

## Plasma Science and Technology

### Room 304 - Session PS-TuM

#### Plasma Surface Interactions I

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

#### 8:20am PS-TuM1 Investigation of Plasma-Surface Interaction by Sheath-Lens Focusing Effects, *E. Stamate, H. Sugai*, Nagoya University, Japan

Present trends in nano-technologies involve reactive plasmas of complex chemistry that makes it difficult to evaluate and control all surface reactions. Recently we discovered that the sheath forming to a biased target interfacing an insulator acts as an electrostatic lens that exhibits two focusing effects. The discrete-focusing led to the formation of a passive surface of no charge impact, near the target edge, and the modal-focusing resulted in the formation of certain modal-spots and/or modal-lines on the active surface. So far, several applications to plasma diagnostics (negative ion detection, sheath thickness measurements) and ion flux control in plasma immersed ion implantation have been reported. In this work we are demonstrating by simulations and experiments the possibility to use the focusing effects to investigate the surface reactions induced by beams of focused positive and negative ions and/or dusty particles. Measurements are done in DC and ICP discharges using Ar/SF<sub>6</sub>, O<sub>2</sub> and CF<sub>4</sub> gases. Sheath accelerated ion beams with energy ranging from 50 to 500 eV are directed by focusing effect to samples of various geometries (disk, square and complex three-dimensional shapes) made of different materials (metals or semiconductors). Surface investigation by AFM and SEM shows the influence of the ion dose and incidence angle to the sputtered profile. Depending on the competition between sputtering and deposition of by products the formation of cluster like structures is also observed. Simulations of the sheath potential structure and ion and dust kinetics are done in three dimension. The ion and dust flux on target surface is found in an excellent agreement with experiments. This work was partially supported by the 21st Century COE Program of MEXT, Japan. E. Stamate and H. Sugai, Phys. Rev. Lett. 94, 125004 (2005).

#### 8:40am PS-TuM2 Effects of Polymer Deposition on Density Stabilization and Loss Rate of Radical Species in Fluorocarbon Plasmas, *K. Kumagai, K. Nakamura*, Chubu University, Japan; *K. Oshima, T. Tatsumi*, Sony, Japan

Fluorocarbon discharges have been widely used for etching processes of dielectric thin films for microfabrication. However, these have suffered from various problems, in particular, repeatability of the etching characteristics. The problem becomes recently severe due to narrow process margin for next generation ULSI devices. One of the major origins is plasma-surface interaction on polymer-deposited vessel wall, leading to significant time-variation of radical composition of the plasma. Alternating ion bombardment (AIB) method has been proposed to reduce such interactions by applying an RF bias to the chamber wall. We reports on the effects of polymer deposition on the density variation and loss rate of radical species in fluorocarbon plasma reactors. 13.56 MHz inductively-coupled plasmas were produced in Ar-diluted C<sub>4</sub>F<sub>8</sub> gases in a stainless steel chamber in which two semi-cylindrical electrodes are set. A 400 kHz RF source serves alternating negative bias to the electrodes, and the AIB could control the deposition rate of the polymer on the biased wall. The radical density reached a steady state more quickly when the polymer deposition was suppressed with the AIB. In order to investigate the mechanism, as a parameter of thickness of the polymer, we measured a decay time of the radical density immediately after only the bias was turned off keeping the plasma-existing conditions. The delay time corresponding to a loss rate of the radical species increased with an increase in the polymer thickness, suggesting that the polymer deposition affected the loss rate. To keep the polymer thickness will be crucial for stabilization of the radical density. K. Nakamura et al: J. Vac. Sci. Technol. A 18 (2000) 137.

#### 9:00am PS-TuM3 Angular Dependence of Si<sub>3</sub>N<sub>4</sub> Etch Rates and the Etch Selectivity of SiO<sub>2</sub> to Si<sub>3</sub>N<sub>4</sub> at Different Bias Voltages in a High Density C<sub>4</sub>F<sub>8</sub> Plasma, *J.-K. Lee, J.-H. Min, S.H. Moon*, Seoul National University, South Korea

