Wednesday Afternoon, October 17, 2007

Plasma Science and Technology

Room: 607 - Session PS2-WeA

Plasmas and Polymers

Moderator: M.A. Creatore, Eindhoven University of Technology, The Netherlands

1:40pm PS2-WeA1 Activation of Polymer Surfaces by Electron Beam Generated Plasmas, *E.H. Lock*, *S.G. Walton, R.F. Fernsler*, Naval Research Laboratory
The activation of polymer surfaces via plasma exposure is one of the most powerful techniques to enhance the bond strength between the polymer surface and molecules, cells and thin films. Even though there are many established plasma techniques for the modification of polymer surfaces, there remain many unresolved questions regarding the most effective use of plasma processing because of the complexity of plasma-surface interactions. In order to guarantee quality and reproducibility of a given plasma process, numerous plasma effects and process parameters need to be taken into account. To ensure the maximum bond strength between a polymer and another material, the chemical and physical changes at the surface need to be well understood. Unfortunately, the conventional plasma sources are limited in their ability to address these problems and the lack of process control leads to problems with efficiency, scalability and material surface damage. Due to its unique characteristics, the electron beam generated plasma system developed at the Naval Research Laboratory allows access to operating conditions not available with traditional plasma methods. This plasma source provides individual control over the plasma parameters including plasma density, ionization region, electron temperature, ion and radical fluxes. Perhaps, the most important advantage of the system is that it minimizes the ion-induced damage to the substrate due to the inherently low plasma potentials. The objective of this work is to study the activation of polystyrene, polyethylene and polypropylene thin film surfaces exposed to plasmas produced in argon and SF6. Argon is inert and should limit surface modification to physical changes through bond breaking. SF6 provides a source of reactive radicals that can directly modify the surface. In both cases a wide range of process parameters was investigated, including pressure, gas flow rate, plasma exposure time, and substrate biasing (to increase ion energy). Ex-situ surface analysis included X-ray photoelectron spectroscopy, atomic force microscopy and various wetting tests are applied to characterize the chemical and physical properties of plasma modified polymer surface.

2:00pm PS2-WeA2 Impact of Plasma Etching Processes on 193 nm Photoresists: Etch Resistance and Line Width Roughness, *E. Pargon*, *J. Thiault, M. Martin*, CNRS, France, *J. Foucher*, CEA-LETI, France, *G. Cunge, O. Joubert*, CNRS, France, *Th. Lill*, Applied Materials Inc.
INVITED
Successful pattern transfer by lithography and plasma etching requires minimal mask erosion, degradation and roughening. However, going to 193 nm based lithography in manufacturing several years ago brought new issues such as poor etching resistance of the photoresist masks during front end and back end processes. Indeed, the transition from 248 nm to 193 nm exposure sources has introduced significant changes in the composition of the photoresist (PR), including the removal of all aromatic functional groups due to their excessive absorption at 193 nm. Due to these important chemical changes, 193 nm PR not only exhibit poor etch resistance but are also thinner limiting strongly the 193 resist budget. Moreover, it was observed that 193 nm PR present severe surface roughening after plasma etching that can lead to wiggling and striations, impacting directly the resist Line Width Roughness (LWR). The critical issue is that PR degradation during plasma etching processes is possibly transferred into the underlayers, resulting in a polysilicon gate LWR above the requirements of the ITRS (1.4nm at 3σ for the 45 nm technological node). So far there is no real understanding on how different manufacturing operations may impact the resist roughness and its transfer into complex stacks of materials. In this work patterned and blanket 193 nm PR have been exposed to typical plasma etching processes involved in gate stack etching. In this work, we will show first correlations between etch rates (measured by ellipsometry), chemical analyses of the resist surfaces after plasma exposure (FTIR, XPS) and physical modifications on blanket resist substrates (using DSC and AFM), in order to better understand the etching and roughening mechanisms of typical 193 nm resists. The evolution of the patterned resist LWR and its transfer into the underlayer during the subsequent lithography and plasma

etching steps are investigated by CD-AFM. We demonstrate that the resist LWR measured before etching is a key parameter in the final polysilicon LWR. Different plasma treatments applied to the 193nm photoresist patterns prior to all the following plasma etching steps can reinforce the 193 nm resist etch resistance and smooth the resist sidewalls thus reducing the LWR of the polysilicon gate. Our results also show that resist faceting induced by the ion bombardment plays a key role in the smoothening or roughening of the resist and pattern sidewalls.

