Wednesday Afternoon, November 5, 2003

Plasma Science and Technology
Room 314 - Session PS1-WeA

Mechanisms in Plasma-Surface Interactions

Moderator: E. Kessels, Eindhoven University of Technology, The Netherlands

2:00pm **PS1-WeA1 PECVD of Thin Films: The Study of the Plasma-surface Interaction by Means of In Situ Plasma and Film Diagnostics*, M.C.M. van de Sanden,*** Eindhoven University of Technology, The Netherlands **INVITED**

Plasma enhanced chemical vapor deposition (PECVD) is now a well established technique to obtain various high quality films for e.g. micro-electronic, photovoltaic, scratch resistant or abrasive applications. Although widely applied in industry, fundamental knowledge on the actual plasma deposition mechanism is to a large extent unknown. The reason is the complexity of the problem: to unravel the deposition mechanism requires a simultaneous investigation of the plasma phase, the plasma-surface interaction and the film properties using in situ plasma and film diagnostics. The need to understand the mechanism is evident since the development and design of new functional materials and up scaling of the technique to large areas involves detailed and generic knowledge of the plasma-surface interaction. In this talk I will discuss the approach our group has undertaken to investigate the deposition mechanism of a limited number of model systems: the fast plasma deposition of hydrogenated amorphous silicon, carbon and silicone films utilizing a remotely expanding thermal plasma. I will discuss the measurement of radical and ion densities using sensitive plasma diagnostics such as cavity ring down spectroscopy and (modulated beam) appearance potential mass spectrometry. From measurements using the time-resolved version of these diagnostics, taken in the afterglow of a small perturbation of the plasma, plasma and surface reaction probabilities of selected radicals are determined. The results are compared with molecular dynamics simulations of the plasma-surface interaction and are discussed in relation to in situ characterizations of the chemical and structural composition of the film surface of the growing film.

2:40pm **PS1-WeA3 Plasma Nitriding and Reactive Deposition in Electron Beam Generated Plasmas*, *C. Muratore*,** *D. Leonhardt, S.G. Walton, D.D. Blackwell, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

A molecular gas based electron beam generated plasma provides a significantly higher atomic ion flux than molecular ion flux. Additionally, the well-defined geometry of the electron beam gives rise to a high spatial dependency of the plasma specie flux due to gas phase reactions between the beam edge and surface to be modified. To investigate the utility of the unique features associated with electron beam generated plasmas for materials processes, planar electron beams were used for plasma assisted nitriding and reactive sputter deposition. Stainless steel and other metals were exposed to electron beam generated plasmas containing mixtures of nitrogen and other gases at appropriate treatment temperatures to produce nitrided surface layers. The activation energy for nitriding was determined for stainless steel and other metals, and found to be lower than values associated with other plasma assisted nitriding processes. Thin films were reactively sputtered at equivalent total ion fluxes with variations in only plasma chemistry (e.g., N@super +@/N@sub 2@@super +@ flux ratios). All materials were characterized using standard techniques including atomic force microscopy, X-ray diffractrometry, electron microscopy and nanoindentation. Observed trends in microstructural features and materials properties correlate well to the measured plasma characteristics. @FootnoteText@ @footnote *@This work is supported by the Office of Naval Research. Muratore, C., NRL/ASEE Postdoctoral Research Fellow; Blackwell, D.D., SFA Inc., Largo, MD 20744.

3:00pm **PS1-WeA4 Angular Dependence of SiO@sub 2@, Si and Si@sub 3@N@sub 4@ Etch Yield in Fluorocarbon Gas Chemistries by using Plasma Beam*, K. Kurihara,*** *A. Egami, M. Nakamura,* ASET, Japan

