Tuesday Afternoon, November 5, 2002

Plasma Science
Room: C-105 - Session PS2-TuA

Plasma Surface Interactions I

Moderator: K.L. Steffens, National Institute of Standards & Technology

2:00pm **PS2-TuA1 Plasma-Wall Interaction Studies during Gate Etch Processes**, ***G. Cunge***, CNRS/LTM, France, *M. Kogelschatz, N. Sadeghi*, CNRS/LSP, France, *L. Vallier, O. Joubert*, CNRS/LTM, France

During a CMOS gate etch process, requirements in terms of Critical Dimension Control are more and more severe and the process reproducibility from wafer to wafer is becoming a serious issue. Process drift are commonly observed in high density plasma sources operating in $HBr/Cl_2/O_2$ and $HBr/Cl_2/O_2/CF_4$, and originate from the deposits of SiOX and SiO-CFX layers on the reactor walls. In the present paper, mass spectrometry and optical emission have been used to investigate the influence of the reactor walls' chemical nature on the recombination rate of halogen atoms, and on the surface loss rate of silicon etch by products. To begin with, the chemical nature of the layers deposited in various chemistry has been characterized by time-resolved actinometry: after a gate etch process, the layer deposited on the reactor walls is sputtered by a pure argon plasma and the emission from etch product and halogen atoms monitored as a function of time. The results gives insight on the chemical nature of the layer as a function of its thickness. Complementary experiment where the layer is sputtered in an $Ar-O_2$ plasma also provides information on the layer deposition mechanism, which proceeds through re-deposition and oxidation of halogenated silicon etch products. As a result, we will show that when a carbon source is provided to the gas phase of an $HBr/Cl_2/O_2$ plasma (either through CF_4 addition, or in the presence of photo-resist) the layer composition change from SiOCl to a mixture of SiOCl-C(F) species. Mass spectrometric measurement demonstrates that the presence of carbon in the layers is accompanied by a drastic increase of the Br and Cl atoms recombination coefficient, whose concentration in the gas phase consequently drops.

2:20pm **PS2-TuA2 Effect of Plasma Chamber Wall Conditions on Atomic Chlorine Concentration and Polysilicon Etch Rate Uniformity**, ***T.W. Kim****, *E.S. Aydil*, University of California, Santa Barbara

The effect of reactor wall conditions on atomic chlorine concentration and polysilicon etch rate uniformity was studied in a high-density inductively coupled plasma reactor. Experimental measurements of etch rate and two dimensional ion flux distributions on the wafer are combined with a simple transport and reaction model for Cl atoms in the plasma to elucidate the effect of reactor wall conditions on the etch rate uniformity. Specifically, we focus on the effects of wafer-to-wafer drifts from the wall conditions and effects of such drifts on the uniformity of etching. The spatially averaged etch rate across the wafer surface increases with time as etch products react with residual oxygen in the chamber and coat the reactor walls with a thin layer of silicon oxychloride film. Etch rate is highest at the center of the wafer when the anodized aluminum reactor walls are maintained in a "clean" state, free of silicon oxychloride deposits. In contrast, the etch rate peaks at the edges of the wafer with a local maximum near the pumping port when the reactor walls are coated with the silicon oxychloride film. The spatially averaged ion flux increases slightly while ion flux uniformity does not change as the reactor walls are covered with the silicon oxychloride film indicating that the drift in etch rate and etch uniformity is primarily due to the drift in atomic chlorine concentration and its spatial distribution. The increase in atomic chlorine concentration is due to its lower recombination probability on the silicon oxychloride film surface as compared to the "clean" anodized aluminum wall. As the reactor walls are coated with the silicon oxychloride film the etch rate distribution changes from a center-fast profile to a edge-fast profile due to a change in the dominant atomic chlorine depletion mechanism from wall recombination to recombination on the wafer surface.

