

# Wednesday Morning, November 15, 2006

## Plasma Science and Technology

### Room 2009 - Session PS1-WeM

#### Plasma-Surface Interactions II

Moderator: V.M. Donnelly, University of Houston

8:00am **PS1-WeM1 Carbon Exposed to Hydrogen Plasma of ITER Relevant Conditions in Pilot-PSI**, *G.J. van Rooij, W.A.J. Vijvers, J. Westerhout, H.J.N. van Eck, W.R. Koppers, V. Veremiyenko, W.J. Goedheer, B. de Groot, P. Smeets*, FOM-Inst. for Plasma Phys., The Netherlands; *R. Engeln, D.C. Schram*, Eindhoven Univ. of Tech., The Netherlands; *H.J. van der Meiden, N.J. Lopes Cardozo, A.W. Kleyn*, FOM-Inst. for Plasma Phys., The Netherlands

Plasma surface interaction (PSI) in the divertor of ITER and fusion reactors beyond ITER, is a critical research area in the development of fusion power. For ITER, power and particle flux densities of 10 MW/m<sup>2</sup> and 1E24 m<sup>-2</sup>s<sup>-1</sup> respectively are foreseen, at  $n_e < 1E21$  m<sup>-3</sup> and Te in the few eV range. Pilot-PSI is a linear plasma generator that studies the production of such plasma conditions with a cascaded arc in magnetic fields up to 1.6 T. These studies are required for the design of the larger linear plasma generator Magnum-psi (Magnetized Plasma Generator and Numerical Modelling for Plasma-Surface Interactions Studies), which is being build by FOM in collaboration with ISTEC partners to address the physics of PSI in this extreme regime. In this contribution, we show on the basis of Thomson scattering and optical emission spectroscopy results that the specified plasma parameters have been realized in Pilot-PSI. We demonstrate how the geometrical details and the operation parameters of the cascaded arc can be optimized for high hydrogen plasma yields in strong magnetic fields. This knowledge is used to produce the record numbers of  $n_e = 5E21$  m<sup>-3</sup> and  $T_e = 5$  eV. Pilot-PSI is already a unique experiment for the field of PSI-studies on the basis of these numbers. In preparation for detailed PSI studies on the hydrogen plasma and carbon surface system, we have performed preliminary experiments by exposing carbon targets to the Pilot-PSI plasma jet. The carbon content in the plasma was monitored in these experiments with optical emission spectroscopy on the CH band and the Balmer  $\gamma$  line. In addition, Cavity Ringdown Spectroscopy was installed for characterisation of the plasma close to the surface. Results will be shown on the detection of CH (around 431 nm) and C2 (around 517 nm). The effect of the exposure on the target was analysed off line by means of the XPS instrument that is available within our PSI-lab.

8:40am **PS1-WeM3 Control of Atomic Layer Degradation on Si Substrate**, *T. Tatsumi*, Sony Corporation, Japan; *Y. Nakamura, T. Harano*, Sony Semiconductor Kyushu Corporation, Japan; *K. Kugimiya*, Sony Corporation, Japan; *T. Kawase, S. Hamaguchi*, Osaka University, Japan; *S. Iseda*, Sony Semiconductor Kyushu Corporation, Japan