A plasma-beam irradiation apparatus, which can control plasma parameters independently, such as ion energy, radical/ion composition and incident angle of ions, is very useful to examine the plasma-surface interactions under a real etching environment for constructing a process simulator without experiments of trial and error. We measured etch yield dependence on the incident angle of ions for Si, SiO@sub 2@, and Si@sub 3@N@sub 4@ substrates under the three conditions of Ar gas and two different fluorocarbon gas chemistries. One provides low selectivity of SiO@sub 2@ to Si using CF@sub 4@/Ar gas mixture (low selective mode), and the other provides high selectivity of that using CF@sub 4@/C@sub 4@F@sub 8@/Ar gas mixture (high selective mode). As for physical sputtering using Ar plasma, the etch yield at incident angle of 60 ° (oblique incidence) was about 4 times larger than that at incident angle of 0 ° (normal incidence) for all substrates at the ion energy of 530 eV, and this tendency was kept at the low ion energy of 120 eV. On the other hand for the case of CF@sub 4@/Ar gas chemistry, the etch yield of the oblique incidence was about 1.4 times larger than that of the normal incidence at the ion energy of 530 eV, but at that of 120 eV the etch yield did not increase with the increase in incident angle. In the case of etching reaction proceeded chemically by fluorocarbon gases, the angular dependence on the etch yield was influenced by the ion energy. The gas chemistry also affected the angular dependence on the etch yield. The etch yield of Si@sub 3@N@sub 4@ weakly depended on the incident angle in the case of the low selective mode, but that strongly depended on the incident angle in the case of the high selective mode. Concerning Si and SiO@sub 2@ substrates the angular dependence has no difference under above two modes. We will discuss the relation between composition of surface reaction layer and the etch yield. This work was funded by NEDO.

3:20pm **PS1-WeA5 Reduction Mechanism of VUV Radiation Damages in Pulse-Time-Modulated Plasma Processes*, Y. Ishikawa*,** *M. Okigawa,* Tohoku University, Japan*; S. Yamasaki,* National institute of Advanced Industrial Science and Technology, Japan*; S. Samukawa,* Tohoku University, Japan

In plasma processing using high-density plasma, vacuum-ultraviolet (VUV) radiation damage is one of the most serious problems. The electrical characteristics of dielectrics directly exposed to plasma are affected by plasma-emitted VUV radiation. VUV radiation with a higher photon energy than the SiO@sub 2@ band gap energy (8.8 eV) can generate electron-hole pairs in the irradiated dielectric films. The generation of electron-hole pair increases the charge densities trapped in the SiO@sub 2@ bulk and SiO@sub 2@/Si interface, affecting the conductivity of the SiO@sub 2@ layer. This results in dielectric breakdown, shorter lifetime of minority carriers, and a flat band voltage shift in transistors. Thus, reducing the VUV radiation damage is important for improving the reliability of semiconductor devices. To realize these requirements, we proposed a pulse-time-modulated plasma (pulsed plasma). In this paper, to understand the reduction mechanism of VUV radiation damages using pulsed plasma, we investigated the time dependence of defects (E' center) generation in the SiO@sub 2@ film by altering the pulse-on and off time. We found that the E' center was increased during the pulse-on-time and was also reduced during the pulse-off time. It is speculated that the generation and loss of E' center was progressed at the time constant of µmseconds. As a result, the pulsed plasma could drastically reduce the generation of E' center in the SiO@sub 2@ film and could eliminate VUV radiation damages in comparison with the continuous plasma.

3:40pm **PS1-WeA6 IRIS Investigations of Gas Phase Species in Fluorocarbon Plasmas*, I.T. Martin*,** *E.R. Fisher,* Colorado State University

Fluorocarbon (FC) plasmas are widely used for FC film deposition and the etching of Si-based materials. Investigating a specific molecule during plasma processing of a substrate can yield information on its role in the chemistry occuring at the plasma surface interface. CF@sub 2@ is a particularly interesting species in FC plasmas because its role differs in various plasma systems. CF@sub x@ and C@sub x@F@sub y@ radicals have been cited as FC film deposition precursors, while other work has shown cases where CF@sub 2@ is not a deposition precursor.@footnote 1,2,3@ We have used our imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of CF@sub 2@ radicals with Si substrates during plasma processing. CF@sub 2@ surface loss coefficients determined for 25-200W C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasmas show relatively high levels of scattering, which indicates that CF@sub 2@ radicals are produced at the surface in these systems. One advantage of the IRIS system is our ability to collect data for multiple molecules in a single plasma system. Experimental excitation spectra have verified the presence of CF in our FC systems and have been used to determine the rotational temperatures (@theta@@sub R@) of CF in the plasmas. Trends in @theta@@sub R@ are discussed as a function of plasma input power and source gas. Surface reactivity studies will determine if CF contributes to CF@sub 2@ scatter in these systems. Preliminary investigations of SiF@sub 2@(g) formation at the surface will also be presented. @FootnoteText@ @footnote 1@ R. d'Agostino, et al., in Plasma Deposition, Treatment, and Etching of Fluorocarbons, edited by R. d'Agostino (Academic Press, Inc., San Diego, 1990) p.95-143.@footnote 2@ S. Samukawa, AIP Conference Proceedings 636, 95-107 (2002).@footnote 3@ K. Sasaki, et al., Thin Solid Films 374(2), 249-255 (2000).

