Friday Morning, November 4, 2005

Surface Science
Room 202 - Session SS1-FrM
Surface Modification through Etching

Moderator: K.T. Queeney, Smith College

8:20am **SS1-FrM1 Creating Si Structures from Meso- to Nano-scale via Chemical and Laser-Assisted Methods***, **K.W. Kolasinski**,* University of Virginia **INVITED**

Nanocrystalline porous silicon is created by etching Si in fluoride solutions. The reaction is initiated by valence band holes that are provided by laser irradiation or suitable oxidants. The composition of the fluoride solution can be used both to elucidate the mechanism of etching as well as to control properties of the resulting microporous film. Several new classes of stain etchants - containing some combination of HF, NH@sub 4@HF@sub 2@, HCl, HNO@sub 3@, Fe(III), Mn(VII) and water - have been investigated. Once porosified, the films exhibit visible photoluminescence (PL). The peak PL wavelength depends on the etchant composition. Properties of the film, such as morphology, porosity and the PL maximum wavelength, respond to the etchant composition. Of particular interest is the observation of a blue shift in PL, which correlates with an increasingly positive electrochemical potential (E@sub 0@) of the oxidant. It is argued that E@sub 0@ plays a role much like wavelength in photoelectrochemical etching and that smaller nanocrystals are produced with more positive values of E@sub 0@. Micrometer scale Si pillars are formed by chemically enhanced laser ablation using nanosecond excimer laser irradiation (308 nm, ~3 J cm@super -2@) of Si in the presence of SF@sub 6@. Smaller pillars are formed using femtosecond irradiation (790 or 390 nm, ~ 1 J cm@super -2@). We can control the initiation of precursor holes by ruling a grating into the Si substrate prior to irradiation. Near-field amplification of the laser intensity enhances the formation of the precursor holes and aligns them parallel to the rule. Continued irradiation leads to the break up of the holes into pillars. The pillars can be thinned and eventually removed by wet chemical etching in aqueous KOH resulting first in ordered arrays of pillars with aspect ratios approaching 10,000 (e.g. tens of microns in length, with ~10 nm tips) and then macropores. Macropore shape is determined by crystallography and the anisotropy of the wet etchant.

9:00am **SS1-FrM3 Optical Second Harmonic Generation as a Diagnostic Tool in Ar@super +@ and XeF@sub 2@ Beam Etching Studies of Silicon***, **J.J.H. Gielis**, A.A.E. Stevens, P.M. Gevers, H.C.W. Beijerinck, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Insight into surface and interface properties during plasma etching of micro- and nanostructures is essential to obtain optimal device performance. In this work we study surface and interface processes during etching of Si by implementing the surface and interface sensitive nonlinear optical technique of second harmonic generation (SHG) in a UHV multiple-beam experiment including an Ar@super +@ ion gun and a XeF@sub 2@ beam. SHG has been applied both spectroscopically and in real-time to study H-terminated Si(100) during ion bombardment and (subsequent) XeF@sub 2@ etching using a fs Ti:sapphire laser. Low-energy (50-1000 eV) ion bombardment of c-Si results in a layer of amorphous silicon (a-Si) with a thickness of several nanometers and is expected to create defects such as dangling bonds and strained bonds in this damaged layer. For the applied fundamental photon energy range of 1.35-1.75 eV the SHG signal for c-Si is mainly governed by a two-photon resonance at 3.3 eV related to strained Si-Si bonds in the surface region. This resonance has been characterized before, during, and after ion-induced etching of H-terminated Si(100). It has for example been observed that the resonance at 3.3 eV substantially increases in amplitude during ion bombardment while an additional broad resonance at 3.2 eV seems to emerge. From comparison with spectroscopic ellipsometry studies and by XeF@sub 2@ dosing experiments, the former resonance is likely to originate mainly from strained Si-Si bonds at the a-Si / c-Si interface while the latter seems to be related to strained bonds in the a-Si surface region. Prolonged XeF@sub 2@ etching of a-Si and c-Si results in an almost complete quenching of the SHG signal, followed by a partial recovery of the SHG signal in which two separate resonances can be distinguished. The dynamics of the spectral SHG signal can aid in understanding the role of strained bonds in the Ar@super +@ and XeF@sub 2@ etching process of silicon.

