## Thursday Afternoon, October 5, 2000

### Plasma Science and Technology Room 310 - Session PS1-ThA

**Plasma-Surface Interactions II** 

Moderator: C.B. Labelle, Bell Laboratories, Lucent Technologies

2:00pm **PS1-ThA1 Plasma Surface Modification of PET and Acrylic Coating Surfaces**, *M.K. Shi*, Pacific Northwest National Laboratory, U.S.; *A. Tyryshkin*, Princeton University; *G.C. Dunham*, *M. Bowman*, *G.L. Graff*, *P.M. Martin*, *G.J. Exarhos*, Pacific Northwest National Laboratory

Plasma treatment has proven to be very effective in modifying polymer surface properties for enhanced surface compatibility and adhesion. The treatment is performed in vacuum and the effect can be achieved within a few seconds. These characteristics make plasma technology extremely appealing for the adhesion promotion of polymer-metal multilayer stacks that can be deposited inline and at high speed in a vacuum web-coater. The surface modification of poly(ethylene-terephthalate) (PET) and UV-cured tripropyleneglycol diacrylate films induced by remote N@sub2@ and Ar microwave (2.45 GHz) plasmas was investigated in order to better understand the plasma/surface interaction mechanisms. In-situ XPS analysis revealed that N@sub2@ and Ar plasma treatments led to removal, in entirety, of the initial oxygen-containing groups on the polymer surfaces. The removal of ester groups was much faster for the acrylic than for the PET, and the removal of ether groups was much faster than that of ester groups within the acrylic film. Electron parametric resonance (EPR) measurements indicated the presence of several types of free radicals. The concentration of these radicals was higher for N@sub2@ than for Ar plasma treatment and for the acrylic than for the PET film, which correlated well with the more pronounced surface modifications measured by XPS. Pulsed EPR measurements suggested that these radicals existed mainly in radical pairs and were distributed within 2000 Å from the top surface. The concentration of free radicals correlated well with the amount of N incorporated into the surface by N@sub2@ plasma treatment. These results strongly supported a free radical-dominated plasma/surface interaction mechanism and highlighted the important role of plasma UV emission. Water contact angle measurements indicated that the incorporated N atoms were responsible for the improved surface wettability.

### 2:20pm PS1-ThA2 Exploring Chemical Mechanisms behind Hydrophilic Surface Modification of Polymeric Membranes by Low-temperature Plasma Treatment, *M.L. Steen*<sup>1</sup>, *E.R. Fisher*, Colorado State University

We recently developed a surface modification strategy that renders asymmetric polymeric membranes permanently hydrophilic.@footnote1@ This entails treating asymmetric membranes with a low-temperature plasma to obtain the desired change in wettability. This treatment is quite versatile as polysulfone, polyethersulfone, and polyethylene membranes are completely hydrophilic as a result of plasma treatment. XPS results indicate that the desired change in wettability observed for plasma-treated membranes is a result of implantation of new, more hydrophilic functional groups by plasma treatment; however, little is known about the chemistry occurring on a molecualr level during plasma modification. Hence, we recently began investigating the mechanisms behind hydrophilic modification of asymmetric polymeric membranes. We have determined the gas-phase composition as well as ion and electron densities with optical emission sepctroscopy (OES), Langmuir probe studies and mass spectrometry. We suspect OH radicals, detected in the OES spectrum, are likely the species predominantly responsible for hydrophilic modification of our porous materials. Therefore, we have studied plasma-generated OH radical/surface reactivites with porous polymeric membranes as the substrate of interest by the IRIS (Imaging of Radicals Interacting with Surfaces) method. This technique is uniquely suited to afford chemical information critical to elucidation of the mechanisms responsible for plasma modification of porous materials. We will report OH reactivites at several porous polymeric substrates including asymmetric polysulfone, polyethersulfone, and polyethylene membranes. We will also present correlations drawn from the aforementioned techniques, proposing the role of OH radicals and other plasma-generated species in plasma processing of porous materials. @FootnoteText@ @footnote 1@M. L. Steen, L. Hymas, E. D. Havey and E. R. Fisher, J. Memb. Sci., to be submitted.

2:40pm **PS1-ThA3 The Mechanisms of Anisotropy Control in Plasma Etching Processes, L. Vallier**, CNRS/LTM, France; G. Cunge, CEA/LETI, France; J. Foucher, D. Fuard, CNRS/LTM, France; R.L. Inglebert, O. Joubert, LTM/CNRS, France INVITED