2:40pm PS2-WeA4 Plasma Etching Performance of Thin Polymeric and Photoresist Films, *N. Vourdas*, *G. Kokkoris, E. Gogolides*, Institute of Microelectronics, NCSR "Demokritos", Greece
In most cases of plasma processing of polymers, plasma etch rate (ER) is treated as being a constant value throughout the plasma process. However some studies have demonstrated that ER is actually a function of film thickness,[1,2] process time[3] or both. Similar observations have been recorded for the dissolution (development) rate (DR) of polymers, revealing a DR variation vs. film thickness. In this work we present plasma ER measurements via in situ spectroscopic ellipsometry (SE) of atactic (a-), isotactic (iso-) and syndiotactic (syndio-) poly(methyl methacrylate)-(PMMA) and poly(styrene)-(PS) films on Si and SiO2 under high density O2 plasma discharges, and observe variations of ER vs. time and thickness. Based on these findings along with data obtained from the literature we try to identify the reasons for these variations and deduce the key mechanisms controlling the plasma etching performance of thin and ultra thin polymeric films. Three kinds of ER variations are recorded: (a) ER increase (~8%) within the first stages of etching (~first 10 sec), followed by a gradual increase of ~20% until ~120 nm remaining film, (b) ~25% ER decrease after ~120 nm remaining film, and finally (c) ER drastic decrease at the final stages of etching (completion of etching) until ER=0. Variations (a) and (b) occur regardless the initial thickness, while the variation (c) strongly depends on process time, correlates with the surface roughness amplitude, and indicates means to control surface roughness of polymers (maximum surface roughness in this point). For ultra thin polymer films (less than ~100 nm) ER increase (region a) is not recorded; we attribute this to thin-film effects. These variations result in a decreased average ER of ultra-thin films compared to the ER of the thicker ones. These results are of interest both when ultra-thin polymers are used e.g. EUV lithography, chemical nano-patterning etc, or when high surface roughness is needed, e.g. antireflective coatings, super-hydrophobic coating fabrication etc.

[1]M. Tatoulian, O. Bouloussa, F. Moriere, F. Arefi-Khonsari et al, Langmuir 2004 20 p.10481
[2]N. Vourdas, A.G. Boudouvis, E. Gogolides, Microelectron. Eng. 2005 78-79 p.474
[3]X. Hua, S. Engelmann, G.S. Oehrlein et al, JVST B 2006 24 p.1850
[4]P. Paniez, M. Pons, O. Joubert, Microelectron. Eng. 1990 11 p.469.

3:00pm PS2-WeA5 Fabrication of Organic Polymers with Tuned Properties and Their Correlation to Plasma-diagnostic Parameters, *G. Franz*, University of Applied Sciences, Germany, *D. Voss*, Plasma-Parylene Coating Services
Poly-parylene is one of the rare organic polymers which have passed the FDA criteria as long-term compatible for the human body. Films of the derivates C and N have been deposited applying cvd and pecvd (microwave). By a combined application of plasma diagnostics and surface analysis, is is possible to tailor the properties of the polymer poly-parylene over a wide range. In the border region, the plasma density rapidly falls with growing distance from the wall due to the strong shielding at microwave frequencies. In contrast to the usual expectation, the plasma density decreases with growing pressure for both ambients, argon and parylene. The electron temperature exhibits the expected hyperbolic behavior vs. pressure. Nevertheless, the higher deposition rate is the most significant proof of the higher density of polymer-building species as compared to cvd. As first consequence, in a pulsed plasma the ratio of the time constants of diffusion can be modeled applying the simplest approach proposed by Brown. For same power input, the plasma density in parylene is lower by more than one order of magnitude compared with argon, which is due to numerous other tracks of molecule excitation and electron loss. At the upper energy end, parylene-C definitely behaves as an electropositive gas, main loss of electrons caused by diffusion, whereas at low or medium energies, pressure-independent electron attachment is supposed to become the dominating loss mechanism leading to significantly lower plasma densities as compared to argon. Infrared spectroscopy shows the conservation of the ring structure during the plasma treatment. The contact angle exhibits a relatively flat response with respect to discharge pressure for cvd, stronger dependence for pecvd. The surfaces of the cvd-films are classically hydrophobic and lipophilic. This behavior is less pronounced in the pecvd-films. Films copolymerized with CF4 are both hydrophobic and lipophobic in character and show very high roll-off angles (super-

hydrophobicity). Subsequent plasma treatment with Ar/O$_2$ significantly reduces the contact angle against water (down to 30°). The dielectric constant has found to be very low with only a slight increase to low frequencies with nearly the same value at optical frequencies. Compared with previous works, the range for influencing these surface properties has been farther opened.