To suppress the fluctuation of transistor properties, the degradation on Si substrate must be minimized. We quantitatively evaluated the relationship between ion energy at high energy peak of IEDF, the thickness of a C-F polymer (T<sub>C-F</sub>) and the thickness of damage (T<sub>d</sub>) formed during the etching of SiO<sub>2</sub> on an Si substrate. CH<sub>4</sub>/CF<sub>4</sub>/Ar/O<sub>2</sub> plasma was used for experiments. The T<sub>d</sub> were evaluated using XPS, TEM, and RBS. The changes of surface layers in the early stage of damage formation were estimated using molecular dynamics (MD) simulations. By increasing the O/CF<sub>4</sub> ratio in the plasma, T<sub>C-F</sub> decreased, and T<sub>d</sub> was a minimum under conditions where the penetration depth of ions (T<sub>ion</sub>) was equal to T<sub>C-F</sub> (the balance point: P<sub>b</sub>). When O/CF<sub>4</sub> > P<sub>b</sub>, T<sub>d</sub> increased when T<sub>C-F</sub> decreased because the ion energy consumption by the polymer was smaller. On the other hand, when O/CF<sub>4</sub> was less than P<sub>b</sub>, T<sub>C-F</sub> increased with time, and T<sub>d</sub> increased when the rate at which the polymer was deposited was increased. We used MD simulations to evaluate the surface around the transition from SiO<sub>2</sub> etching to Si etching. Damage started forming just before the SiO<sub>2</sub> was completely removed, and when the SiO<sub>2</sub> was etched off, the highest T<sub>d</sub> was observed. Then, T<sub>C-F</sub> began to increase, and T<sub>d</sub> slightly decreased by desorbing unstable SiC<sub>x</sub>F<sub>y</sub> species. When T<sub>C-F</sub> became larger than T<sub>ion</sub>, the damaged layer was buried, and changes in T<sub>d</sub> stopped. T<sub>d</sub> can only decrease until T<sub>C-F</sub> reaches the ion penetration depth. We carefully adjusted T<sub>ion</sub> to be equal to T<sub>C-F</sub> under low ion energy conditions; T<sub>d</sub> was reduced to

below 1 nm. Thus, the precise control of ion energy and the prediction of several atomic layers on an actual etched surface will be indispensable in the fabrication of 32nm-node devices.

9:00am **PS1-WeM4 Modifications of Advanced Photoresist Polymers after Plasma Processing**, *S. Engelmann, R.L. Bruce, B.F. Smith, T. Kwon, R. Phaneuf, G.S. Oehrlein*, Univ. of Maryland College Park; *C. Andes*, Rohm & Haas Electronic Materials; *D.B. Graves, D.G. Nest, M. Goldman*, UC, Berkeley; *E.A. Hudson*, Lam Research Corp.; *P. Lazzeri, E. Iacob, M. Anderle*, ITC-irst, Center for Sci. and Tech. Res., Italy

Plasma based transfer of photoresist patterns onto underlying substrates is basic to micro- and nano-fabrication, but suffers from problems like introduction of surface and line edge roughness in the photoresist/underlying features as a result of plasma processing. In this collaboration, we seek to develop a deeper understanding of this behavior along with the formulation of design criteria for new photoresist systems. Etch rates, chemical and morphological evolution of fully formulated photoresist systems as well as carefully selected model polymers have been studied using Ellipsometry, Atomic Force Microscopy, Time-of-Flight Secondary Ion Mass Spectrometry and X-Ray Photoelectron Spectroscopy. We find that the polymer structure in the top surface layer is destroyed within the first 2-3 seconds of plasma exposure accompanied by hydrogen-loss and densification. Furthermore we observed a strong correlation between polymer structure, plasma-induced surface chemistry, and morphological evolution of the sample. We also observed that acrylate content improves the etch performance of our materials and that the plasma etching rate and surface roughening of a fully formulated photoresist is essentially the same as that of the polymer backbone of which it consists. Varying the physical properties of the plasma attack can greatly modify these chemical and morphological changes. The role of process chemistries as well as the effect of ion energy or ion/neutral ratio and the effect of materials modifications for selected conditions will be addressed.

9:20am **PS1-WeM5 Study of Energetic Ion and Radical Beams Interacting with Advanced Photoresist Polymers**, *D.G. Nest, M. Goldman, D.B. Graves*, UC Berkeley; *S. Engelmann, R.L. Bruce, B.F. Smith, T. Kwon, R. Phaneuf, G.S. Oehrlein*, Univ. of Maryland; *C. Andes, Rohn and Haas Electronic Materials; E.A. Hudson*, Lam Research Corp.; *P. Lazzeri, M. Anderle*, ITC-irst, Italy

