Plasma Science and Technology

Room: 607 - Session PS2-WeM

Plasma-Surface Interactions I

Moderator: J.P. Chang, University of California at Los Angeles

8:00am **PS2-WeM1 Measurement of Electron Shading and its Depletion by Ultraviolet Radiation using Scanning Surface Potential Microscopy**[1], *G.S. Upadhyaya*, ***J.L. Shohet***, University of Wisconsin-Madison, *J.B. Kruger*, Stanford University

Electron Shading, or topography-dependent charging, is believed to occur during plasma exposure when the depth-to-diameter ratio (aspect ratio) of pattern features is greater than 0.5. We present preliminary direct experimental evidence of the existence of electron shading. In addition, we present evidence of removal of the electron shading by exposure of the charged structure to UV radiation produced by a Hg-Ar lamp A patterned test structure was exposed to a d.c. nitrogen plasma operating at a pressure of 120 mTorr. The pattern was composed of a layer of thermally grown oxide with circular pits of 800 nm diameter and 1 micron depth. The pit pitch was 1.6 microns. The structure was placed on the cathode of the discharge to which -500 V was applied to break down the gas and to bombard the surface with ions. The structure was exposed to the plasma for a total of 10 seconds. A Digital Instruments multimode Atomic Force Microscope was modified to operate as a Kelvin probe in order to measure the surface potentials with sufficient spatial resolution to determine the potential inside the pit regions. To enhance the resolution beyond the standard AFM tip dimensions a carbon nanotube was attached to the apex of the AFM tip. Three two dimensional surface potential scans were made. First, a scan of the unexposed test structure showed that the surface potential was less than 10 mV over the surface of the unexposed structure. After plasma exposure, a second scan showed d.c. surface potential of the order of 6 volts over the entire structure. In addition, higher potentials (of the order of 200 mV) were observed directly over the pit regions, thus showing that electron shading appears to be present. The third scan (after UV exposure) shows removal of all surface potentials inside and out of the pit region and returns the structure to the uncharged state before plasma exposure.

[1] Work Supported by NSF under grant DMR-036582 and under grant ECS-9731293.

8:20am **PS2-WeM2 Surface Reaction Enhancement by UV Irradiation during Si Etching with Chlorine Atom Beam**, ***B. Jinnai***, Tohoku University, Japan, *F. Oda, Y. Morimoto,* Ushio Inc., Japan, *S. Samukawa*, Tohoku University, Japan

The surface atomic layer chemical reactions must be accurately controlled in future nanometer scale ULSI devices to enable precise patterning without any irradiation damage being caused during plasma etching processes. Many investigations have been conducted to understand surface reactions during silicon etching in chlorine plasma. Such research has focused on the effects of energetic ion and radical species using high-energy ion beam experiments. However, we recently found that the UV photon irradiation from plasma also plays a very important role in surface reactions during silicon etching in chlorine plasma. In this study, we discuss the effects of UV photon irradiation from chlorine plasma during silicon etching with our developed low-energy chlorine atom beam. A silicon substrate was etched by combining a low-energy chlorine atom beam and UV photon irradiation. When the silicon substrate was irradiated to the UV photons from 200 nm to 380 nm during etching with the chlorine atom beam, the etching rate of silicon was drastically increased. The results suggest that UV photons with wavelengths between 200 nm to 380 nm enhance the silicon surface reactions in the chlorine plasma. Additionally, a total photon irradiation density must be greater than 20 mW/cm^2 to increase the etching rate of silicon. Namely, the silicon surface reactions strongly depend on the wavelength (the energy) of the UV photons and the UV photon flux in the chlorine plasma. Our results are the first to clarify that UV photon irradiation from plasma plays very important roles in silicon surface atomic layer reactions in chlorine plasma.

8:40am **PS2-WeM3 Vacuum-Ultraviolet Radiation-Induced Charge Depletion in Plasma-Charged SiO2/Si by Electron Photoinjection and Fowler-Nordheim Tunneling**[1], ***G.S. Upadhyaya***, *J.L. Shohet*, University of Wisconsin-Madison

Vacuum-ultraviolet (VUV) radiation emitted from processing plasmas can damage dielectric materials by creating electron-hole pairs. However, the resulting increased dielectric conductivity during VUV irradiation can also be beneficial in either partially or completely depleting previously deposited plasma charge. The underlying mechanisms that can be responsible for VUV-induced charge depletion are determined by exposing plasma-charged SiO2/Si samples to monochromatic-synchrotron radiation with photon energies in the range from 8 to 18 eV. Charge depletion was observed only for photon energies smaller than 13 eV. For photon energies between 8 and 11 eV, photoinjection of electrons from the Si into SiO2 conduction band is identified as the process responsible for charge depletion. For photon energies between 11-13 eV, field emission of electrons from Si into the oxide due to electric-field enhancement at the Si-SiO2 interface is believed to be the charge-depletion mechanism. Qualitative photoinjection and field-emission models convincingly explain all experimental measurements.

