

Wednesday Afternoon, October 30, 2013

Advanced Surface Engineering

Room: 203 C - Session SE+PS-WeA

Atmospheric Pressure Plasmas

Moderator: H. Barankova, Uppsala University, Sweden

2:00pm **SE+PS-WeA1 Tailoring Surfaces using Atmospheric Plasma Technologies : Examples, Challenges, Limits, Future, F.A.B. Reniers, Université Libre de Bruxelles, Belgium** **INVITED**

Atmospheric plasma present nowadays numerous applications in the treatment of surfaces. They can be used for the cleaning of metals, for the reduction of surface oxides, to increase the adhesion of polymers, to deposit a wide variety of coatings from anticorrosion ones to biocompatible ones, including hybrid multifunctional coatings. They also have an effect on the surface roughness. Although the principles of the main technologies used (dielectric barrier discharge, RF discharges,...) are well known, the mechanisms involved in the different processes are still partly to be determined. Through a few detailed examples, the talk will try to go deeper in the understanding of what is going on in the process. The current limitations of atmospheric plasma technologies (what can be done, and what cannot be done (yet)) will conclude the talk.

Some detailed examples :

- Understanding the mechanisms for etching PTFE by atmospheric plasma to make it superhydrophobic. Through a combined study of the gas phase and the polymer by optical emission spectrometry, dynamic water contact angle, AFM, XPS and weight measurements, we will evidence the selected effect of atomic oxygen, metastable helium and UV photons on the etching process. The etching study is extended to a range of other polymers, ranging from PE to PTFE, with an increasing number of fluorinated atoms. Different mechanisms are proposed.

- The deposition of atmospheric plasma coatings usually leads to coatings exhibiting a good adhesion to the substrate. This adhesion, evidenced by peeling test, can be studied at the molecular level. The case of poly-AMA coatings and Silane coatings on aluminum will be presented.

- Plasma polymerization is strongly influenced by the chemical reactivity of the precursor molecule. A wide selection of molecules of precursor molecules, liquid at room temperatures have been injected in dielectric barrier discharge (from pure C_xH_y , to C_xCl_y and C_xF_y , and esters such as nPIB, nPMA, AMA). We will show the effect of the double bonds on the final chemical structure of a coating, and on the deposition rate. We will also show that double bonds known to be unreactive in conventional polymerization can easily be activated in plasma. The effect of halogenated atoms present on the precursor is also studied

Finally, some perspectives regarding the future applications of atmospheric plasma will be discussed. Geometrical aspects, frequency range, hybrid coatings, microtexturing, deposition rates, will be approached.

2:40pm **SE+PS-WeA3 Defining Atmospheric Pressure Air Plasma Treatment Parameters for Bonding Sheet Molding Compound, L.P. Haack, A.M. Straccia, Ford Motor Company**

Sheet molding compound (SMC) is used in the automotive industry for constructing body closure panels, typically on vehicles of low volume where tooling costs can be kept to a minimum. SMC is a reinforced composite material consisting of dispersed strands of chopped glass fibers in a polyester/polystyrene blended resin along with surface additives and inorganic fillers. The SMC body panels are typically constructed with an inner structure and an outer skin that are mated by adhesive bonding. Epoxy adhesives are used to join the panels. Although the resin chemistry should allow for a strong covalent bond with the epoxy adhesive, instead poor bonding is often noted in production. This is mostly attributed to the use of internal and external mold release agents. Physical sanding will help improve bonding, but the process creates substantial amounts of dust and debris and is prone to human error. Atmospheric pressure air plasma is therefore being evaluated as an alternative to prepare the surfaces for bonding. Plasma was shown to improve bond reliability at low to moderate levels of treatment. Interestingly, it also yielded impeccable bond durability at high to extremely high levels of treatment; conditions that would be deleterious to many plastics, especially polyolefins that can revert treatment at elevated temperatures. Measurements were conducted in an attempt to elucidate how this material interacts with the plasma to produce a surface exceedingly robust to bonding at an unexpectedly wide range of treatment conditions. Atomic force microscopy measurements gave insight into the amount of surface roughness created by the plasma treatments, while chemistry was determined by surface energy measurements and X-ray

photoelectron spectroscopy (XPS). Dyne level testing was unable to accurately discern varying treatment levels since measurements reached 72 dynes/cm (the wetting point of water) even at lower treatment levels, while robust bonding occurred at still considerably higher dosage levels. Solvent wiping experiments along with XPS measurements revealed that, under the time constraints of the automotive manufacturing process, plasma treatments essentially achieve a condition of steady state that will remove material and yet still present a highly oxidized surface that is conducive to bonding. Thus, in practice, a condition of overtreatment is essentially unattainable.

