Wednesday Morning, October 4, 2000

Semiconductors

Room 306 - Session SC+EL+SS-WeM

Passivation and Etching of Semiconductors

Moderator: Y.J. Chabal, Bell Laboratories, Lucent Technologies

8:20am SC+EL+SS-WeM1 Infrared Study of the Initial Stages of Etching of Si Electrode Surfaces in HF Solution, Y. Kimura, Y. Kondo, J. Nemoto, M. Niwano, Tohoku University, Japan

Porous Si has been a promising class of materials used for light-emitting devices and nano-scale electronic devices, and a number of theoretical and experimental investigations have been performed on the formation and optical properties of porous Si. A conventional method of synthesizing porous Si is to apply an anodic (positive) potential to a Si electrode in aqueous etching solutions such as dilute hydrofluoric acid (HF) solution. However, the mechanism of pore formation has not been fully understood. In order to control the structure of porous Si, we need an understanding of the microscopic etching process of Si electrode surfaces during immersion in etching solution. In this study, we have investigated in-situ and in real time the etching process on p-Si(100), (111), and (110) electrode surfaces in dilute HF solution, using infrared absorption spectroscopy (IRAS) in the multiple internal reflection (MIR) geometry, and analyzed infrared absorption spectra in the Si-H stretching vibration region of the electrode surface to examine how surface Si atoms are removed. At electrode potential below approximately 1 V, surface roughening occurs to produce hydride species in the vicinity of the electrode surface. At initial stages of etching of a Si(100) electrode, monohydride species is dominantly populated by the removal of dihydride species on the topmost layer of the electrode surface. We suggest that removal of monohydride species is favored over that of dihydride species, leading to the formation of pores on the etched surface. At electrode potential above 1 V, all the hydride species are etched away, leading to electropolishing of the surface. For electrochemical etching of Si(110), monohydride species are removed from the topmost layer to populate dihydride species on the second layer of the surface. For etching of the Si(111) surface, it appears that removal of surface Si atoms more favorably takes place at step sites than on terraces.

8:40am SC+EL+SS-WeM2 Electrical Transport at Chemically Modified Silicon Surfaces, O. Hul'ko, R. Boukherroub, C. Mark, S.N. Patitsas, H.Z. Yu, G.P. Lopinski, National Research Council Canada

We are exploring methods for tailoring the electrical conductivity of silicon surfaces via the covalent attachment of atomic and molecular adsorbates. A method for studying the electrical transport properties of wet-chemically modified silicon surfaces has been developed and applied to study of chlorine terminated Si(111). Resistivity measurements (4-probe, van der Pauw geometry) were performed on low doped n-type Si (111) substrates patterned with titanium silicide contacts. These contacts were found to withstand the RCA clean and ammonium flouride etching procedures required to prepare the atomically flat, highly ordered hydrogen terminated Si(111) surfaces that are the starting point for fabricating chemically modified Si(111) surfaces. Chlorine-termination was achieved by UV irradiation of H/Si(111). The resulting surfaces were characterized by STM and Auger, indicating a monolayer of Cl in an ordered (1x1) structure. These Cl/Si(111) surfaces showed a significant (at least one order of magnitude) increase in conductivity with respect to H/Si(111). Under ambient conditions the conductivity decreased exponentially with a time constant of ~1hr., eventually returning to the value measured before chlorination. The enhanced conductivity of the Cl/Si(111) surface is attributed to increased carrier density in the near surface region due to upward band banding caused by the electron withdrawing nature of the adsorbed chlorine. In order to explain the increased conductivity this band bending must be sufficient to cause inversion (>0.6eV). Capacitance measurements indicate that the near surface carrier concentration is increased by at least a factor of 1000 upon chlorination, consistent with the observed conductivity change. Results on other chemically modified surfaces will also be presented.