This work was supported by the National Science Foundation under grant No. DMR-0306582. The SRC is a national facility, funded by NSF under grant No. DMR-0084402.

9:00am **PS2-WeM4 The Characteristics of a Neutral Beam Angle using a Low Angle Reflected Neutral Beam Etching System**, ***D.H. Lee***, *S.W. Hwang, J.S. Lee, S.H. Oh, Y.H. Lee, Y.-J. Kim, S.W. Choi, W.-S. Han*, Samsung Electronics Co. Ltd., S. Korea

Plasma etching is one of the key technologies in the fabrication of deep submicron silicon based integrated circuits. However, plasma etching has a serious disadvantage due to the energetic charged particles such as positive ions and photons generated in the plasma which causes radiation damage causing physical defect, increased gate oxide breakdown, charging, etc. To avoid these charge-related and physical impact-related damages, several low-damage processes have been proposed. One possible alternative to avoid these problems is a low energy neutral beam etching. The neutral beams recently investigated for the anisotropic etching are generated by a low angle charge exchange collision of an ion beam in the range from 50 to 500eV (hyperthermal ions) with a flat surface. The characteristics of the neutral beam formed after the charge exchange collision such as the neutralization efficiency, neutral beam energy and its distribution, scattering angle of the neutral beam, etc. are the important in the nanoscale device etching characteristics. When an energetic ion collides with the surface, various reactions of the incident ions with the surface are occurred. The collision of ions having a high energy or a high incident angle with the surface increases the possibility of sputtering or implantation, however, the collision of ions having a low energy or a low incident angle with the surface increases the possibility of reflection. The reaction phenomena between the surface and incident ions have been mostly studied with the incident ion energy range from keV to MeV for ion implantation or surface analysis, however, the reactions phenomena with the energy range less than 1 keV, which is important in the application of neutral beam etching, have not been investigated. Therefore, in this study, the variation of angle distributions of neutral beam after the low angle reflection of the low energy (<600eV) ion beam on the flat surface were investigated using double faraday-cup and the etch characteristics for the angle distribution changes were also investigated.

9:20am **PS2-WeM5 Quantitative Characterization of Ions and Si Surface Interactions - Estimation of Plasma-Induced Defect Generation Probability**, ***K. Eriguchi***, *D. Hamada, M. Kamei, H. Fukumoto, K. Ono*, Kyoto University, Japan

The plasma damage induced by ion bombardment has become one of crucial issues from the viewpoints of the physical thickness in scaled devices. Quantitative analysis of the plasma-induced defects is requisite for understanding the mechanism and realizing high performance devices. In this article, ions and Si surface interactions during plasma processing are quantitatively analyzed by novel techniques, providing the defect (charge trapping site) density and defect generation probabilities. Samples were exposed to two different plasma sources, DC and ECR with various biasing, gas mixtures and process time. N-type Si wafers with the low resistivity of 0.02 Ωcm were mounted on the stage and exposed to plasma sources. Combined with plasma diagnostics, two optical analyses, spectroscopic ellipsometry and photoreflectance (a modulation spectroscopy) were conducted to identify the damaged layer thickness with the 4-layer (air/layer-1/layer-2/Si substrate) model, the mechanical strain developing in the vicinity of the surface determined by the Si transition energy change, and the defect density (charge trapping site) by a novel method based on the surface potential change calculation. Also the surface layers were evaluated by a resistivity measurement. We have observed the characteristic structure change in the damaged layers with the relaxed mechanical strain (approximately 0.1 %) and the charge trap site generation with significant densities of 10^{12} cm^{-2}, along with plasma exposure time. Hence we have finally determined the defect generation probabilities per an impinging ion as 10^{-3} - 10^{-5} s^{-1} in the present ion energy and plasma density ranges. The difference is attributed primarily to that in the measured bias voltage (-300 V for DC and -50 V for ECR) dominating the energy of ions accelerated in the sheath, although the ion energy distribution function has to be taken into account for further discussion. This ion energy effect is confirmed from the difference in damage-layer thickness by ellipsometry as well as from the etching simulation. The calculated defect densities in the damaged layer are considered to affect device performances in terms of the increase in power consumption by plasma-induced junction leakage. The obtained defect generation probability is a key parameter for understanding the mechanism of ions and Si surface reactions as well as plasma process designs.