2:40pm **PS2-TuA3 Abrupt Changes with Mixture Composition in the Surface Coverage and Etch Rate During Si Etching by Cl_2-Ar Plasmas**, *N.C.M. Fuller*, ***I.P. Herman***, Columbia University, *V.M. Donnelly*, University of Houston

Laser desorption of the adlayer, with laser-induced fluorescence and plasma-induced emission detection of the desorbed adsorbates, has been used to investigate Si etching in inductively coupled Cl_2-Ar plasmas. These techniques show that the relative coverage of $SiCl_x$ species and etch rate increase and the coverage of Si decreases very abruptly as the chlorine fraction is increased for a 75% Cl_2 plasma with the bias set for 80 eV ions. The Cl_2 fraction required to produce this abrupt change increases with an increase in ion energy. There is no corresponding abrupt change in the Cl, Cl^+, and Ar^+ densities or electron temperature at this mixture condition, as measured by optical emission spectroscopy. The implications of these results and the reaction mechanism will be discussed. This work is supported by NSF Grant No. DMR-98-15846.

3:00pm **PS2-TuA4 Generating High-efficiency Neutral Beams by Using Negative Ions in an Inductively Coupled Plasma Source**, ***S. Samukawa***, *K. Sakamoto*, Tohoku University, Japan, *K. Ichiki*, Ebara Research Co., Ltd., Japan

To minimize radiation damage caused by charge build-up or ultraviolet and x-ray photons during etching, we developed a high-performance neutral-beam etching system. The neutral-beam source consists of an inductively coupled plasma (ICP) source and parallel top and bottom carbon plates. The bottom carbon plate has numerous apertures for extracting neutral beams from the plasma. When a direct current (DC) bias is applied to the top and bottom plates, the generated positive or negative ions are accelerated toward the bottom plate. Most of them are then efficiently converted into neutral atoms, either by neutralization in charge-transfer collisions with gas molecules during ion transport and with the aperture sidewalls in the bottom plate, or by recombination with low-energy electrons near the end of the bottom plate. We found that negative ions are more efficiently converted into neutral atoms than positive ions. The neutralization efficiency of negative ions was almost 100%, and the maximum neutral flux density was equivalent to 4.0 mA/cm^2. A neutral beam can thus be efficiently produced from the ICP source and apertures in our new neutral-beam source.

3:20pm **PS2-TuA5 Direct Detection of Radical and Stable Species Impacting and Desorbing from Surfaces**, ***Y. Kimura***, *J.W. Coburn, D. Fraser, D.B. Graves*, University of California, Berkeley

We present results from a new vacuum beam apparatus that has been designed to measure directly the radical and stable species fluxes impacting surfaces and the products that form as a result of these interactions under high vacuum conditions. The Radical- and Ion-Surface Interaction Analysis System (RISIAS) is equipped with an external plasma source that creates a beam of radicals, and a threshold ionization quadrupole mass spectrometer (TIQMS) that is aligned with the beam's line of sight. This setup allows us to measure all the radical and stable species in the beam. The TIQMS is vertically translatable to allow a horizontal insertion of a sample surface into the beam path via a load lock. With the sample surface in place, all species desorbing from the surface can also be detected with the TIQMS through a separate aperture. Choppers are used for background subtraction, allowing a direct measurement of the incident beam and product components. The addition of ion bombardment from a separate ion source on the chamber before or during radical beam exposure allows us to simulate processes with substrates in direct contact with a plasma. We demonstrate operation of RISIAS with O, N, NH, and F radicals impacting a variety of surfaces. In particular, we report the etch product composition for a nanoporous silica film (hydrogen silsesquioxane, or HSQ) etched with fluorine. The products include SiF_4, SiH_4, O_2 and a variety of carbon-containing species, apparently due to carbon contamination in the film.