4:00pm PS2-WeA8 Study of Plasma-Surface Interactions of Styrene and Vinylpyridine Polymers in Ar/C$_4$F$_8$/N$_2$ Discharges, *R.L. Bruce*, *T. Kwon, S. Engelmann, F. Weilnboeck, M. Sumiya, R. Phaneuf, G.S. Oehrlein,* University of Maryland, College Park, *B. Long, G. Willson,* University of Texas, Austin, *D.G. Nest, J.J. Vegh, D.B. Graves,* University of California, Berkeley, *A. Alizadeh,* GE Electrics Global Research Center

Ar/C$_4$F$_8$/N$_2$ gas mixtures are being used for plasma etching low-k dielectric films. It is not fully understood how addition of N$_2$ affects the polymer surface of an organic masking material in a fluorocarbon-rich plasma environment. Therefore, the effects of N$_2$ addition in fluorocarbon plasma on polymers containing nitrogen (polyvinylpyridine) and without nitrogen (polystyrene) were investigated. The polymer surface after plasma exposure was analyzed using a number of characterization tools: ellipsometry (etch resistance), atomic force microscopy (AFM) (surface roughness), and x-ray photoelectron spectroscopy (XPS) (chemical composition). Through ellipsometric analysis, we found that the etch resistance was dependent on the steady state fluorocarbon (FC) layer created during plasma etching. With AFM, we have shown that the surface roughness decreased with %N$_2$. Using XPS, it was found that while the fluorine content in the polymer surface continually decreased with increasing %N$_2$, the nitrogen content increased until reaching a saturation level. Furthermore, significant differences in etch resistance, surface roughness, and chemical composition were found between polystyrene and polyvinylpyridine. We investigated whether the nitrogen in the polymer enhances the effect of the nitrogen in the plasma during exposure. In addition, we examined the relationship between the reduction of FC film thickness in remote plasma conditions and the enhanced etch rate of polymers in direct plasma conditions.

4:20pm PS2-WeA9 Advanced Plasma Treatments for Cleaning and Protection of Metal Artefacts, *A. Milella,* University of Bari, Italy, *F. Palumbo,* CNR-IMIP, Bari, Italy, *S. Grassini, E. Angelini,* Polytechnic of Turin, Italy, *R. d'Agostino, F. Fracassi,* University of Bari, Italy

In the framework of conservation of cultural heritage, protection of metal artefacts from corrosion and degradation phenomena which take place during burial and /or during storage and exhibition, is of outstanding importance. Restoration procedures must be non-destructive, reversible, they have to respect the integrity of the objects and to satisfy specific requirements for preserving their aesthetic appearance. In this contribution we present the development of a non-destructive and reversible procedure for cleaning and protecting precious archaeological objects, mainly Ag-based alloys, in low pressure plasma. Reference Ag alloy with micro-chemical and micro-structural features similar to ancient artefacts were used for the plasma treatments. To mimic the real artefacts, the specimens have been buried in the archaeological site of Tharros (Sardina, Italy) for 6 months. To accelerate the corrosion degradation 5% of NaCl has been added to the soil, since chlorides play a key role in the degradation of silver alloys during burial. Furthermore, to better mimic the patina present on real ancient artefacts (mainly consisting of AgCl and Ag$_2$S), the Ag-based alloys were also immersed in a solution of Na$_2$S. Cleaning of the tarnished specimens was carried out in RF hydrogen plasma. As detected by XRD and EDS analyses, the treatment effectively decreases the thickness of the patina to an extent which depends on the plasma treatment time. The hydrogen plasma removes the chlorides by forming HCl and this is accompanied by the reduction of oxidized silver (Ag$^+$) to metal silver (Ag^0). The conversion to Ag^0 can represent an advantage of the plasma cleaning with respect to conventional methods, generally leading to removal of silver from the artefact. Furthermore it is important to mention another benefit: existing cleaning methods are based on chemicals with environmental concerns. For protection of the Ag-based alloy from tarnishing, SiO$_2$-like coatings were deposited from a RF plasma fed with tetraethoxysilane/oxygen/argon mixture and the protective effectiveness was tested by electrochemical Impedance Spectroscopy (EIS) analyses. Results show that serious tarnishing of the coated samples only occurs after 72 h of immersion in 0.1 M Na$_2$S solution. Chemical (FTIR, XPS) and morphological (AFM, SEM) characterization of the films will be also presented.