9:40am **SS1-FrM5 157 nm Laser Interactions with Fused Silica@footnote 1@***, **S.R. John**, J.A. Leraas, S.C. Langford, J.T. Dickinson,* Washington State University

The F@sub 2@ excimer laser, with a wavelength of 157 nm and a photon energy of 7.8 eV, has been shown useful for micromachining a number of technologically useful materials and has potential applications in developing optics, resists, and scanners for DUV lithography. Two materials that have been examined extensively are fused silica and PTFE (Teflon). Little has been done to understand the detailed mechanisms underlying the superior etching behavior of these materials at 157 nm. Here we present a summary of our initial studies. Beginning at fluences well below threshold for plasma formation, we have examined the direct desorption of atomic ions from fused silica surfaces at 157 nm. We used time resolved mass spectroscopy to identify the species and determine their kinetic energies. Both Si@super +@ and O@super +@ are observed. Prolonged irradiation reduces the emission intensities, consistent with the consumption of defects by the emission process. Molecular dynamics simulations of the silica surface suggest that silicon ions bound at surface oxygen vacancies (analogous to E' centers) provide suitable configurations for emission. Direct emission involving antibonding chemical forces (Menzel-Gomer-Redhead model) are suggested as the origin of the observed kinetic energies. If time permits, results on PTFE will be presented, showing significant neutral and ion emissions (with high kinetic energies). @FootnoteText@ @footnote 1@This work was supported by the Department of Energy.

10:00am **SS1-FrM6 Ion-induced Initiation of Defects on Graphite at Hyperthermal Beam Energies***, X. Liu, **T. Tzvetkov**, X.D. Qin, D.C. Jacobs,* University of Notre Dame*; N. Mateljevic, J.C. Tully,* Yale University

Ion beams of O@super +@, O@sub 2@@super +@, and Ne@super +@ with incident energy of 5-20 eV are used to etch a Highly Oriented Pyrolytic Graphite (HOPG) surface. The study is focused on the initial stages of defect initiation when well-ordered HOPG is damaged by ion bombardment. The defects generated by the ion beam are observed with ex-situ Scanning Tunneling Microscopy (STM). The density and size of the defects are analyzed as a function of the dose, incident energy, and chemical identity of the ion. Kinetic Monte-Carlo simulations reveal that the probability of an incident ion removing a carbon atom from an intact basal plane are orders of magnitude smaller than removing a carbon atom from a site adjacent to a defect.

10:20am **SS1-FrM7 Etching of Carbonaceous Thin Films by Atomic Oxygen: The Influence of Chemical Composition, Substrate Temperature and Gas Phase Environment***, **H. Fairbrother**, J. Gorham,* Johns Hopkins University

The etching of carbonaceous thin films by atomic oxygen (AO) is an important component of many industrial plasma cleaning and decontamination strategies. AO is also the central species responsible for the degradation of polymers exposed to Low Earth Orbit (LEO). To improve the mechanistic understanding of AO mediated erosion processes, the surface reactions of AO with various carbonaceous thin films have been studied using X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). In situ XPS analysis revealed that AO mediated erosion rates with carbonaceous films increase rapidly as a function of substrate temperature. This effect was correlated in part with the thermal stability of the oxidized carbon species produced as intermediates during the etching process. In low pressure plasma cleaning processes surfaces are typically exposed to a variety of reactive species. As an initial step towards identifying the existence and magnitude of co-operative effects between AO and other reactive species contained in plasma discharges results will also be presented on the erosion of carbonaceous thin films exposed simultaneously to AO and low energy (< 100eV) electrons. In these studies XPS analysis will be augmented by AFM studies, using HOPG as a model substrate for carbonaceous films. To identify their suitability as protective coatings for spacecraft vehicles exposed to LEO the surface reactions of AO with amorphous carbon phosphide films have also been examined. In these studies phosphorous incorporation was found to retard the rate of AO erosion due to the formation of a passivating surface layer that contains highly oxidized phosphorous species.

10:40am **SS1-FrM8 Consequences of Exposing Ionic Single Crystals to UV Laser Light, keV Electrons, and Low Pressure Water Vapor@footnote 1@***, J.T. Dickinson, K. Kjelgaard, **S.C. Langford**,* Washington State University

At low pressures, water often does not stick to clean, room temperature surfaces, including surfaces of insulating inorganic materials. Nevertheless sorption, including dissociative sorption, can be strongly enhanced by defects, such as atomic steps, vacancies, and adatoms. We have examined

the consequences of exposing ionic, single-crystal surfaces simultaneously to energetic radiation (UV photons, keV electrons) and relatively low pressures of water vapor. Dramatic synergisms are observed, presumably due to chemisorption-induced bond weakening. We describe mechanistic studies of this phenomenon, including time-resolved measurements of the response of the radiation-induced particle emission to transients in water pressure (@DELTA@P@sub H2O@ 10@super -9@ to 10@super -5@ Pa). Both ion and neutral particle emission rates respond to these transients on time scales of micro- to milli-seconds. We use scanning electron and atomic force microscopies to image the surface modifications associated with this loss of material, beginning with the removal of single atomic layers along step edges and eventually yielding micron-scale pits. We present AFM evidence that material removal is highly localized and defect mediated. We suggest that radiation-induced defects produce atomic-scale structures along steps (e.g., kinks) that peel off when the associated chemical bonds are weakened by sorbed, water-derived radicals. Supporting evidence from spectroscopic and microscopic data on exposed surfaces will be presented. We also show novel nanostructures produced by exposure to energetic radiation in the presence of water vapor. @FootnoteText@ @footnote 1@This work was supported by the Department of Energy.

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