.D. Short,* ***S. Al-Bataineh****, E. Szili, C. Priest, Ph. Gruner,* University of South Australia*, E. Anglin,* Flinders University, Australia*, H.J. Griesser,* University of South Australia*, N. Voelcker,* Flinders University, Australia*, D. Steele*, University of South Australia

Microplasmas, a rapidly growing technology, are normally operated at or near atmospheric pressure with dimensions ranging from microns to millimetres. [1] We are developing this technology for surface modification without using a physical mask or additional processing steps to increase the versatility and cost-effectiveness of the technology. Micropatterning of various chemistries and biomolecules is seen as vital to the successful development of new and emerging technologies, such as microfluidics and high throughput cell screening tools. [1, 2] In this presentation, the fabrication process of microcavity plasma array devices will be introduced, followed by a demonstration of the utility of these devices for generating specially well-controlled micron-scale surface treatment and polymer deposition. Two issues regarding the utility of these devices for localised surface modification were investigated: 1) Can these devices be used to modify a surface with micron-scale features without having the substrate pressed against the array? 2) Can this be achieved with control over diffusion of the plasma reactive components? We explored this through XPS imaging and small spot analysis, which gave insights into the surface chemistry of the micron-scale modified areas. Finally, we demonstrate the utility of microcavity plasma array surface engineering in the development of biological cell arrays.

1. Iza, F., et al., *Microplasmas: Sources, particle kinetics, and biomedical applications.* Plasma Processes and Polymers,

2008. 5(4): p. 322-344.

2. Klages, C.-P., et al., *Microplasma-Based Treatment of Inner Surfaces in Microfluidic Devices.* Contributions to Plasma

Physics, 2007. 47(1-2): p. 49-56.

11:00am **SE+PS-MoM9 Electrical Characterization of Dielectric Barrier Discharges of Various Electrode Geometries**, ***V. Rodriguez-Santiago****, J.K. Hirvonen, B.E. Stein,* U.S. Army Research Laboratory*, D.R. Boris, S.G. Walton,* U.S. Naval Research Laboratory*, D.D. Pappas*, U.S. Army Research Laboratory

The increased use of atmospheric-pressure plasmas for the surface modification of materials has drawn particular interest in understanding the basic phenomena underlying dielectric barrier discharges (DBDs). One of the main advantages of using DBDs is the generation of cold, non-equilibrium plasma at atmospheric pressure conditions without the need of vacuum equipment. A typical DBD setup consists of one or both electrodes covered with a dielectric material with a sufficiently high applied voltage to ignite the plasma. The plasma can be either filamentary or spatially uniform depending on parameters such as dielectric and electrode material, interelectrode gap, carrier and reactive gas mixture, and the type of applied voltage among others. Another important aspect is the geometry of the electrode assembly, which will determine the electric field configuration and thus influence the discharge characteristics.

In this study, we investigate the electrical characteristics of He and He-O_2 dielectric barrier discharges using a pulsed, sinusoidal signal in the kHz frequency range with a (1-10) kV peak-to-peak amplitude. Full characterization of the plasma will be carried out using rod, sheet and planar electrode assemblies, while materials of various dielectric constants such as mica, quartz and polyethylene will be employed. Voltage, current and power distributions will be analyzed aiming to identify the optimal electrode geometries and dielectric materials needed to produce uniform and large scale plasmas for materials processing.

11:20am **SE+PS-MoM10 ICP Atmospheric Plasma Torch with Saddle-like Antennas for Yttrium Oxide Nanocoating**, ***Y. Glukhoy****, H. Schiesser*, American Advanced Ion Beam Inc.

ICP atmospheric plasma torch is the most powerful electrode-less heat generating system with relatively small dimensions and a reasonable consumption of power and gases. It serves as an universal tool for nanocoating of surfaces where the gaseous, liquid as well as powder precursors can be used. A total melting, evaporation and plasma chemical reaction of precursor can be achieved with torches that provide a sufficient residential time a high temperature plasma fluid. But a conventional torches are supplied by a coil inductor pinching this fluid due to an axial magnetic filed. In result, a high temperature area is reduced and a sufficient part of precursor is converted in dust. In order to broaden and lengthen this area for a sufficient increasing of a residential time the inductor has been replaced with two saddle-like ICP antennas with the different frequencies, i.e. 27.12 and 13.56 MHz. Each antenna comprises two or more spiral coils in a mirror position and in series or parallel connection. These coils are distributed with an angular uniformity and envelop a quartz tube of a plasma reactor. Such an non-axisymmetric design allows generation of a transversal RF field directed normally to axis of this reactor. But a plasma fluid is fixed on the axis due to buoyancy in the centrifugal force field created by a swirling injection of a discharge and sheath gases. However, the temperature gradient and a pressure drop caused by a cold carrier gas injected with a high velocity axially into a plasma bulk generate turbulence disrupting and distorting the plasma fluid. In result, a heat transfer from plasma to the wall is increased, becomes non-uniform and creates a hot spot melting the quartz wall. Mechanisms of the non-axisymmetric coupling, torch generation, contribution of different factors in distortion of the plasma fluid and method elimination of the hot spot have been investigated. In addition, we will discuss recent effort to extend applications such a torch in different areas including fabrication of yttrium oxide anti-corrosive nanocoating of focusing rings used in plasma etching processes in semiconductor industry.

1. Y.Glukhoy, I. Ivanov RF Atmospheric Plasma Systems for Nanopowder Production and Deposition of Nanocrystallines. AVS 53rd International Symposium, San Francisco, California, November , 2006 CA, USA .

2. Y.Glukhoy. Saddle-like ICP Antenna for RF Atmospheric Plasma Processes. AVS 56th International Symposium, San Jose, California, November , 2009 CA, USA .

Authors Index

Bold page numbers indicate the presenter