Electronic Materials and Processing Division
Room 608 - Session EM-TuM

Si Surface Chemistry and Etching, Passivation, and Oxidation

Moderator: J.E. Crowell, University of California, San Diego

8:20am **EM-TuM1 Structural Transition Layers at the Interface of SiO@sub 2@/Si(100) Fabricated by Ozone***, **K. Nakamura**, H. Itoh, A. Kurokawa, S. Ichimura,* Electrotechnical Laboratory, Japan*; K. Koike, G. Inoue, T. Fukuda,* Iwatani International Corporation, Japan

A novel processing technique for oxidation with rapid growth kinetics at lower substrate temperature is strongly required to fabricate a much thinner silicon dioxide film 1nm thickness. This was confirmed by a change of the etching rate of SiO@sub 2@ film with dilute hydrofluoric acid solution. Such thinner region of transition layers in the ozone-oxide was implemented either on clean Si(100)2x1 or on Si(100) with an already existing native oxide film at 300°C or more. However, exposure of ozone to Si(100) with an already existing thermally grown oxide film, for example at 350°C, caused no change in the distribution of transition layers in the oxide. This contrast indicates that the oxide growth by ozone or the further oxidation of lower oxidized silicon atoms in the native oxide by ozone formed transition layers with much less thickness, while highly oxidized silicon atoms in the thermally grown oxide film remained unreacted even by reactive ozone. Structural transition layers on the opposite side of the interface, i.e. in the substrate, will also be discussed.

8:40am **EM-TuM2 Infrared Spectroscopy as a Probe of Semiconductor/Dielectric Interfaces: Growth and Structure of SiO@sub 2@ on Si***, **K.T. Queeney**, M.K. Weldon, Y.J. Chabal, K. Raghavachari,* Bell Laboratories, Lucent Technologies **INVITED**

The structure and quality of the Si/SiO@sub 2@ interface are crucial to the performance of transistors with gate oxide thicknesses < 20 Å. We have exploited the intrinsic sensitivity of infrared absorption spectroscopy to microscopic chemical environment in order to elucidate structural details of this interface between crystalline Si and amorphous SiO@sub 2@. Infrared spectra of thermally grown SiO@sub 2@ are acquired as a function of film thickness by etchback of device-quality films. Modeling the mechanical and optical properties of these films reveals that substoichiometry at the Si/SiO@sub 2@ interface dominates the spectra of ultrathin (< 10 Å) SiO@sub 2@; different thermal histories are shown to affect the quality of this "transition region." To understand the microscopic structure of this interfacial substoichiometry, we have grown and characterized a model Si/SiO@sub x@ interface via controlled H@sub 2@O reaction of Si(100)-(2x1) in ultrahigh vacuum. Coalescence of dimer-based silicon epoxide species (capped by triangular Si-O-Si linkages) into an extended silicon-oxygen network results in the birth of SiO@sub x@ phonon modes (975 and 1130 cm@super -1@) whose microscopic structural origins are for the first time well understood. This epoxided interface is trnasformed at room temperature into high-quality SiO@sub 2@, and the mechanism for room-temperature H@sub 2@O-induced oxidation is compared to that observed for technologically relevant surface terminations.

9:20am **EM-TuM4 Real Time Observation on Si(001) Surface Oxidation by Scanning Tunneling Microscopy***, **K. Miki**,* Electrotechnical Laboratory, Japan*; Y. Kudo, M. Murata, K. Yamabe,* Tsukuba University, Japan

We have succeeded in real time observation on oxidation of Si(001) surface by scanning tunneling microscopy at elevated temperatures up to 1100 K. First we made clear the boundary between etching and oxidation regions. At the 900 K, etching both from step edges and in the terrace was dominant at low oxygen partial pressure under $1 \times 10^(-5) Pa$ while we observed oxidation island nucleation over this critical pressure. Under low rate oxidation, we found that etching is allowed together and it stops in the vicinity of the oxidation island. Our map whether etching or oxidation occurs is consistent of the previous reports. At the high temperature region the boundary is good agreement with the previous report by Gelain and et al. [Oxidation of metals 3 (1971) 139]. In the low temperature region under 870 K the oxidation speed of the first 1 ML is independent of temperature and this results is consistent with reflection electron microscopy experiment by Watanabe and et al. [Phys. Rev. Lett. 80 (1998) 345] We found three types of absorbant. Although the one type is still a misery, we could identify that one is atomic oxygen adsorbant in the center of a Si dimer and the other is back bond oxidation. First one was well seen in the initial stage, as oxidation proceeded the latter became more dominant. This observation suggests that oxidation of Si(001) surface has dual species at least, which is previously reported by Engstrom and et al. [Surf. Sci. 256 (1991) 317]. Backbond oxidation extended normal to dimer rows as ordered spots. The ordering eventually came to have disordering around 1ML oxidation. This suggests that stress during is very important even in the initial stage.