4:00pm **PS2-TuA7 Film Formation, CF_2 Reactivity and Ion Effects in Fluorocarbon Plasma Systems**, ***I.T. Martin***, *E.R. Fisher*, Colorado State University

Fluorocarbon plasmas are widely used for the deposition of fluoropolymer films possessing a variety of useful properties, such as hydrophobicity, chemical inertness, and low surface energies. Ions play an important role in plasma film deposition, either as precursors to film deposition or as bombarding species that sputter or cross-link the depositing film. In order to better understand the mechanisms of film formation, gas phase and gas-surface interaction studies are combined with the results of the characterization of films deposited from C_3F_8 and C_4F_8 plasmas. Plasma Ion-Mass Spectrometry (PI-MS) is used to identify nascent ions in the

***** PSTD Coburn-Winters Student Award Finalist

plasma systems at different RF powers, which can then be linked to film structures and reactivity measurements. Plasma conditions that minimize the formation of ions lead to the deposition of less cross-linked fluorocarbon films; conditions that enhance fragmentation of the parent gas lead to higher deposition rates within the plasmas. In addition to film characterization, we have used our Laser Induced Fluorescence (LIF) based imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of CF_2 molecules with Si substrates during plasma processing. CF_2 surface loss coefficients determined for 25-100 W C_3F_8 and C_4F_8 plasmas show relatively high levels of scattering, which indicates that CF_2 molecules are produced at the surface in these systems. Overall, scatter coefficients measured in the C_4F_8 system are higher than those measured in the C_3F_8 system. These data are correlated with the identity of the nascent ions in the plasma systems. Results for ion free conditions are also discussed. Collectively, the data presented provide a fairly comprehensive picture of these fluorocarbon systems, from the gas-phase to the material to the plasma-surface interface.

4:20pm **PS2-TuA8 Surface Reaction Analyses for Si/SiO_2 Selective Etching Processes using Molecular Dynamics Simulations**, ***S. Hamaguchi***, Kyoto University, Japan **INVITED**

Molecular dynamics (MD) simulations are used to study surface reaction dynamics during dry etching processes of Si and SiO2 surfaces. First simulation results of Si and SiO2 etching by Cl and F beams are presented. In these processes Si is selectively etched over SiO2, the mechanism of which can be easily understood from the observation of surface conditions obtained from MD simulations. We also discuss the difference between beam etching and plasma etching (where a large number of low-energy charge-neutral reactive species exist) for these processes. Secondly we present simulation results of SiO2 etching by CxFy. Thirdly enhanced surface diffusion effects by relatively low-energy ion bombardment (the energy of which is below etching threshold) are presented. To perform these MD simulations, we have developed classical interatomic potential functions using potential energy data obtained from ab initio calculations of electronic states for various molecules and radicals. To model Si and SiO2 etching by halogens, we have constructed Stillinger-Weber type potentials for Si-O-Cl and Si-O-F systems. The potential functions for SiO2 and Si etching by CxFy, are of hybrid type of Stillinger-Weber type functions and Abell-Tersoff-Brenner type functions. The details of these potential functions are also discussed in the presentation.

5:00pm **PS2-TuA10 Subsurface Diffusion and Reaction of Fluorine Atoms in Photoresist**, ***F. Greer***, *D. Fraser, J.W. Coburn, D.B. Graves*, University of California, Berkeley

Radicals created in plasmas are known to play important roles in thin film etching, deposition, cleaning, stripping and surface modification. The present study is aimed at developing a more quantitative model of radical-surface interactions. Room temperature measurements of F atoms abstracting D atoms from a deuterated photoresist surface to form DF were made in a vacuum beam apparatus, with simultaneous monitoring of film mass change with a quartz crystal microbalance. These measurements were interpreted as abstraction of D by F, followed by F saturation of dangling bonds previously occupied by D. However, the rate of DF formation and mass uptake due to F saturation showed a relatively long-lived tail, inconsistent with surface-only reactions. After the initial stage, subsequent DF formation and mass uptake appeared to be limited by F atom diffusion into the sub-surface since the measured rate of mass change and DF flux from the surface both varied inversely as $t^{1/2}$. The surface abstraction probability of D by F was inferred to be 0.25, and the value of the F atom diffusivity was consistent with values reported for diffusion in polymers. These results will be discussed in terms of studies with other halogen radicals as well as nitrogen radicals. The application of these results to atomistic scale models of plasma etching will also be discussed.

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