9:00am SC+EL+SS-WeM3 Using Micromachined Test Patterns to Study Surface Chemistry: An Investigation of Etchant Anisotrophy, *M.A. Hines*, *R.A. Wind*, Cornell University

We have developed a new technique for the rapid quantification of etchant anisotropy (i.e. orientation-dependent etch rates), which uses micromachined test patterns. Although macroscopic anisotropy cannot be inverted to provide detailed atomic mechanisms, macroscopic anisotropies do provide important clues to the underlying chemical reactions. For example, an etchant that produces atomically flat silicon surfaces -- a "perfect" etchant -- must selectively etch all defect sites, while leaving the flat surface virtually untouched. Macroscopically, this implies that a perfect etchant must attack vicinal surfaces much more rapidly than flat surfaces. Our standard test pattern consists of 180 1°-wide wedges arranged in an evenly spaced, circular array. Each wedge is bounded by a different set of vertical planes, so the sides of each wedge etch with a characteristic, facedependent rate. Anisotropic etching leads to the development of a "flower pattern," which can be analyzed to yield absolute, face-spec ific etch rates of 180 surfaces simultaneously. Etch rates measured with this technique are in good agreement with those previously reported in the literature. This technique opens to door to a pseudo-combinatorial approach to etchant development. For qu a ntitative interpretation of these data, we constructed a simple model of orientation-dependent etching that is based on step-flow etching. We tested this model on a number of different anisotropic etchants, and the model performed surprisingly well. Interestingly, there was no evidence of direct step-step interactions or step coalescence on vicinal Si(111) surfaces during etching (within approx. 20° of the close-packed plane).

9:20am SC+EL+SS-WeM4 Etching of BPSG Films Using Anhydrous HF, A. Thorsness, G. Montano, A. Muscat, University of Arizona

The absorption of water within BPSG films and its affect on the rate and the product distribution on the surface during etching with anhydrous HF (AHF) has been studied with transmission FTIR and ellipsometry. Gas phase HF chemistries are currently used to selectively etch doped oxide films relative to undoped films for both DRAM and MEMs applications, but often require a post-process water rinse. BPSG films containing 3.5%B/4.0%P were deposited to a nominal thickness of 5K Å on 8" Si wafers containing a 2K Å TEOS buffer layer. Sets of 25 wafers were annealed after deposition to four different temperatures: as deposited (400°C), 500°C, 750°C, and 900°C. The films were etched at atmospheric pressure and at temperatures from 25 to 75°C in a commercial gas phase oxide etching tool (FSI Excalibur ISR) using AHF in a nitrogen carrier. Water uptake by the films did not saturate but increased at a steady rate as a function of annealing temperature during storage in a cleanroom. Absorbed water reacted with P=O producing P-OH groups. The induction time to start etching decreased with water absorption and loss of P=O. Based on relative bond strengths AHF attacks the P-O bonds first opening up the silicon dioxide lattice and producing both a P-bearing acid and product water. The product water H-bonds to the P-bearing acid creating a thin liquid film on the wafer surface. The liquid film supports etching of the stronger Si-O-Si and B-O-Si bonds and solvates etching products. The water H-bonded to the P-bearing acid lowers the activation barrier to breaking Si-O bonds by forming a (SiO)HOH complex. The weakened Si-O bond is more amenable to attack by a polar HF molecule. Metaphosphoric acid, pyrophosphoric acid, boric acid, boron trifluoride, and water were present in the liquid films after etching. The relative amount of these products was a strong function of the annealing temperature.

9:40am SC+EL+SS-WeM5 Etching of Polymer-like a-Si:H Films by Impact of H, *T. Zecho, B. Brandner,* Universitaet Bayreuth, Germany; *J. Biener, J. Kueppers,* Max-Planck-Institut fuer Plasmaphysik (EURATOM Association), Germany

Etching of a-Si:H thin films with H atoms is a well known phenomenon from earlier studies. Nevertheless, the product distribution and the temperature dependence of the absolute etching rate could not be unambiguously determined. The present study was performed in order to quantify the etching rate by direct detection of the etching products during H admission and to determine to what extent higher silane species contribute to the etching process. A-Si:H films in a thickness range ca 1 to 100 nm were deposited at 300 K by ion-beam-deposition on a Pt(111) substrate and characterised by AES, TPD, HREELS and ELS. The films grow in a twodimensional fashion and show a polymer like structure with a hydrogen content of about 40 %. The thermal stability of the films is limited by the formation of a Pt silicide commencing ab about 500 K which proceeds at the a-Si:H/Pt interface. In accordance with the exothermic formation of volatile silanes a constant etching rate of about 1 % between 100 K and 300 K was found with about equal contributions from the silane and higher silanes channels. In this temperature range even minor impurities lead to a decrease of the etching rate. From 300 K to 500 K the etching rate decreased roughly linear to 0.1 % due to the growing thermal instability of the higher silanes. Therefore at 500 K silane was the only detected etching product. The formation of both silane and higher silanes proceeds via a

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direct interaction of atomic hydrogen and the corresponding precursor species.