4:00pm **PS1-WeA7 Fluorocarbon-based Plasma Etching: The Role of the Energy Distribution of Bombarding Ions***, R. Silapunt, S. Williams,* ***A.E. Wendt,*** University of Wisconsin, Madison*; K.H.R. Kirmse, L. Losey,* Texas Instruments

In fluorocarbon-based plasma etching of dielectrics, an overlying thin fluorocarbon film, deposited on the substrate during etching, strongly affects etch rate and etch selectivity.@footnote 1@ Here we report on recent results that suggest that the energy distribution of bombarding ions (IED) has a significant effect on the thickness of this polymer layer, subsequently affecting etch rate and selectivity as well. Specifically, we have narrowed the IED while keeping other process conditions unchanged by tailoring the shape of the RF voltage waveform used for substrate bias. Significant improvements in etch selectivity for SiO@sub2@ over silicon, SiO@sub2@ over photoresist and organosilicate glass (OSG) over silicon nitride and silicon carbide have been obtained by using a narrow IED compared to the broad IED resulting from a sinusoidal bias waveform. X-ray photoelectron spectroscopy (XPS) has been used to determine the thickness of the overlying fluorocarbon film as a function of bias voltage for both narrow and broad IEDs. The results show a strong inverse correlation between film thickness and etch rate, suggesting that the sensitivity of this polymer film to the IED is the key to observed improvements in selectivity.@footnote 2@@FootnoteText@@footnote 1@ G. S. Oehrlein et al., JVST A 15, 1881 (1997)@footnote 2@ Supported by SRC (TI custom funding) .

4:20pm **PS1-WeA8 Investigating the Fundamental Mechanism of Surface Smoothening of Plasma-Deposited Amorphous Silicon Thin Films through Atomistic Simulations***,* ***S. Sriraman****, S. Agarwal, E.S. Aydil,* University of California, Santa Barbara*; D. Maroudas,* University of Massachusetts, Amherst

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition from SiH@sub 4@ containing discharges are widely used in photovoltaic and flat-panel display technologies. Nevertheless, the deposition mechanism of a-Si:H films and the fundamental surface processes that determine the surface morphology during deposition are still not well understood. Under conditions of low SiH@sub 4@ dissociation in the plasma, the dominant precursor for deposition is the SiH@sub 3@ radical. The remarkable smoothness of the a-Si:H films grown under these conditions has been used to conclude that the deposition precursor is very mobile and that it can fill surface valleys after adsorbing onto the film. Using molecular-dynamics (MD), molecular-statics, and Monte Carlo methods, we studied the growth of a-Si:H on initially H-terminated Si(001)-(2x1) surfaces; the films were grown through MD simulations of repeated impingement of SiH@sub 3@ precursor. The relationship between the structure, H coverage, morphology, and reactivity of plasma deposited a-Si:H film surfaces was investigated. Surfaces of a-Si:H films grown with SiH@sub 3@ as the sole deposition precursor were found to be remarkably smooth due to a valley-filling mechanism where mobile precursors, such as SiH@sub 3@ and Si@sub 2@H@sub 6@, diffuse and react with dangling bonds present in surface valleys. Surface transport of these adsorbed species may be driven by the surface Si-Si bond strain distribution, as well as the surface reactivity and morphology. Mobility of the surface species maybe mediated through the formation of over-coordination defects as weakly chemisorbed SiH@sub 3@ diffuse on the surface. Our analysis of the mechanism of SiH@sub 3@ precursor diffusion on the c-Si and a-Si:H surfaces will be presented. In particular, we emphasize the role of Si-Si bond strains in mediating the valley-filling mechanism leading to smooth film surfaces and the identity of the mobile precursor state.