4:40pm PS2-WeA10 Cell Growth on Plasma Deposited Micro- and Nano Patterned Teflon-Like Coatings, *P. Favia, E. Sardella, F. Intranuovo,* University of Bari, Italy, *P. Rossini,* Plasma Solution Srl, Spin off of the University of Bari, Italy, *R. Gristina,* Institute of Inorganic Methodologies and Plasma (IMIP) CNR, Italy, *M. Nardulli*, University of Bari, Italy

Plasma processes are widely used for biomedical applications.[1] Surface chemistry and morphology of substrates to be used in cell-adhesion and growth experiments can be modified by means of plasma (RF 13.56 MHz) PE-CVD from fluorocarbon feeds. Smooth and nano/micro-structured coatings could be obtained by tuning plasma parameters. Discharges fed with hexafluoropropylene oxide (HFPO) were run in continuous mode, and teflon-like coatings with different roughness values have been obtained by changing the afterglow distance with respect to the gas inlet of the plasma reactor.[2] In our previous work,[3] a study of nano-structured surfaces obtained from C$_2$F$_4$ was related to the deposition time. FT-IR, XPS, WCA, AFM and SEM analysis were used to analyze the chemical composition and the morphology of deposited coatings that were obtained by varying the substrate position in the plasma reactor. Nano-structured and flat coatings deposited on PET substrates were coated with a very thin homogeneous plasma deposited teflon-like film from C$_2$F$_4$ (6 sccm C$_2$F$_4$, 200 mtorr, 100 W, 21 s) to obtain surfaces with different roughness but identical chemical composition, to be used in cell-growth experiments. FT-IR, XPS and AFM data show that the "teflon character" (amount of the CF$_2$/C1s component) of the coating increases with the afterglow distance, as well as the hydrophobic character and the roughness (R$_{RMS}$ from 1± 0.2 nm to 350±43 nm). AFM images show different coating structures (e.g. nanopitted and cauliflower-like) as a function of the afterglow distance. Two coatings deposited at different positions, thus characterized by different morphology/roughness, have been selected for cell-growth experiments with 3T3 fibroblasts. Cell culture tests showed a different behavior when cell adhesion and growth were compared between nano-structured and flat coatings with the same surface chemistry. Acknowledgements: The MIUR-FIRB RBNE01458S project is gratefully acknowledged for the financial support.

[1]Plasma Processes for Biomedical Applications, Plasma Processes and Polymers 3(6/7), 2006, Special issue
[2]Castner, Favia, Ratner; Surface Modifications of Polymeric Biomaterials, Castner and Ratner eds, Plenum Press, 45, 1996
[3]Gristina, D'Aloia, Senesi, Sardella, d'Agostino, Favia; European Cells and Materials, 7, 1, 2004.

5:00pm PS2-WeA11 Studies of Plasma Surface Activation for Adhesion Enhancement of Polymer Materials in Nanotransfer Printing, *D.Y. Lee, G.S. Oehrlein, D.R. Hines,* University of Maryland College Park, *C.M. Stafford, C.L. Soles, D.M. DeLongchamp, E.K. Lin*, National Institute of Standards and Technology

Recently, nanoimprint lithography (NIL) and nanotransfer printing (NTP) have attracted much attention because these techniques can be used to fabricate submicron structures at a lower cost and with higher throughput than conventional photo and electron-beam lithographies. For NTP involving thermoplastic polymer materials, a low processing temperature (below the glass transition temperature (Tg) of the polymers) is attractive to minimize distortion of printed layers and to control volume shrinkage of the polymers. One key factor influencing pattern transfer is the strength of adhesion between a printed polymer layer and a thermoplastic substrate. In this study, we systematically survey the factors controlling the adhesion between two polymer surfaces treated by plasma activation. Plasma treated poly(methyl methacrylate) (PMMA) films were transfer printed onto plasma treated polyethylene terephthalate (PET) substrates using NTP at 80 and 100 °C, 500 psi for 3 min. An inductively coupled plasma (ICP) process employing either O2 or N2 was used for surface activation of the polymers. In addition, we compared direct and remote plasma with gap structure to investigate the effect of ion bombardment on interfacial adhesion. With plasma activated samples, pattern transfer using NTP was possible at temperatures below the glass transition temperature (Tg) of both polymers. The enhancement of the polymer-polymer adhesion has been attributed to terminated functional group generated by the plasma surface activation and it mainly depends on the processing temperature and chemical composition of polymer and plasma chemistry. In-situ ellipsometry was used to measure changes in the refractive index and the thickness of the surface modified layer. Atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) measurements were performed on the plasma treated polymers immediately after treatment to minimize contamination effects due to atmospheric exposure. Surface energy and water contact angle of the modified films were also measured. Adhesion was evaluated both from a wedge test and from the NTP transfer efficiency, i.e., the aerial % of PMMA film successfully transferred to the PET substrate.

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