9:40am **PS2-WeM6 Plasma-Catalytic Removal of Nitrogen Oxides**, ***M.M. Morgan***, *E.R. Fisher*, Colorado State University

Nitrogen oxides (NO_x), pollutants produced primarily from engine exhaust, contribute significantly to global air pollution. To reduce NO_x emissions, catalysts involved in exhaust treatment must be improved. A greater understanding of fundamental chemical gas-phase and gas-surface processes is, therefore, required. One promising solution is plasma-catalytic processes for removal of pollutants, specifically nitric oxide (NO), from exhaust gases. Our imaging of radicals interacting with surfaces (IRIS) technique allows us to simultaneously examine the gas-phase, perform surface analyses, and probe the gas-surface interface. Here, we have used IRIS to address the fundamental issue of NO_x removal by measuring relative gas-phase densities and by examining the steady-state surface reactivity of plasma-generated species on catalytic surfaces. Data from relative gas phase density studies suggest that increased water content and applied rf powers are required to diminish a majority of NO emissions. Preliminary IRIS data suggest that NO scatters off of surfaces with a high probability. Additional data on the internal temperature of NO in these systems as a function of plasma parameters will also be discussed.

10:40am **PS2-WeM9 New Insight into Fundamental Ion-Surface Interactions**, ***M.J. Gordon***, *X. Qin*, *K.P. Giapis*, California Institute of Technology **INVITED**

Collisions of ions with surfaces at low energy (<1 keV) are important in reactive ion etching of semiconductors, dielectrics, and metals. For example, ion bombardment can have a strong effect on etch rates, profile anisotropy, and selectivity through physical sputtering, momentum-assisted product removal, and modification of reaction rates. Fundamental understanding of these issues requires detailed information about the scattering processes which occur under different bombardment conditions. To this end, we have conducted scattering experiments involving mass-filtered ions (F^+, CF_x^+, NF_x^+) with tunable energy (50-1000 eV) and high flux (monolayers/s) on several surfaces (Si, Al, Ag) to look critically at collision kinematics, charge exchange processes, and surface reaction products. Topics to be discussed include: (1) electronic excitations in hard collision events (inelastic losses and F^{++} formation); (2) pre-collision fragmentation of CF_x^+ ions which result in fast exit products such as C^+, F^-, and CF^-; (3) high yields of fast F^-; and (4) bimodal energy distributions of F^+ and F^- species leaving Si and Ag surfaces. For instance, energy losses measured for single-scatter events of F^+ off Si and Al show that F^{++} can be formed through a double electron promotion mechanism which “turns-on” above a critical collision energy. Velocity analysis of daughter fragments from CF_3^+ impact on Si and Ag point to several situations where fast exit species (C^++F^- and F^++CF^+ with energies > binary collision predictions) are formed as a result of the projectile ion breaking apart before the hard collision step. Finally, energy analysis of F^+ and F^- leaving Si and Ag surfaces shows two distinct scattering channels: one associated with a binary-like, single-scatter elastic event and another narrow, low-energy channel that cannot be explained as simple sputtering. These results illustrate that in many instances, product species can show significant inelastic losses as well as faster-than-SIMS behavior which may have a dramatic impact on profile evolution in plasma etching. In addition, energy analysis of both the positive and negative ion products associated with fluorinated ion scattering provides indispensable clues about the physics of reactive ion etching.

11:20am **PS2-WeM11 Investigating Fundamental Etch Limits: Molecular Dynamics Simulations of Sub-10 nm Feature Fabrication**, ***J.J. Végh***, *D.B. Graves*, University of California, Berkeley

As semiconductor devices are continually scaled down in size, individual device features are approaching the molecular scale. Fundamental knowledge of the mechanisms of the etch process at very small scales will be necessary to effectively design future etch-enabled pattern transfer schemes. Additionally, it is currently unclear how small features can be made using conventional processing methods. Molecular dynamics (MD) simulations have been carried out to examine the fundamental characteristics of etching very small features on silicon and diamond carbon surfaces. These features are created in simulation through bombardment of surfaces by idealized ion and radical beams (i.e. with perfectly controlled confinement, directionality, and energy). For very small beam diameters (less than 2 nm) a novel mode of hole formation is seen in MD in which the substrate atoms are displaced laterally by the ion beam, but not sputtered. This results in uniform holes with high aspect ratios and the formation of a densified, amorphized region laterally surrounding the hole. Lateral densification occurs from atoms that have been displaced from the hole void region during bombardment. As the beam diameter is increased to ~2 nm and beyond, sputtering is seen with yields comparable to those at steady state on bulk flat surfaces. The effects of redeposition on the side walls of the hole in relation to hole uniformity, achievable aspect ratios, and other feature characteristics are discussed. The effects of ion mass, quality of beam confinement, and the dynamics of ion-surface collisions are also addressed. The addition of chemistry to the inert ions (fluorine and fluorocarbon radicals and ions) is also discussed, and its effects on the hole formation processes are illustrated.