4:40pm **PS1-WeA9 Study of SiO@sub 2@ Plasma Etching with Off-normal Mass-analyzed CF@sub x@@super +@ Ion Beam Irradiation***,* ***K. Yanai,*** *K. Karahashi, K. Ishikawa, M. Nakamura,* Association of Super-Advanced Electronics Technologies, Japan

To clarify the elementary surface reactions in the fluorocarbon plasma etching, the mass-analyzed CF@sub x@@super +@ (x = 1-3) ion beam was irradiated on the SiO@sub 2@ surface at various incident angles. The noble gas ions, such as Ne@super +@, Ar@super +@, Kr@super +@, and Xe@super +@, were also irradiated to compare chemically active CF@sub x@@super +@ ions. The angular dependence of the etch yield depends on the kind of CF@sub x@@super +@ ion. In the case of CF@sub 3@@super +@ ion irradiated at 1 keV, the etch yield increases little with the incident angle below 60°, and decrease rapidly due to the reflection of the ion at the surface over 60°. The ratio of the etch yield at 60° to that of 0° is about 1.2. On the other hand, in the case of CF@sub 1@@super +@ ion at 1 keV, the etch yield increases rapidly with the incident angle below 60°. The ratio of the etch yield at 60° to that of 0° is about 2.3. In the case of the noble gas ions, the angular dependence of the etch yield does not depend on the species, indicating cos@super -2@@theta@ below 60°. The etch yields of CF@sub x@@super +@ ions were analyzed on the basis of an etching model, involving two components originated from different removal mechanisms. The chemical component, due to the thermally desorbed molecules generated through the chemical reactions between incident species and substrate materials, is constant with the incident angles. The physical component, due to the atoms sputtered away from the substrate by the momentum transfer through collision cascade, depends on the incident angle like cos@super -2@@theta@. This model can explain the angular dependence of the etch yields of CF@sub x@@super +@ ions at 1 keV very well. The chemical component of each CF@sub x@@super +@ ion is proportional to the number of the fluorine atoms in the ion with the coefficient of 1/2, consistent with the observation that SiF@sub 2@ is the main desorbed product. This work was funded by NEDO.

5:00pm **PS1-WeA10 Reactive Surface Coefficients for Radicals in a Vacuum Beam System***,* ***Y. Kimura****, J. Coburn, D. Fraser, H. Winters, D.B. Graves,* University of California, Berkeley

We present direct measurements of reactive surface coefficients for various radicals on a range of surfaces. The reactive surface coefficients are determined using the Radical- and Ion-Surface Interaction Analysis System (RISIAS). RISIAS is equipped with two external radical sources and an external ion beam source, all of which can be simultaneously trained on a surface. A threshold ionization quadrupole mass spectrometer (TIQMS) is aligned with one of the radical beamâ€™s line of sight to measure radical flux in the beam. After measuring the radical flux, the TIQMS is vertically translated to allow insertion of a sample surface into the beam path via a load lock. With the sample surface in place, reflected radicals are measured with the TIQMS through a separate aperture. Choppers are used for background subtraction, allowing a direct measurement of the incident beam and reflected components. Experiments conducted with a temperature-controlled quartz crystal microbalance allow measurements of net deposition or etching with various beam components on a range of surfaces. The beam-to-background ratio of the radical beam in the TIQMS is measured to be 15 for the direct line of sight, and about 1 for reflected radicals. RISIAS can measure reactive surface coefficients from ~ 0.01-1. Measurements of CF@sub 3@, CF@sub 2@, CF, NH, NH@sub 2@, F and O radicals reacting with stainless steel, silicon, silicon dioxide, hydrocarbon and fluorocarbon surfaces will be presented.

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