The effects of ions and radicals in plasmas on current and future photoresists (PR) are poorly understood, even though PR degradation is known to be an increasingly important problem for micro- and nano-fabrication. We report results from a collaborative study of etching and roughening mechanisms on fully formulated methacrylate-based 193 nm photoresists as well as on model polymers that make up the fully formulated compounds. We measure the effects of beams of ions and radicals impacting selected materials in vacuum to simulate plasma-photoresist interactions under controlled conditions. We highlight the importance of rare gas ion energy and mass and surface temperature on surface roughening and etching, both with and without chemical effects associated with radical impact. For example, Ar<sup>+</sup> impact at normal incidence and 1 keV results in a smooth PR surface, but 300 eV ion impact steadily roughens the surface. Surfaces impacted by Ar<sup>+</sup> at normal incidence and 500 eV are smooth at 25°C but steadily roughen at surface temperatures above about 40°C. Results of ion sputtering of patterned contact holes and trenches will be presented. Results are compared to measurements in plasmas where possible.

9:40am **PS1-WeM6 Investigation of Plasma-Polymer Interactions for Plasma/Energetic Beam Templating of Materials**, *R.L. Bruce, C. Dutton, G.S. Oehrlein, S. Engelmann, T. Kwon, R. Phaneuf*, Univ. of Maryland, College Park; *B. Long, G. Willson*, Univ. of Texas, Austin; *D.B. Graves, D.G. Nest, J. Vegh*, UC, Berkeley; *A. Alizadeh*, GE Electric Global Research Center

Plasma processing of nanoscale patterned organic masks can lead to surface and line edge roughening and can also lead to changes in dimensions and properties of completed nanostructures for reasons that are not well understood. Using an inductively coupled plasma chamber, tailored polymers were processed in well-characterized controlled plasmas (O<sub>2</sub>, Ar, Ar/C<sub>4</sub>F<sub>8</sub>) and then analyzed using a number of characterization tools: ellipsometry, atomic force microscopy, Fourier-transform infrared spectroscopy, and x-ray photoelectron spectroscopy. Similar polymers (polystyrene, poly(alpha-methylstyrene), poly(para-methylstyrene)) exposed to the same plasma conditions were found to behave very differently in etch yield, rms roughness, and refractive index evolution. Characterization of chemical bonding and

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composition in the damaged layer of these polymers by x-ray photoelectron spectroscopy and infrared spectroscopy give insights into the different plasma-polymer interactions in similar polymers. We discuss the different behavior of the polymers in the plasma environment in terms of fundamentally different responses to radiation environments, including cross-linking and scission.

**10:40am PS1-WeM9 Molecular Dynamics Simulations of Interactions of Ions and Radicals with Organic Masking Materials, J.J. Végh, D.G. Nest, M. Goldman, D.B. Graves, University of California at Berkeley; R.L. Bruce, S. Engelmann, T. Kwon, R. Phaneuf, G.S. Oehrlein, University of Maryland, College Park; B. Long, G. Willson, University of Texas, Austin; A. Alizadeh, GE Electric Global Research Center**

Plasma-organic polymer surface interactions are important in etching, deposition, surface treatment and modification. Organic polymers are used as etch masks in both conventional photoresists and in novel masking schemes such as imprint lithography and self-assembled block copolymer masks, but the mechanisms of etching are poorly understood. We describe studies of ion and radical impacts on organic polymer surfaces using molecular dynamics (MD) simulations, focusing on etch mechanisms for model polymers such as polystyrene. Experiments have revealed that polymers, including commercial photoresists, initially experience a rapid, drastic reduction in sputtering yield before reaching a much lower steady state value. The MD simulations reproduce this drop in sputtering yield, and are also able to predict the ion fluence necessary to reach steady state. Simulations reveal that the near-surface region becomes hydrogen-depleted with Ar<sup>+</sup> bombardment, leading to an amorphous carbon layer that reduces the sputtering yield by as much as two orders of magnitude. We present further results explaining polymer etch in the presence of F and CF with Ar<sup>+</sup> bombardment, contrasting polymer etch mechanisms with those of materials such as silicon. Results are compared with energetic beam and plasma experimental measurements.