The dependence of Si<sub>3</sub>N<sub>4</sub> etch rates and the etch selectivity of SiO<sub>2</sub> to Si<sub>3</sub>N<sub>4</sub> on the ion-incident angle was studied at different bias voltages in a high density C<sub>4</sub>F<sub>8</sub> plasma. A Faraday cage and specially designed substrate holders were used to accurately control the angle of ions incident on the

substrate surface. The normalized etch yield (NEY), defined as the etch yield normalized to one obtained on a horizontal surface, was unaffected by the bias voltage in Si<sub>3</sub>N<sub>4</sub> etching but increased with the bias voltage in SiO<sub>2</sub> etching, in the range of -100 V ~ -300 V. The NEY changed characteristically, showing a maximum, with the ion-incident angle in the etching of both substrates. In Si<sub>3</sub>N<sub>4</sub> etching, the maximum NEY of 1.7 was obtained at 70° in the above bias voltage range. However, the increase in the NEY with the ion-incident angle was smaller for SiO<sub>2</sub> than for Si<sub>3</sub>N<sub>4</sub> and, consequently, the etch selectivity of SiO<sub>2</sub> to Si<sub>3</sub>N<sub>4</sub> decreased with the ion-incident angle. The etch selectivity decreased with the ion-incident angle to smaller extents at high bias voltages because the NEY of SiO<sub>2</sub> was high under this condition. To understand the characteristic changes in the NEY for different substrates, we estimated the thickness of a steady-state fluorocarbon (CF<sub>x</sub>) film formed on the substrates. The thickness of a film on Si<sub>3</sub>N<sub>4</sub> changed with the ion-incident angle, showing a minimum at 70°, and the film thickness was reduced at high angles to smaller extents on SiO<sub>2</sub> than on Si<sub>3</sub>N<sub>4</sub>. These results indicate that the NEY can be correlated with the thickness of a steady-state CF<sub>x</sub> film formed on the substrate surfaces.

#### 9:20am PS-TuM4 Fluorocarbon Film Deposition in a Gap Structure and Correlation With Trench Sidewall Angle for Fluorocarbon Chemistries in Capacitively Coupled Discharges, *L. Ling, X. Hua, B. Orf, G.S. Oehrlein*, University of Maryland at College Park; *E.A. Hudson*, Lam Research Corp.; *P. Jiang*, Texas Instruments; *Y. Wang*, National Institute of Standards and Technology

A small gap structure\* has been used to study surface chemistry aspects of fluorocarbon (FC) film deposition for FC plasmas produced in a mechanically confined dual-frequency capacitively coupled plasma (CCP) reactor. The small gap structure provides a completely shadowed region without direct ion bombardment, similar to surfaces of sidewalls of trench patterns. On both trench sidewalls and the shadowed surface portions of the small gap structure, very thin fluorocarbon layers are formed by neutral diffusion. The lack of ion bombardment also increases the retention of the chemical structure of the FC film precursors in the deposited films. For C<sub>4</sub>F<sub>8</sub>/Ar, C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub>/Ar/N<sub>2</sub> discharges the deposition rate, composition, and bonding of deposited FC films are determined as a function of processing conditions using ellipsometry and X-ray photoemission spectroscopy. The deposition rate and surface chemistry of FC film deposited in this region depend strongly on discharge chemistry, and atomic force microscopy shows significant nanoscale topography that differs markedly from films produced with simultaneous ion bombardment. The inclinations of feature sidewalls formed for different conditions qualitatively correlate with the deposition rates measured for shadowed surfaces of the gap structure. Results of mass spectrometric investigations are also reported in an attempt to relate the observed compositional differences to radicals produced in the gas phase. L. Zheng, L. Ling, X. Hua, G. S. Oehrlein, and E. A. Hudson, J. Vac. Sci. Technol. A 23, xxx (2005).

#### 9:40am PS-TuM5 The Spontaneous Etching of Silicon by F Atoms, Cl Atoms and XeF<sub>2</sub>: A Unified Model Supported by Experiment and Simulation, *H. Winters*, University of California at Berkeley; *D. Humbird, D.B. Graves*, University of California, Berkeley

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Insights gained from a recent molecular dynamics simulation (denoted HG) are used to refine a model that quantitatively predicts spontaneous etch rates of silicon and explains various experimental observations. This model is based on the electronic structure of Si and the electron affinity of the incident gas, and assumes that the rate-limiting reaction step is associated with negatively-charged particles in the halogenated Si surface layer. The density of such charge centers in the layer is a function of its thickness and can be calculated using a formalism similar to one previously published. HG predicts a ~5 Å-thick SiF<sub>x</sub> layer on undoped silicon exposed to F atoms; XPS data agree with this prediction, and indicate that the layer is about twice as thick for XeF<sub>2</sub> exposure. Layer thickness is observed via XPS and temperature programmed desorption to be independent of incident halogen flux and temperature over significant ranges of these parameters, also consistent with the HG simulations. Closed-form expressions for the reaction probability of Si (111) as a function of various parameters will be presented. These expressions correlate well with experiments, including reaction probability measurements as a function of temperature (200K--1000 K), dopant concentration (~10<sup>15</sup> - 10<sup>20</sup>)

