Plasma Science and Technology
Room 2011 - Session PS2-ThM

Plasmas and Polymers

Moderator: E.C. Benck, National Institute of Standards and Technology

8:00am **PS2-ThM1 Tuning Polymer Surfaces by Cold Plasma Technology***, **R. d'Agostino**,* University of Bari, Italy **INVITED**

Polymers modification by means of low pressure plasma processes for different applications are currently investigated in the University of Bari and in the spin off Plasma Solution. Our research follows several applicative directions, however while in the University we mostly deal of fundamental issues, in the spin off we aim to develop industrial customized processes and plasma reactors. Our traditional approach for studying plasma modification of polymers is generally based on a combined use of plasma and surface diagnostics. This, along with performance analyses, allows often to set proper on-line diagnostics for process control and to tune the morphology/composition/performance of treated polymers. The issues covered in the talk include some of our best processes as transparent barrier coatings, nano- and micro-structured polymer films, super-hydrophobic materials, non fouling, corrosion protection, tissue engineering, bacterial resistant coatings, atmospheric pressure glow discharges for Teflon-likes.

8:40am **PS2-ThM3 Morphological and Chemical Evolution of Model Resist Polymers for Plasma/Energetic Beam Templating Materials****, R. Phaneuf, **T. Kwon**, R.L. Bruce, S. Engelmann, G.S. Oehrlein,* University of Maryland*; B. Long, G. Willson,* University of Texas, Austin*; D.B. Graves, D.G. Nest, M. Goldman, J. Vegh,* University of California, Berkeley*; A. Alizadeh,* GE Electric Global Research Center

The control of the line edge / surface roughness induced by plasma etching, one of the essential process steps in IC fabrication, may ultimately limit the minimum critical dimensions obtainable in nanoscale-devices. This issue is thus crucial in the development of the new generation of organic mask materials for advanced lithographic techniques. In the work presented here we have investigated the evolution of surface roughness of five prototypical resists, polystyrene (PS), poly (4-methylstyrene), poly-@alpha@-methylstyrene (P@alpha@MS), poly-3-hydroxy-1adamantyl methacrylate (HAMA), and poly-3-hydroxy-1-adamantyl acrylate (HAdA), during inductively coupled plasma (ICP) etching with O@sub 2@, with Ar, and with C@sub 4@F@sub 8@/90%Ar plasmas. Our AFM measurements show a strong correlation of the rate of roughening of these resists with type and position of chemical functional groups, the tendency toward chain scission vs. cross-linking in the presence of ionizing radiation, and with the composition of the etching gas. In particular, we find that for the C@sub 4@F@sub 8@/90%Ar plasma, poly (4-methylstyrene) shows the smallest surface roughness among all the samples, and HAMA the highest. We compare the morphological and chemical changes of these model resists under plasma etching to the extreme case of ion sputtering during Ar@super +@ beam bombardment. *Work supported by the National Science Foundation under NIRT, # CTS-0506988.

9:00am **PS2-ThM4 Advanced Plasma Polymerization Methods to Deposit Multifunctional Coatings***, **D. Hegemann**, M.M. Hossain, D.J. Balazs,* Empa, Swiss Materials Science & Technology, Switzerland

Products made with the help of flexible porous webs, e.g. textiles, become more and more sophisticated and 'multifunctional'. Tailored surface modifications are required to meet customer needs and to assure a share in the market. However, conventional finishing techniques applied to textiles (dyeing, stain repellence, flame retardance, antibacterial treatments) generally use wet-chemical process steps and produce a lot of waste water. Plasma polymerization, on the other hand, as a dry and eco-friendly technology, is offering an attractive alternative to add new functionalities such as water repellence, long-term hydrophilicity, mechanical, electrical and antibacterial properties as well as biocompatibility due to the nano-scaled modification on textiles and fibers. At the same time, the bulk properties as well as the touch of the textiles remain unaffected. Of great potential are nanoporous plasma coatings which can be achieved by adjusting the deposition/etching conditions at the growing film surface. Depending on functional groups incorporated during the plasma polymerization process, permanent hydrophilic surfaces can be achieved which are mechanically stable. Moreover, dye molecules can be attached to the accessible functional groups within the plasma coatings, thus enabling substrate independent dyeing of textiles. Different other molecules might be added as well, e.g. biomolecules for enhanced cell growth. Co-sputtering of silver during plasma polymerization enables the controlled incorporation of Ag nanoparticles into a functional plasma polymer matrix in a one-step process inducing an antimicrobial activity. Hence, nanostructured, multifunctional textile surfaces can be achieved. However, suitable plasma reactors and scalable processes are required for an economical treatment of textiles. The scale-up of plasma processes is thus an important issue and is demonstrated using a continuous web coater.