**11:00am PS1-WeM10 Scattering Dynamics of Fluorinated Ions on Surfaces of Relevance to Plasma Etching, M.J. Gordon, LTM/CNRS, France; X. Qin, J. Mace, K.P. Giapis, California Institute of Technology**

Fluorocarbon plasmas are extensively used for SC, dielectric, and metal etching; in particular, F-based etching of Si has been studied for many years. However, little is known about specific interactions (kinematics/charge exchange/reaction dynamics) of F-containing ions at collision energies relevant to plasma processing (0.1-1 keV). This talk will focus on experiments involving mass-filtered ions (F<sup>+</sup>, CF<sub>x</sub><sup>+</sup>) with tunable energy (50-1000 eV) and high flux scattered off a variety of surfaces. Beam studies were carried out in an ICP-based accelerator system with simultaneous energy/mass analysis of products leaving the target. We first highlight two new effects in the F<sup>+</sup>-Si/Al systems: electronic excitation during the hard collision to form inelastic F<sup>+</sup>/F<sub>2</sub><sup>+</sup> and stimulated desorption of hyperthermal (10-20 eV) F<sup>+</sup> (HT-F<sup>+</sup>). Inelastic losses and F<sub>2</sub><sup>+</sup> were attributed to the formation of doubly-excited autoionizing states of F and F<sup>+</sup> (analogous to Ne) in the hard collision. HT-F<sup>+</sup> is thought to originate from core-hole charge transfer involving a surface-bound F atom. These two effects are potentially important for profile evolution because F<sup>+</sup> scattering becomes inelastic at low collision energies (300/500 eV for Al/Si) and desorbing HT-F<sup>+</sup> may enhance the reactivity at surfaces not accessible to plasma ions. In the second part of the talk, collision kinematics of CF<sub>x</sub><sup>+</sup> ions off Si and metals will be discussed. Velocity analysis of scattered fragments suggests that neutralization induced dissociation of the projectile occurs before the hard collision (CF<sub>3</sub><sup>+</sup> is neutralized on approach and dissociates to form CF or CF<sub>2</sub>). The resulting CF/CF<sub>2</sub> fragments then scatter elastically off the surface to form a hot positive ion, which dissociates to F<sup>+</sup>C or F<sup>+</sup>CF, with both fragments leaving at similar velocities. This reaction scheme was seen to depend on both the incident energy and target material. Implications of these findings for plasma etching and profile evolution will be discussed.

**11:20am PS1-WeM11 Plasma-Surface Interactions During Deposition of Hard Carbon Materials, D. Liu, J.M. Stillhan, E.R. Fisher, Colorado State University**

Hard carbon-based materials such as carbon nitride and diamond-like carbon (DLC) have many desirable properties such as high hardness, good thermal conductivity, and high electrical resistance. Although plasma deposition and etching of these materials has been widely studied, very little has been reported on gas-phase ion and electron kinetics in these systems and even less is available on plasma-surface interactions. We have performed Langmuir probe and energy analysis-based mass spectrometry

measurements to characterize the gas-phase of low pressure, 13.56 MHz inductively coupled plasma molecular beams. In addition, hydrogenated DLC and a-C:N films were deposited on silicon wafers at different substrate potentials to determine the effect of ion bombardment on film properties. Films were characterized via FTIR, SEM, AFM and nanoindentation measurements, and results demonstrate that ion energy has a significant effect on the composition and morphology of plasma deposited DLC films. Most importantly, we have used our unique imaging of radicals interacting with surfaces (IRIS) technique to directly examine surface interactions of radicals during plasma deposition. IRIS data for CH and C@sub 2@ radicals in hydrocarbon plasmas and CH, CN, NH, and NH@sub 2@ radicals in a-C:N deposition systems will be presented. These species display very different surface reactivity that is dependent on plasma parameters, feed gases, and the electronic configuration of the molecule. For example, CH and CN are highly reactive during a-C:N deposition, whereas C@sub 2@, NH and NH@sub 2@ display intermediate reactivity that is highly dependent on substrate bias. IRIS results will be correlated to gas-phase and surface analysis data to provide more comprehensive mechanisms for hard carbon deposition systems.