10:00am SC+EL+SS-WeM6 Reaction Mechanism of Si(100) Etching by Mass- and Energy-Selected Cl+ Beams, S.M. Lee, M. Lu, J.W. Rabalais, University of Houston

Plasma etching of semiconductor materials is a standard manufacturing technique used in integrated semiconductor industries. Due to the high operational pressures used in this process, it is difficult to study the basic etching mechanism. While plasma etching is a dynamic process, many studies have been done on the more static systems using analysis techniques like temperature programmed desorption (TPD). In this work, the kinetic energy and temperature dependencies of CI+ beam etching of Si (100) have been studied by Auger electron spectroscopy (AES), X-rav photoelectron spectroscopy (XPS), reflection high energy electron deflection (RHEED), and positive and negative energy-filtered secondary ion detection. Ion kinetic energies were varied over the hyperthermal range of 1 - 500 eV and sample temperatures were varied over the 25 -700° C range. Chemical etching dominates in the low energy range, while both chemical and physical etching processes are prevalent at the higher energies. Both the AES and XPS results demonstrate that the amount of CI deposited on the surface is a strong function of the ion energy. The RHEED study of the surface crystallinity clearly showed the existence of synergetic effects due to simultaneous ion bombardment and annealing. A nearly ideal (2x1) surface reconstruction was obtained under the conditions of 100 eV Cl+ etching at 600°C. AES analysis demonstrated that the main source of surface disordering at lower temperatures and lower kinetic energies is residual CI in the surface region. The etching products, the kinetic energy distribution of each species, and the critical kinetic energy for the etching process have been measured for different temperatures by using the positive and negative ion detector. The overall reaction mechanism is discussed based on the results obtained.

10:20am SC+EL+SS-WeM7 Deuterium Etching of the Si-rich SiC(0001)-(3x3) Surface Reconstruction, C.R. Stoldt, C. Carraro, R. Maboudian, University of California, Berkeley

The low-energy electron (LEED) pattern of the SiC(0001)-(3x3) surface reconstruction undergoes a conversion from (3x3) to (1x1) upon exposure to atomic hydrogen (and deuterium). Using high-resolution electron energy loss spectroscopy, Auger electron spectroscopy, LEED, and temperature programmed desorption, we have determined that this conversion is due to etching and disordering of the uppermost Si layers. With increasing deuterium exposure at 320 K, etching results in depletion of the Si adlayer and formation of SiD surface species. At high deuterium exposure, observation of the C-D stretch mode indicates the onset of bulk silicon carbide etching. SiD@sub 2@ and SiD@sub 3@ surface species, known intermediates in the Si etching process, are observed with deuterium exposure at 180 K.

10:40am SC+EL+SS-WeM8 Variable Temperature Study of Hydrogen and Deuterium Passivation of the Si(100)-2x1 Surface using the Scanning Tunneling Microscope, M.C. Hersam, N.P. Guisinger, K. Cheng, J. Lee, J.W. Lyding, University of Illinois

Deuteration of dangling bonds at the Si/SiO@sub 2@ interface has led to a significant reduction of hot carrier degradation in complementary metaloxide-semiconductor (CMOS) circuits. Although CMOS transistors are annealed in a D@sub 2@ environment, the presence of H in the oxide leads to the interface being unavoidably exposed to both H and D during the passivation process. Thus, an understanding of the parameters that affect the equilibrium quantities of H and D on Si surfaces is of notable interest. In this paper, the relative concentrations of H and D on the Si(100)-2x1 surface are studied following in situ passivation under conditions of equal H and D pressure. Electron stimulated desorption with a scanning tunneling microscope allows for atomically precise determination of the H and D levels. The ratio of D to H on the Si(100) surface is measured to be ~50 and ~5 following monolayer passivation at 350 K and 650 K respectively. This behavior can be gualitatively understood through a statistical thermodynamics model. Ultimately, the magnitude of the D:H ratio and its inverse relationship with passivation temperature result from the difference in the vibrational frequencies for Si-H and Si-D bonds. These results imply that the optimal deuteration of silicon dangling bonds in the presence of background H should occur at low sample temperatures. Since CMOS processes are continually reducing their thermal budgets to accommodate additional metal layers and novel materials (e.g., low k dielectrics), this paper fundamentally suggests that

deuteration of the Si/SiO@sub 2@ interface could improve as processing temperatures are inevitably lowered in the future.

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