3:00pm **SE+PS-WeA4 Correlation of Spectral Emissions of a He-O₂ RF Atmospheric Plasma Discharge with Polymer Surface Activation, V. Milosavljevic, M. Donegan, University College Dublin, Ireland, P.J. Cullen, Dublin Institute of Technology, Ireland, D.P. Dowling, University College Dublin, Ireland**

Atmospheric pressure non-thermal helium plasma jets are increasingly used in many processing applications due to their combination of inherent plasma stability and excellent reaction chemistry. Despite their widespread usage, it remains largely unknown whether cold atmospheric plasma jets maintain characteristics, such as gas temperatures and particle flux, when they breakdown while arcing or whether they possess different operating modes. From an application point of view, the activation of polymer surfaces can help to overcome the chemical inertness and low surface energy generally associated with these types of materials. Polymers, such as PET, are thermally damaged at relatively low temperatures and so a delicate balance must be reached where surface activation of the polymer is maximised, while thermal damage is prevented.

The atmospheric plasma system employed generates plasma using He-O₂ (in the range of 100-200 W), operates at a frequency of 27.12 MHz and uses a 5 cm wide beam applicator. The input variables on this system were: helium gas at a constant flow rate of 30 l/min, while secondary gas input: plasma power ratios are set by the manufacturer.

This work employs optical emission spectroscopy as a diagnostic technique for the measurement of atomic and molecular spectral emissions generated using the plasma jet system. The OES of neutral atomic spectral lines and molecular bands are investigated over a range of plasma process parameters. Wavelength resolve optical emission profiles suggest that the emission of helium's spectral lines shows that the high energy electrons have a larger influence than helium metastables on the overall spectral emission. Furthermore, the experimental data indicates that the use of high helium flow rates limits the significance of air impurities, e.g. N₂, for the creation and sustainability of plasma discharges in He-O₂ gas chemistry. The level of polymer surface activation was evaluated based on changes to the water contact angle of PET samples after plasma treatment. For the first time a direct correlation was obtained between polymer water contact angle changes and the OES measurement of the atomic hydrogen Balmer H α and molecular OH line emission intensities. Further work will be presented how the high helium flow rate is used in an attempt to minimize the ratio of gas convection to chemical reaction time scale (recombination). This is also favours the rapid transport of newly created radicals and excited species to the surface under treatment.

This work was a funded by SFI under the Precision cluster, the 'Fresh-Pack' project funded by the National Development Plan of Republic of Ireland and grant OI171006.

4:00pm **SE+PS-WeA7 Atmospheric Plasma Polymerization Enhanced by Simultaneous UV Irradiation, N. Vandencastele, J. Bossert, Université Libre de Bruxelles, Belgium, A. Kakaroglou, Vrije Universiteit Brussel, Belgium, B. Nisol, Université Libre de Bruxelles, Belgium, H.A. Terry, Vrije Universiteit Brussel, Belgium, F.A.B. Reniers, Université Libre de Bruxelles, Belgium**

Plasma polymerization is now commonly used to deposit a wide variety of films for various applications (corrosion protection, biocompatibility, ultrahydrophobic layers...). Atmospheric plasma polymerization is a very promising technique for thin film deposition in industry. Indeed it does not require the use of organic solvent and it is not limited by vacuum requirement. Furthermore the high reactivity of the plasma medium allows for a rapid deposition of a large number of molecules on virtually any kind of substrate.

However there are still some issue remaining: the degree of crosslinking is not always sufficient to ensure good barrier and mechanical properties of the films. In some instance the adhesion of the films to the substrate is not strong enough. In this study we looked at the plasma polymerization of Allyl methacrylate on gold substrate using a high frequency (17 kHz) dielectric barrier discharge (DBD). The effects of the classical plasma

polymerization parameters (monomer concentration, power, deposition time...) are studied as well as the effect of in situ ultra violet (UV) irradiation. The UV source is a mercury discharge lamp commonly used to cure polymers. Our experimental setup consists of a 2 mm thick quartz plate (acting as the dielectric) covered with a stainless steel grid (diameter 0.018 mm, spacing 0.045 mm) acting as the powered electrode. The second electrode is made of a grounded copper plate. It is separated from the powered electrode by a 3mm gap. The UV lamp is placed directly above the quartz electrode, illuminating the sample through the grid. Argon is used as the plasma gas. Its flow ranges from 1 to 3 liter per minute (LPM). The precursor vapor is carried in the plasma by a secondary argon line with flow ranging from 1 to 3 LPM. The total gas flow is kept constant at 4 LPM.