**11:40am PS1-WeM12 In Situ Surface Diagnostics during Room Temperature Plasma Deposition of Polycrystalline Si Films, E.S. Aydl, University of Minnesota; R.C. Mani, Applied Materials**

The ability to deposit crystalline silicon at room temperature would be very attractive for a variety of applications. Crystalline silicon films are obtained when silane is highly diluted in hydrogen, or under conditions where silane is highly dissociated such that there is high concentration of H in the gas phase. In fact, amorphous silicon films undergo disorder-to-order transition upon exposure to H atoms created by plasma dissociation of hydrogen. The mechanism of this disorder-to-order transition was uncovered recently; specifically, it was shown that hydrogen inserts into the strained bonds Si-Si bonds in amorphous silicon, and induces bond-breaking and bond reforming reactions, which eventually lead to nucleation of crystalline silicon. This chemically-induced crystallization of silicon occurs in the temperature 150-300 C range. However, despite extensive experimental studies, unambiguous room temperature nucleation and growth of microcrystalline Si has not been demonstrated. We demonstrate the deposition of thin films containing nanocrystals of silicon using an inductively coupled plasma source and silane diluted in hydrogen at room temperature. In situ attenuated total internal reflection - Fourier transform infrared spectroscopy and in situ spectroscopic ellipsometry were used to monitor the film structure, temperature and thickness during deposition. The films were also characterized using ex-situ techniques such as Raman spectroscopy and TEM. Both in situ and ex-situ characterization techniques clearly indicated the presence of crystalline domains in the deposited films. In situ spectroscopic ellipsometry revealed that Si nanocrystals nucleate in the bulk and grow beneath an amorphous silicon crust validating the theory of hydrogen-induced crystallization. Crystals as large as 100-150 nm were observed at room temperature. Thus, silicon nanocrystals not only nucleate but also grow substantially in the bulk at room temperature.

**12:00pm PS1-WeM13 In-situ Spectroscopic and Kelvin Probe Studies of the Modification of Passive Films on Metals in Low Temperature Plasmas, M. Giza, T. Titz, G. Grundmeier, Max-Planck-Institut fuer Eisenforschung, Germany**

Low temperature plasma processes are of increasing interest for the surface modification of engineering metals such as iron, zinc, aluminium, copper or titanium. Many studies have been devoted to the deposition of thin protective, adhesion promoting or biocompatible films on these metal substrates. However, less attention was paid to the influence of the plasma treatment on the passive films between the metal and the deposited plasma polymer. Since the adhesive properties as well as the corrosion behaviour of metals strongly depend on the chemical composition, morphology and electronic structure of their oxides, it is of high interest to reveal principle processes of oxide modification on metals in reducing and oxidising plasmas. Moreover, the question arises how stable these modified oxides are in contact with the underlying metal and with the environment. To answer these questions in-situ analytical set-ups have been designed that allow studies of the plasma modification as well as ageing processes of modified oxides in defined environments. An in-situ set-up for vacuum and atmospheric plasma studies combines a quartz crystal microbalance, FTIR spectroscopy under grazing incidence and a Kelvin Probe. For studies in ultra high vacuum an in-situ cell was developed that consists of Auger Spectroscopy in combination with a Kelvin Probe. This plasma cell is connected to an UHV system with ToF-SIMS, XPS and STM. The presentation will cover principle aspects of

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relevant passive film structures, the introduction of the in-situ analytical set-ups, oxide modification in vacuum and atmospheric plasmas, the stability of these modified oxides and finally the relevance of the oxide modification for aspects of polymer/metal adhesion and corrosion.  
@FootnoteText@ @footnote 1@ Raacke, J., Giza, M., and Grundmeier, G., Surface and Coatings Technology, 2005. 200(1-4): p. 280-283.

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