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dopants/cm@super 3@), and incident species (F, Cl, and XeF@sub 2@). The model rationalizes the observation that the doping effect in Cl is large relative to F, even though the opposite trend is observed for the spontaneous etch rate. Finally, the HG result that etch products desorb with significant kinetic energy allows modulated beam mass spectrometry data to be quantitatively calibrated, making measured etch reaction probabilities absolute. @FootnoteText@@@footnote 1@ D. Humbird and D. Graves, J. Appl. Phys. 96 791 (2004) @footnotes 2@ H.F. Winters and D. Haarer, Phys. Rev. B 36 6613 (1987) See also erratum @footnote 3@ H.F. Winters and D. Haarer, Phys. Rev. B 36 6613 (1987)

10:20am **PS-TuM7 Molecular Dynamics Simulations of Ar@super +@ Bombardment of Si: Characterizing Ion-Induced Disorder at Surfaces, D. Humbird**, Lam Research Corporation; D.B. Graves, University of California at Berkeley; W.M.M. Kessels, Eindhoven University of Technology, The Netherlands, Netherlands

Previous molecular dynamics (MD) simulations of energetic Ar@super +@ ions bombarding initially crystalline Si surfaces indicated the formation of an amorphous phase of Si on top of crystalline Si. This amorphous phase is established within 1 monolayer of Ar@super +@ fluence, and under continuous bombardment it reaches a steady-state thickness that is a function of the impacting ion energy. We revisit some of these calculations with a different potential energy function that predicts the same general behavior, but also permits accurate simulation of F atoms interacting with a Si surface. We discuss changes to the average Si-Si bond length, bond angle, and other local order parameters as a result of Ar@super +@-induced amorphization. We note sharp transitions of these properties at the interface between amorphous and crystalline Si. Finally, we discuss differences in uptake and etch rate when thermal F atoms adsorb on and spontaneously etch the amorphous and crystalline surfaces. Some parallels are drawn between the simulations and recent real-time ellipsometry and second harmonic generation experiments, which give information on amorphous layer formation, and on bond disorder at the interface and surface of the amorphous layer, respectively.

10:40am **PS-TuM8 Fluorocarbon Polymer Layers and Etching: the Role of Fluctuations, Cluster Ejection, and Redeposition, J.J. Vegh<sup>1</sup>, D. Humbird, D.B. Graves**, University of California, Berkeley

Fluorocarbon (FC) plasma etching is known to result in the formation of a FC-containing 'polymer' film during etch, but the nature of this film remains poorly understood. Understanding and control of this film are essential to meet goals for etch of novel materials (e.g. ultra low-k (ULK) dielectrics) and to minimize photoresist loss and surface roughening during FC plasma etch. Molecular dynamics (MD) simulations of Si etch with FC radicals, F atoms, and argon ions suggest that local film thickness fluctuations are common. These fluctuations result from ejection of clusters of FC (~C@sub 20@F@sub 20@) by Ar@super +@ impacts. Temporary, local thinning of the FC film by cluster removal allows subsequent Ar@super +@ impacts to penetrate into the underlying substrate and facilitate Si etch through the deposition of kinetic energy. Similarly, transport of F atoms to the underlying Si and of etch products to the vacuum are both facilitated by this mechanism. These phenomena have been observed in simulation previously, but the relationships between cluster removal and the formation and persistence at steady state of the fluctuating FC film are not yet clear. This fluctuation effect has not been reported experimentally, to our knowledge. We have collected statistics on the FC clusters formed during etching simulations. We report the relationship between cluster size and composition to various local and instantaneous properties in the near-surface region. These properties include the average FC film thickness and Si etch yield; fluctuations in FC film thickness and surface coverage; incident FC species type and energy; density of the FC film, and incident Ar@super +@ energy. We have simulated cluster re-deposition as well. We conclude that film fluctuation through cluster ejection and perhaps redeposition of clusters play an integral role in the maintenance of the FC overlayer.