Three separate cases are studied: plasma polymerized films (pp-film) without UV irradiation, pp-films with post plasma UV irradiation and finally pp-films with UV irradiation during the plasma polymerization.

The pp-films are characterized by FTIR, XPS, contact angle and ellipsometry. Differences between the pp-film compositions have been evidenced for the 3 types of treatments. Increased O/C ratios have been observed for the films exposed to UV irradiation. The FTIR spectra are also strongly affected by the presence of UV irradiation. Changes in the C=O/C-C peaks ratio are observed for the 3 types of treatments. This allows us to conclude that the irradiation during the films growth leads to different results than the usual UV post treatment (UV curing).

4:20pm SE+PS-WeA8 Plasma Polymerization of (3-aminopropyl) Trimethoxysilane using a Micro-plasma Printing Setup, J.R.G. Schalken, Eindhoven University of Technology; InnoPhysics B.V., Netherlands, A.A.E. Stevens, P. Verhoeven, InnoPhysics B.V., Netherlands, M. Creatore, Eindhoven University of Technology, Netherlands

Amino-functionalities are introduced in biosensors in order to specifically bind proteins using biomolecules for the detection of diseases from human blood samples. Plasma polymerization of amine-containing precursor molecules such as (3-aminopropyl) trimethoxysilane (APTMS) can be used to deposit films with amino-functionalities.

The μ PlasmaPrint technique utilizes a pin-to-plate dielectric barrier discharge at atmospheric pressure. A dielectric substrate is placed on a high-voltage plate electrode. An array of needles is moved above the substrate, while individual needles are allowed to move towards the surface and back based on a digital pattern. According to the Paschen law, a reduction of the distance between a grounded needle electrode and the high-voltage substrate holder from about 800 μ m to 200 μ m can lead to the ignition of a plasma. Within a millisecond the plasma is turned off by moving the needles up again. The dot-wise exposure of the surface to short micro-plasmas enables a local plasma treatment with a minimum feature size of 100 μ m.

Thin films of plasma polymerized APTMS have been deposited on a fluorinated ethylene propylene copolymer (FEP) using the μ PlasmaPrint technique. The thickness of the deposited films varied in the range of 5 to 100 nm. The surface characteristics and ageing behavior of the films have been investigated by X-ray photoelectron spectroscopy (XPS), fluorescence microscopy and water contact angle measurements, respectively. Depending on the number of print repeats of the μ PlasmaPrint system, the concentration of amino-functionalities in the deposited film as derived from XPS peak analysis varied from 9.1% for a single print repeat, down to 4.7% for 20 print repeats.

Water contact angle measurements showed an increase from 10° for a single print repeat up to 40° for 20 print treatments, while the water contact angle of the FEP substrate was measured to be 110°. The increase in water contact angle with increasing print repeats suggested a reduction of polar components at the surface and was therefore consistent with the relative reduction of amino-functionalities as measured with XPS.

Based on the experimental results, a polymerization process of APTMS is proposed. It is suggested that polymerization mainly takes place by the abstraction of methyl- and methoxy- groups to develop siloxane chains. For an increased number of print repeats, which results in a prolonged plasma exposure, it is proposed that the creation of reactive sites for the cross-linking of APTMS polymer chains also takes place in the aminopropyl chains, resulting in a decreased concentration of amino-functionalities.

4:40pm SE+PS-WeA9 Evaporative Coating at Atmospheric Pressure (ECAP), Y.L. Wu, J. Hong, D. Peterson, J. Zhou, T.S. Cho, D.N. Ruzic, University of Illinois at Urbana-Champaign

Recently, the Center for Plasma-Material Interaction (CPMI) has developed innovative coating method of Evaporative Coating at Atmospheric Pressure (ECAP). This new idea is an atmospheric pressure based process following the similar concept as the Laser Pressure LAPCAP purely at Atmospheric Pressure (LAPCAP) [1], the material captured by the plasma plume is

atomic in nature (the evaporated metal atom) and should therefore end up deposited molecule-by-molecule in a PVD fashion. By using the thermal energy from the microwave plasma solid 99.99%+ purity aluminum are evaporated and then produce a PVD-like alumina coating on a workpiece. The Aluminum target is inserted in the center of the microwave torch feeding a melt pool and evaporates into the surrounding plasma plume. A bottle neck was made in the antenna and could reduce the heat loss by 84%. The film was deposited as Al_2O_3 using oxygen from the environment. Alpha and other metastable phases of aluminum oxide were found on the deposited films. Deposition rate was around 2 μ m/min. Gas flow rate around the antenna tip was about 0.9 m/s, and temperature of the plasma was about 1400°C at 1350W input power from simulations. Gas shield was used to keep the work gas pure. A much higher thermal energy of the plasma plume will make a superior coating microstructure as compared to a purely evaporated film.