11:40am **PS2-WeM12 Fragmentation Dynamics of Energetic Fluorinated Ions on Inert and Reactive Surfaces**, ***X. Qin***, *M.J. Gordon*, *K.P. Giapis*, California Institute of Technology

Fluorinated ions with energies between 50-1000eV are important in plasma etching and deposition of materials used in the semiconductor industry. However, the scattering dynamics of molecular ions with surfaces are still not well understood in terms of fragmentation and energy transfer. We report results on the collision of mass-selected ions, such as SF^+ and SiF^+, with Si and Ag surfaces under UHV at impact energies relevant to plasma processing conditions (< 1 keV). Positive and negative products leaving the surface were analyzed in both mass and energy under high flux bombardment conditions (~monolayer/s) to compare with fragmentation of CF_x^+. Results show that daughter ions leaving a relatively inert surface (Ag) are much more energetic (not SIMS-like) than those from a reactive surface like Si. Characteristic overlaps in the velocity spectrum of species leaving the target surface suggest that a pre-dissociated projectile scatters nearly elastically off a target atom and breaks apart after the hard collision step. For instance, several daughter ions (S^+, F^+, F^-, SF^+) leave the surface at velocities much larger than expected for an elastic deflection of the molecular ion projectile. Product distributions (chemical identity and energy content) with respect to impact energy for a similar series of projectile ions (i.e., SF_3^+, SiF_3^+, CF_3^+) will be compared to understand the dynamics of how molecular ions fragment upon impact. Detailed reaction channels that lead to the formation of scattered products and etching of the surface will be discussed.

12:00pm **PS2-WeM13 Optical Second-Harmonic Generation to Study Plasma-Surface Interaction in Silicon Materials Processing**, ***J.J.H. Gielis****, *P.M. Gevers*, *P.J. van den Oever*, *A.A.E. Stevens*, *H.C.W. Beijerinck*, *M.C.M. van de Sanden*, *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Surface and interface properties increasingly govern device performance in microelectronics, therefore, obtaining profound knowledge of these properties in real time during plasma processing is essential. In this respect, the nonlinear optical technique of second-harmonic generation (SHG) is very promising, as it has proven to be an ultra-sensitive probe for surface and interface states such as dangling bonds and strained Si-Si bonds in crystalline Si (c-Si) surface science.[1] In this work the real time and spectroscopic SHG response of amorphous silicon (a-Si) will be addressed in two areas of plasma processing, ion-assisted etching of c-Si and deposition of hydrogenated amorphous silicon (a-Si:H). In addition, spectroscopic ellipsometry was used to deduce linear optical properties. The experiments were carried out under well-defined conditions in high vacuum setups, using ion and radical beams to circumvent the complexity of the plasma.[2] Ion bombardment of c-Si using a low-energy Ar^+-ion gun (70-1000 eV) results in a layer of a-Si with a thickness of several nanometers. For fundamental photon energies from 1.35-1.75 eV, the SHG signal increases with an order of magnitude upon ion bombardment and it is shown that the SHG signal is governed by a two-photon resonance at 3.36 eV, related to modified Si-Si bonds at the a-Si/c-Si interface with an additional a-Si surface contribution. In the 0.8-1.1 eV fundamental photon energy range the increase in SHG signal is even stronger. It is discussed that the time-resolved SHG signal is governed by dangling bond creation and annihilation dynamics at the a-Si surface and a-Si/c-Si interface. Thin films

---

***** PSTD Coburn-Winters Student Award Finalist of a-Si:H deposited on c-Si by a SiH_3 dominated beam have been investigated with SHG in the same photon energy ranges. For many applications, such as heterojunction solar cells, the abruptness of the a-Si:H/c-Si interface is crucial. Also in this system the SHG signal displays a strong resonance at ~3.3 eV from the a-Si:H/c-Si interface. It will be demonstrated that real time SHG provides a method to distinguish between direct heterointerface formation and nanometer-level epitaxial growth at a very early stage of film growth.

[1] U. Höfer, Appl. Phys. A 63, 533 (1996).

[2] J. W. Coburn and H. F. Winters, J. Appl. Phys. 50, 3189 (1979).

Authors Index

Bold page numbers indicate the presenter