11:00am **PS-TuM9 Molecular Dynamics Investigation of the Etching of Passivated SiOCH Low-@kappa@ Dielectric Films, V. Smirnov, A. Stengatch, K. Gainullin, V. Pavlovsky, SarovLabs, Russia; S. Rauf, P. Ventzek, Freescale Semiconductor, Inc.**

Fluorocarbon plasmas are widely used for etching of dielectric thin films (conventional and low-@kappa@) in the microelectronics industry. Fluorocarbon radicals and ions are known to produce a nanometer-scale passivation layer on the dielectric surface, whereupon energetic ion

bombardment leads to dielectric material etching. As the passivation films are extremely thin and in-situ monitoring is difficult during etching, very few experimental studies have been able to probe into the fundamental nature of fluorocarbon based etching of low-@kappa@ dielectrics. This paper reports about a computational molecular dynamics (MD) investigation of the etching of SiOCH low-@kappa@ dielectric films by CF@sub x@@@super +@ (x=1, 2, 3), SiF@sub x@@@super +@ (x=1, 2, 3), CHF@sub x@@@super +@ (x=1, 2), and Ar@super +@ ions. The MD model is 3-dimensional and uses the velocity-Verlet method for particle acceleration. Pseudo-potentials for two and three body interactions of Si, O, C, H, F, and Ar have been assembled either using Gaussian based quantum chemistry computations or data available in the literature. The test structures for the MD studies are prepared by starting with crystalline Si and depositing mixtures of SiO@sub x@@@super +@, CH@sub x@@@super +@ and H@super +@ ions. Film stoichiometry and density can be controlled by means of ion fluxes and energies. A passivation layer is grown on the low-@kappa@ test structures through low energy fluorocarbon ion bombardment. Impact of energetic (100-300 eV) ions on passivated dielectric films is investigated in this paper, and modeling results are used to determine ion etching yields, nature of sputtered clusters, and their energy and angular distributions.

11:20am **PS-TuM10 Scattering Dynamics of Energetic F@super +@ Ions on Si and Al Surfaces, J. Mace, M.J. Gordon, K.P. Giapis**, California Institute of Technology

Fluorine is a significant component of many processing plasmas. Its reactions with surfaces have been extensively studied in the presence and/or absence of ion bombardment. Yet, little is known about the interaction of energetic F@super +@ ions with fluorinated semiconductor and metal surfaces, perhaps because of the difficulty in conducting well-defined experiments with F@super +@ beams. Using high flux (monolayers/sec) of F@super +@ extracted from an inductively-coupled plasma (ICP) source coupled to a mass-selective beamline accelerator, we have studied the scattering dynamics of 50-1000eV tunable F@super +@ ion beams with Si and Al surfaces. Energy and mass analysis of all scattered products was performed by a triply-differentially pumped electrostatic energy analyzer preceeding a quadrupole mass spectrometer capable of detecting single ions. We observed a transition from elastic to inelastic behavior at 500 and 300eV for Si and Al, respectively, where the directly scattered F@super +@ exits the surface with energy considerably lower than that predicted from binary collision theory due to quantum mechanical effects. At the threshold energy, we observed the onset of F@super ++@ production at considerably lower energy than F@super +@. The inelastic energy losses were attributed to formation of doubly-excited auto-ionizing states of F and F@super +@. In addition, we also saw in much greater yield low-energy (5-20eV) scattered F@super +@, believed to be generated via a stimulated desorption process involving charge transfer to the incident ion from an F atom bound to the surface, leaving the latter in a highly repulsive state. We have also monitored all scattered ionic products as a function of beam energy and identified SiF@super +@ as the dominant fluorinated species emitted from a Si surface, while SiF@sub 2@@@super +@ was barely detectable. The implications of these findings for plasma etching and profile evolution will be discussed in the talk.

11:40am **PS-TuM11 IRIS Studies of SiCl@sub x@ Surface Interactions in SiCl@sub 4@ Plasmas, I.T. Martin, D. Liu, E.R. Fisher**, Colorado State University

Chlorine based plasmas, such as SiCl@sub 4@, are widely used for Si etch processes. Additionally, SiCl@sub 4@/H@sub 2@ plasmas are utilized to deposit a-Si materials. We have characterized SiCl@sub 4@-based plasma systems using LIF, OES, and MS measurements. Density measurements indicate that relative SiCl@sub 2@ densities strongly rely on plasma parameters such as power and pressure. We have used our imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of SiCl@sub 2@ radicals with Si substrates in SiCl@sub 4@-based etch and deposition systems. Preliminary data show significant SiCl@sub 2@ surface production (S(SiCl@sub 2@)>2) in all etch systems. These results will be compared to SiF@sub 2@ and CF@sub 2@ IRIS data, as these molecules are isoelectronic to SiCl@sub 2@. Our results indicate all three molecules behave similarly under etching conditions. Surface interaction data from power, pressure and feed-gas ratio dependence studies will be presented for both etching and deposition plasmas. SiCl@sub 2@ IRIS data will also be compared to previous experimental and theoretical work on SiCl@sub 2@ surface interactions.

<sup>1</sup> PSTD Coburn-Winters Student Award Finalist

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