Reference:

[1] Laser-assisted plasma coating at atmospheric pressure: production of yttria-stabilized zirconia thermal barriers, Zihao Ouyang *et al* 2011 *J. Phys. D: Appl. Phys.* 44 265202

5:00pm SE+PS-WeA10 Selection of an Atmospheric Plasma Source for 450mm Backside Wafer Cleaning, F.T. Molkenboer, J. Van Veldhoven, Y.L.M. Creyghton, O. Kievit, T.W. Versloot, N.B. Koster, TNO Technical Sciences, Netherlands

TNO is working on the selection and development of a non-thermal atmospheric plasma source for backside wafer cleaning. This selection started with a theoretical comparison of the potential candidates. Main criteria for the selection are cleaning speed, the amount of contamination that can be removed in a certain time and plasma temperature. Further criteria are the dependency of plasma homogeneity on substrate conductivity, the distance between the plasma source and the substrate as well as scalability of the source up to a 450 mm wide cleaner. Backside wafer cleaning is important for the semiconductor industry to enable the transition from 300 mm wafers to 450 mm wafers. Contamination on the backside of a wafer can lead to printing errors and can negatively influence post lithography processing like metal deposition.

The selection of the plasma source is part of a TNO project that has the objective to build and deliver a complete backside wafer cleaner to the 450 mm pilot line to be installed at IMEC, Belgium. The final selection will be made on the basis of a series of experiments. Candidates already tested are surface- and volume- dielectric barrier discharge (SDBD and VDBD) plasma sources.

In this presentation we will report the outcome of our selection of the plasma source, supported by the validated source inventory and experimental results.

This work is funded by the ENIAC Joint Undertaking and AgentschapNL. It has the goal to enable the European semiconductor industry to make the transition to 450mm wafers

5:40pm SE+PS-WeA12 Rapid Atmospheric Pressure Plasma Jet Treatment on ZnO for rf-sputtered MgZnO/ZnO Heterostructures, S.T. Lien, H.C. Li, Y.J. Yang, C.C. Hsu, I.C. Cheng, J.Z. Chen, National Taiwan University, Taiwan, Republic of China

MgZnO/ZnO heterostructures have shown great potential for optoelectronic device applications. The polarization field at MgZnO/ZnO heterojunction can induce charge accumulation at the interface to form two-dimensional electron gases (2DEGs). This has been observed in high quality materials grown by molecule beam epitaxy (MBE) or pulse laser deposition (PLD) as well as in defective MgZnO/ZnO heterostructure system deposited by rf-sputtering. Although high quality MgZnO/ZnO is desirable for its high electron mobility, the required deposition technique such as MBE or PLD is not suitable for the processing of large-area electronics. In regard to large-area deposition, rf-sputtering technique is the preferred process in spite of the more defective nature of the deposited materials. In our previous studies, we have demonstrated that the electron Hall mobility of $\sim 40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and field-effect mobility of $\sim 84 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the rf-sputtered $\text{Mg}_{0.4}\text{Zn}_{0.6}\text{O}/\text{ZnO}$ heterostructure and the top-gated $\text{Mg}_{0.2}\text{Zn}_{0.8}\text{O}/\text{ZnO}$ thin film transistor, respectively. The mobility exceeds the typical value (6 to $9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) of a-InGaZnO TFT, which is the most promising technique for large-area oxide electronics nowadays.

One key step to obtain 2DEGs in the defective rf-sputtered MgZnO/ZnO heterostructures is the thermal annealing process on ZnO prior to the deposition of MgZnO material. This paper reports that atmospheric pressure plasma jet (APPJ) treatment can be used for the same purpose with a much shorter processing time. A thirty-second APPJ anneal on ZnO with a maximum temperature of 340 °C can replace a 30 min, 400 °C furnace-anneal to promote the formation of 2DEGs in the rf-sputtered MgZnO/ZnO heterostructure. The APPJ treatment also increases the crystallinity of ZnO

films and releases the compressive residual stresses, verified by XRD and UV-Vis transmission measurements. The ultra-short processing time is attributed to the synergy of plasma reactivity and temperature of APPJ.

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