Anisotropic plasma etching of microelectronic materials is achieved thanks to the bombardment of energetic ions, allowing the etch directionality to be achieved, and the formation of volatile etch products, through ionassisted chemical etching reactions. In this talk, we demonstrate that the anisotropy control of an etch process is obtained via the re-deposition of heavy non-volatile etch products on the feature sidewalls. Experiments have been conducted on a very powerful plasma etch system dedicated to advanced studies. It consists in a Decoupled Plasma Source (DPS) from Applied Materials modified to host in situ diagnostics such as UV-visible ellipsometry, mass spectrometry, fast injection Langmuir probe and X-ray photoelectron spectroscopy (XPS). Etch processes have been developed for silicon gates, low k polymers as intermetal dielectrics and Aluminum as metal for interconnect. Strong correlations have been observed between sidewall passivation layer formation (analyzed by XPS), profile control (through SEM inspection) and etch products analyses (using mass spectrometry analyses). For each material investigated, we have observed that the anisotropy control is only achieved if a passivation layer is formed on the feature sidewalls. At the same time, ion mass spectra clearly shows the presence of non-volatile species: heavy carbon chains for low k polymer etching, and silicon oxide and their derivatives for silicon etching. Mass spectrometric results also indicate that the number density of theses species is varying as the square root of ion energy (DC bias), suggesting that they are produced by the sputtering of the reactive layers formed at the bottom of the etched features. Finally, these experiments show that passivation layers can be designed by tuning the etch product formation. An example of sidewall passivation engineering for poly gate etching will be shown with the formation of a controlled notched profile.

## 3:20pm **PS1-ThA5 Pulsed Plasma Polymerisation of Acrylic Acid**, *S. Fraser*, *D.B. Haddow, R.D. Short*, University of Sheffield, UK

The synthesis of thin plasma polymer films from radio frequency sustained glow discharges of small organic compounds is well documented. Films containing a high degree of retention of the starting monomers original functionality and structure can be deposited using a low power plasma. These plasmas can be sustained by continuous wave (CW) or by pulsing a higher input power to achieve a lower average power. Although there is substantial literature on the use of pulsed plasmas there has not been any investigation made of the pulsed rf plasma environment of monomers containing C, H, O, or N. We describe the application of mass spectrometry and ion energy analysis to probe the pulsed plasma environment of acrylic acid. Analysis of the deposited films was carried out by XPS. The input power was fixed at 50W and the effect of plasma off time was investigated with respect to a fixed on time (eg 5ms/40ms=11% duty cycle). In terms of functional group retention the pulsed 50W plasma at a duty cycle of 11% is equivalent to a 3-3.5W CW plasma. It was shown that in the pulsed plasma the amount of intact acrylic acid was greatly reduced. There is no evidence in the pulsed plasma gas phase neutrals for significant radical-neutral or radical-radical combination. Any neutral species detected can be explained by homolytic cleavage of the carboxyl group and subsequent addition or loss of H. The positive ion mass spectrum of the pulsed acrylic acid plasma shows extensive gas phase oligomerisation was detected. This oligomerisation has been previously described in low power CW plasmas of acrylic acid. The similarities between pulsed 50W and 5W CW plasmas include gas phase chemistry, plasma polymer chemistry and deposition rates. This might suggest that the pulsed plasma environment is a continuation of the low power CW environment, but to lower average powers than can be sustained using a CW signal generator. Measurements of ion energies suggest a more complex system.

3:40pm **PS1-ThA6 Control of Ion Energies in RF Plasmas used for the Surface Modification of Polymers**, *D. Barton*, UMIST, UK; *J.W. Bradley*, UMIST, UK, U.K.; *D.A. Steele*, *R.D. Short*, University of Sheffield, UK

Despite the widespread use of low pressure (~10mTorr) radio frequency (13.56MHz) plasmas for the surface modification of polymers the importance of the various plasma species, e.g. positive ions and VUV photons, in effecting these changes remains the subject of some debate. To investigate the role of positive ions in the argon plasma treatments of various polymers, we have developed a technique which allows for the in situ control of the ion energies at the polymer surface. The technique does not perturb the bulk plasma, and in particular leaves the VUV flux unchanged. A further advantage is that that no grids or optical windows are

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placed in front of the sample. The technique is similar in principle to the active compensation of Langmuir probes, in that it relies on feeding an RF signal onto the polymer which is phase and amplitude matched to the (RF) sheath potentials. By increasing the amplitude of this signal, we force the self-bias potential of the sample more positive and thereby reduce the ion energy at the polymer surface. This contrasts with the well known technique of biasing substrates with an unmatched RF signal which greatly increases ion energy to the surface. By varying the contribution from positive ions to the total energy deposition on the polymer surface, we are able to estimate the respective roles of ions and VUV in the surface modification of polystyrene, an important biomedical plastic. The effects of plasma exposure are measured by X-ray photoelectron spectroscopy, XPS. Although demonstrated for a particular plasma reactor, polymer and gas, the approach is generic and could be applied more widely.

### 4:00pm **PS1-ThA7 Surface Chemical Patterning by Plasma Polymerization**, *R.D. Short*, *N. Bullett*, *A.J. Beck*, University of Sheffield, UK; *C. Blomfield*, Kratos Analytical, UK

Plasma polymerization has been used to create chemically-patterned surfaces. The fidelity of the patterns is demonstrated by means of imaging TOFSIMS and XPS. The sequential plasma deposition of a hydrocarbon compound (1,7 octadiene) and a functionalized compound (allyl amine or acrylic acid) through electron microscope grids has been used to create surface patterns of amine and carboxyl, respectively, on polymer sheets. By this approach it has been possible to fabricated surfaces containing stripes of 75-150 microns and squares, of similar dimensions, of amine and carboxyl functionalities. These patterns have been used to spatially control protein adsorption, demonstrated using a fluorescent marker, and cell attachment and spreading.