9:20am **PS2-ThM5 Low Temperature PECVD of Silicon Oxynitride Thin Films from Dimethylaminosilanes: Role of Oxygen Addition***, R. Di Mundo, F. Fracassi, **R. d'Agostino**,* University of Bari, Italy*; F. Palumbo,* IMIP-CNR

Silicon oxynitride (SiON) coatings are important materials as dielectrics and optical components. So far attempts to replace hazardous silane in SiON PECVD processes with organosilicon precursors have led to organic SiC@sub x@N@sub y@O@sub w@H@sub z@ films. However, considering the good features of SiN coatings deposited at low temperature from inductively coupled discharges fed by bis(dimethylamino)dimethylsilane (BDMADMS) and argon,@footnote 1@ we tested the addition of O@sub 2@ to this novel system for SiON films deposition. The O@sub 2@-to-monomer ratio was varied at low and high input power until transition to oxide was observed. The chemical composition of the coatings was characterized by means of FT-IR and XPS analyses while a deep investigation on the plasma phase was carried out by Optical Emission Spectroscopy (OES) in order to gain insight into the role of oxygen atoms in the deposition mechanism. Results indicate that at high input power and low O@sub 2@-to-BDMADMS ratio highly inorganic SiON films can be obtained. The sharp increase of the O/Si ratio in the coating, as the O@sub 2@ concentration in the feed rises, is accompanied by a significant reduction of the N/Si ratio, which is even faster than the decrease of the C/Si ratio. This particular chemical evolution can be correlated with the trends of relative density in plasma phase of N-containing species (NH, CN) as well as of oxidation products (CO, OH) detected with OES, suggesting some favourite reaction paths within the process.@FootnoteText@@footnote 1@R. Di Mundo, R. d'Agostino, F. Fracassi, F. Palumbo, Plasma Process. Polym., 2, 612-617 (2005).

9:40am **PS2-ThM6 Plasma-Assisted Growth of Moisture Diffusion Barriers on Polymers: From Chemical Vapor Deposition to Atomic Layer Deposition***, **M. Creatore**, E. Langereis, I. Volintiru, A. Milella,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

Polymer- based technologies are rapidly growing in fields such as flexible solar cells and OLEDs, but long-term stability devices are desired and, therefore, high moisture diffusion barrier films are required (water vapor transmission rates (WVTRs) as low as 10@super -6@ g/m@super 2@day). Sputtering and plasma-enhanced chemical vapor deposition (PE-CVD) are the most investigated technologies for the deposition of barrier films, although only µm-thick multi-layer systems appear to meet the above-mentioned requirements. Very recently, however, Atomic Layer Deposition (ALD) has been addressed as an attractive route towards excellent and thinner barriers. Also in this case, plasmas can assist the growth (plasma assisted ALD, PA-ALD) by providing a radical source, which replaces one (molecular) deposition precursor (e.g., O radicals replacing H@sub 2@O for Al@sub 2@O@sub 3@ deposition). Here we address the PA-ALD deposition of Al@sub 2@O@sub 3@, consisting of cycles of trimethylaluminum dosing alternating with O@sub 2@ plasma exposure. WVTR values as low as 0.005 g/m@super 2@day are reported for thin (20 nm) PA-ALD Al@sub 2@O@sub 3@ on polyesters, while 100 nm- thick oxides (SiO@sub 2@ and Al@sub 2@O@sub 3@) deposited by means of PE-CVD in a remote plasma configuration are characterized by WVTR values of 0.15 g/m@super 2@day. The superiority of the PA-ALD layers is attributed to the control of the film microstructure during the growth: chemical (XPS), optical (spectroscopic ellipsometry) and morphological (atomic force microscopy) analyses have pointed out towards lower hydrogen content-, higher refractive index- and smoother PA-ALD films in comparison with PE-CVD layers. Routes for the microstructure control in PE-CVD will be also addressed: ion bombardment (via an external rf bias), in terms of ion energy and ion-to-radical flux ratio, was found to be a key parameter in tuning the film microstructure and improving the moisture permeation barrier properties.

10:00am **PS2-ThM7 Super-Hydrophobic Transparent Polymer Surfaces Fabricated by Plasma Etching and Deposition***, **N. Vourdas,** M.E. Vlachopoulou, A. Tserepi, E. Gogolides,* Institute of Microelectronics, NCSR Demokritos, Greece

Wettability control is of great importance in many industrial and scientific areas; from manufacturing of water repellent surfaces to droplet frictionless motion in microfluidics, and biocompatibility tuning. Wetting or repellent behavior is governed by both surface chemistry and topography. In particular, super-hydrophobicity is attained by combining low surface energy coatings and high-aspect-ratio (HAR) geometrical characteristics. Liquids contact only the upper part of HAR surfaces (Cassie-Baxter regime). In this study we present a novel, simple, generic and fast technique to fabricate stable super-hydrophobic, yet transparent surfaces by means of high-density plasma etching and deposition.@footnote 1@ An Inductively Coupled Plasma (ICP) reactor is used to treat two different kind of polymers; an organic one (PMMA) and a hybrid one (PDMS). Different plasma chemistries pertinent to each polymer are implemented to etch the surfaces followed by a fluorocarbon deposition to control the surface roughness and the surface chemistry respectively. AFM is used to characterize morphology and water contact angle (CA) and CA hysteresis to characterize wetting properties. We demonstrate high aspect ratio pillars with height ranging from ca. 350nm to several microns depending on the processing time, and contact angles of 150@super o@ with hysteresis lower than 15@super o@. Surfaces with pillar height less than 400nm are also transparent. @FootnoteText@@footnote 1@Greek Patent application number 20050100473; PCT application number GR2006/000011.