#### 4:20pm PS1-ThA8 The Relationship between Deprotection and Film Thickness Loss during Plasma Etching of Chemically Amplified Resists, *A.P. Mahorowala*, *D.R. Medeiros*, IBM T.J. Watson Research Center

Positive-tone chemically amplified (CA) resists provide the sensitivity, contrast and resolution necessary to print state-of-the-art sub-wavelength features using KrF (248 nm) and more recently ArF (193 nm) lithography. These materials are also being looked at for printing sub-100 nm features with F@sub 2@ (157 nm) and next-generation lithography technologies such as EUV (13 nm) and E-beam projection lithography (EPL). Beyond the desired exposure-induced reactions, the acid-catalyzed deprotection reactions responsible for the solubility differential can also occur in unexposed resist areas when etched in a plasma due to uv-exposure, high energy ion bombardment, plasma composition and elevated substrate temperatures. Deprotection has been associated with resist mass loss and film shrinkage during plasma etch that can adversely affect the tight resist budget. In this paper, we determine the film thickness loss during etching of several unexposed CA resists in a variety of plasmas while simultaneously monitoring the film composition by FTIR. These results will be compared with theoretical predictions based on well-known deprotection mechanisms. It will be demonstrated that the acidic nature of certain plasmas such as Cl@sub 2@/O@sub 2@ can deprotect the resist film even in the absence of a photoacid generator (PAG). It will also be shown that the nature of the resist polymer and the identity of the deprotection products directly influence resist mass loss and etch rate linearity both of which can be controlled by careful selection of resist materials.

### 4:40pm PS1-ThA9 Study of Defects Induced on Graphite Surface by Low Pressure Argon Plasma, A.L. Thomann, P. Brault, GREMI (CNRS), France; H. Estrade-Szwarckopf, B. Rousseau, CRMD (CNRS), France; C. Andreazza-Vignolle, P. Andreazza, CRMD (Universite d'Orleans), France

Since several years, we have been studying ultra-thin metal film deposition by a plasma sputtering method giving rise to low deposition rates (< 5 Å/min). Previous works have shown that the metal growth mode depends on the deposition conditions, which are tailored by the plasma conditions. For example, Pd metal has been found to form either 3D nanometer clusters, or very thin continuous layers.@footnote 1@ These results are interesting because they evidence that, with this deposition method, the film morphology may be easily chosen for a given application. Our aim is now to study how argon plasma pretreatment may modify the substrate surface state and thus, change growth modes. This will lead to an integrated plasma process allowing surface preparation followed by metal deposition. To study the induced defects, a plasma reactor has been added to an UHV-chamber equipped with STM, AFM, XPS and UPS analyses. This system allows chemical, electronic and morphological characterizations of the substrates before and after plasma treatments of different durations (30 s to 1 h). For these experiments, Highly Oriented Pyrolytic Graphite (HOPG) substrate has been used because it has been thoroughly studied as well as the surface defects created by ions beam techniques. First results show that small (D= some Å) and large (D= tens of Å) size defects are created on HOPG surface, that appear on STM images as hillocks of some Å height. Close to the large defects, a graphite lattice superstructure is observed. After a long lasting plasma treatment, the C1s XPS spectrum of the HOPG surface is completely modified ; on STM images, the hexagonal lattice is no longer observed and the superficial atomic structure appears as highly distorted although with a very small roughness (< 2 Å). @FootnoteText@ @footnote 1@ P. BRAULT et al, Recent Research Development in Vacuum Sci. And Technol., 2, R.A. Gottscho R.J. Pearton Eds. (Transworld Research Network, India, 1000).

### 5:00pm PS1-ThA10 Novel Technique to Enhance Etch Selectivity of Carbon ARC over PR based on O@sub 2@/CHF@sub 3@/Ar Gas Chemistry, J. Hong, J.S. Jeon, Y.B. Kim, Samsung Electronics, South Korea; T.-H. Ahn, Samsung Electronics, South Korea, Korea

New Anti-Reflective Coating (ARC), amorphous carbon (C-ARC) substitute for inorganic ARC (SiON) is gaining attention recently in DRAM process as device scales down requiring more fine control of submicron (0.8) was achieved with annealing of amorphous carbon. The presence of hydrogen radical in the plasma produced similar result with C-ARC phase transition from sp@sub 3@ to sp@sub 2@ resulting from hydrogen-hydrogen abstract reaction. Deposition temperature of C-ARC determined hydrogen content on the surface. Hydrogen behavior on the surface appeared to be dominant factor to control etch selectivity and surface reaction mechanism of amorphous carbon will be discussed.

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