10:20am **PS2-ThM8 Fabrication and Characterization of Plasma Processed Surfaces with Tuned Wettability***, **P. Colpo**, A. Ruiz, L. Ceriotti, A. Valsesia, F. Brétagnol, G. Ceccone, D. Gilliland, F. Rossi,* European Commission, Institute for Health and Consumer Protection, Italy

Plasma treatments have been extensively applied to polymers, metals or elastomers for fabricating engineered surfaces. Among others, applications of plasma processing include the alteration of the wetting properties of surfaces to create either hydrophilic or hydrophobic surfaces. The wettable behaviour of surfaces is determined by several parameters, being the surface energy and the surface roughness the most important ones. Tailoring the roughness of surfaces has been proved to be an effective method for enhancing its hydrophilic or hydrophobic character. Therefore, studying the wetting capacity of rough surfaces has attracted special interest in the last years. In this scope, we have used a combination of plasma processes including etching and polymerization to prepare rough surfaces with different hydrophilic/hydrophobic character. The surfaces have been then analysed in terms of chemistry, roughness and wettability. Surfaces with different roughness have been fabricated by etching with several gases and different treatment duration a layer of polymer resin deposited on silicon and glass substrates. The etched surfaces were analysed by XPS, ToF-SIMS, SEM, and the results were compared with the wettability and roughness, given by contact angle and surface profile measurements respectively. We found a correlation between the contact angle, i.e. the hydrophilic character, the roughness and the chemical composition of the surface. Teflon-like, acrylic acid and PEG layers were deposited on the rough plasma treated surface by plasma polymerisation. Selected wettability has been achieved combining plasma etching and plasma deposition processes. Superhydrophilic and superhydrophobic surfaces have been obtained with a fast, easy to implement method, which has also the advantage of mass production, repeatability and reliability. The surfaces fabricated have interest in a variety of applications (coatings, medical devices, biosensors, ...).

10:40am **PS2-ThM9 Plasma-Polymerised Surface Chemical Gradients as Platforms for Making Biomolecule Gradients***, **D.E. Robinson**, R.D. Short, D.J. Buttle,* University of Sheffield, UK*; T. Day, A. Marson,* University of Manchester, UK*; K. Parry,* Plasso Technology

A continuous variation in a surface chemical feature (i.e. a gradient) is important in controlling a variety of processes, biological@footnote 1@ and chemical.@footnote 2,3@ The production of such features on the millimetre and sub-millimetre scale length on a material surface is a challenge, and the methods employed currently are only suitable for one-off experiments. Gradients of chemical functionalities may be fabricated by plasma polymerisation, using a moving slot, to separate plasma from the collecting substrate (and simultaneous control of two monomer gas ratios).@footnote 4@ This method offers advantages over others, vis-a -vis the robust (stable) nature of the gradients, and the scalability of the method, an exact precision in the start and end point and shape of the gradient, gradients can be fabricated onto a wide range of substrates, e.g. plastics, glass and metals. A gradient of functional heparin (a gylcosaminogylcan(GAGs)) is fabricated by depositing a plasma-polymerised gradient of allyl amine (the co monomer is octadiene). A gradient of plasma-polymerised allyl amine is incubated with native heparin, forming a functional gradient. Functionality is demonstrated by binding of known heparin-binding proteins.@footnote 5@ Gradients of GAGs are important in functional diversity, playing fundamental roles in biological processes such as blood clotting, tissue structure and organisation, development and morphogenesis and many disease processes. The fabrication of a heparin gradient provides an important research tool by which some of these processes can be studied in vitro. @FootnoteText@ @footnote 1@N L Jeon, K W Dertinger, G M Whitesides, et al., Langmuir 2000, 16, 8311@footnote 2@J Aizebnberg, A J Black, G M Whitesides, Nature 1999, 398, 495 @footnote 3@B S Gallardo, V K Gupta, et al., Science 1999, 283, 57 @footnote 4@J D Whittle, D Barton M Alexander, R D Short, Chem. Comm., 2003, 14, 1766 @footnote 5@D J Mahoney, A J Day, R D Short et al., Anal. Biochem. 2004, 330, 123-129.

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