9:40am **EM-TuM5 Scanning Tunneling Microscopy Study of Surface Morphology of Si(111) after Synchrotron Radiation Stimulated Desorption of SiO@sub 2@***, **Y. Gao**, T. Miyamae, H. Mekaru, T. Urisu,* Institute for Molecular Science, Japan

We have used scanning tunneling microscopy to investigate the surface morphology of Si(111) after the native SiO@sub 2@ layer was removed by synchrotron radiation stimulated desorption at 650 °C. The surface shows large regions of atomically flat Si(111)-7x7 structure. An interesting feature of the surface is the formation of atomic steps nicely registered to the crystal structure, and the pinning of the steps by nanometer scale dust is evident. This is in sharp contrast to Si(111) surfaces after thermal desorption of SiO@sub 2@ at temperatures 880°C and above, where the surface steps are much more irregular. The registration of the surface steps to the underlying crystal structure indicates that the surface atomic layer reaches thermodynamic equilibrium under synchrotron radiation at temperatures much lower than that necessary for thermal desorption of SiO@sub 2@.

10:00am **EM-TuM6 How Important are Second Nearest Neighbor Effects in Silicon 2p Photoemission Spectroscopy of Si/SiO@sub 2@ Interfaces?***, **J. Eng, Jr.**, K. Raghavachari,* Bell Labs, Lucent Technologies

The proper interpretation of Si 2p photoemission spectra of Si/SiO@sub 2@ interfaces has been a controversial topic since 1993, when Banaszak-Holl and McFeely proposed that second nearest neighbor effects can cause significant chemical shifts in Si 2p photoemission features.@footnote 1@ Their claims were based upon model Si/SiO@sub 2@ surfaces produced by the adsorption of H@sub 8@Si@sub 8@O@sub 12@ clusters on Si(100) at room temperature. Arguing that the clusters are bonded to Si(100) dimers through a single vertex (due to Si-H bond cleavage), they proceeded to correlate the relative peak positions and peak intensities with different Si species at the interface. This correlation led them to conclude that the entire formal oxidation state framework is inadequate for interpreting Si 2p photoemission spectra of Si/SiO@sub 2@ interfaces, and that second nearest neighbor effects are important. The key issue in this controversy is understanding how the H@sub 8@Si@sub 8@O@sub 12@ clusters bond to the Si(100) surface. Using transition state calculations, we present detailed mechanistic arguments which show that the clusters do not react with the Si(100) surface through Si-H bond cleavage, but rather through Si-O bond cleavage. The resulting "cracked" cluster allows us to predict the Si 2p photoemission features of the clusters on Si(100) using the conventional formal oxidation state model, without invoking second nearest neighbor effects. Finally, the normal mode frequencies of the "cracked" cluster are in excellent agreement with infrared studies of the clusters on Si(100). @FootnoteText@ @footnote 1@ M. M. Banaszak-Holl and F. R. McFeely, Phys. Rev. Lett., 71(15) (1993) p.2441.

10:20am **EM-TuM7 FTIR Studies of the Nitridation of Si(100)-(2x1) and Oxidized Silicon***, K.T. Queeney, **Y.J. Chabal**, J. Eng, Jr., K. Raghavachari,* Bell Laboratories, Lucent Technologies*; X. Zhang, E. Garfunkel,* Rutgers University*; S.B. Christman, E.E. Chaban,* Bell Laboratories, Lucent Technologies

We have investigated the incorporation of N into Si and SiO@sub 2@ with IR absorption spectroscopy, in order to elucidate the mechanisms by which nitridation and oxynitridation influence the structure and thus the electrical characteristics of Si/SiO@sub 2@ interfaces. Studies of the adsorption and decomposition of NH@sub 3@ on Si(100)-(2x1) demonstrate that the chemistry of this nitriding agent is governed by a combination of dissociative and molecular adsorption, with metastable NH@sub 3(a)@ characterized by a dramatically redshifted NH@sub 3@ deformation mode. Higher coverages and temperatures favor NH@sub 3@ dissociation into H and NH@sub 2@, followed by competing desorption and decomposition. The mechanism for N insertion into the Si substrate is studied via repeated cycles of NH@sub 3@ dosing and annealing with post-dosing of atomic H to identify discrete N-containing structures by the perturbation in @nu@(Si-H) frequencies. Oxynitride growth by reaction of NO on Si(100)-(2x1) reveals the interplay between oxygen and nitrogen, as both Si-O (~900 cm@super -1@) and Si-N (~775 cm@super -1@) modes exhibit frequencies distinct from those observed for pure oxide and nitride films. These fundamental growth studies are used to interpret structural details contained in the complex spectra of device-quality nitride and oxynitride films grown on Si.

10:40am **EM-TuM8 Silicon Passivation Chemistry for MEMS Technology*,*** ***R. Maboudian,*** University of California, Berkeley **INVITED**

Adhesion, friction , and wear are prevalent problems in a majority of micro-electro-mechanical systems (MEMS) devices. Since gravity is negligible at the dimension of most microstructures, understanding of surface interactions in MEMS is of paramount importance for controlling stiction phenomena. After a brief introduction to Si micromachining, I will discuss the use of various micromachined testing devices, such as cantilever beam arrays, in conjunction with other surface characterization techniques, such as X-ray photoelectron spectroscopy and atomic force microscopy, to measure the surface forces present between polycrystalline silicon surfaces and to manipulate them by utilizing various surface passivation treatments.

11:20am **EM-TuM10 STM Studies of the Site-specific Reactivity of Isopropanol in Aqueous Silicon Etching: Controlling Morphology with Surface Chemistry***, **M.A. Hines**, T.A. Newton, Y.-C. Huang, L.A. Lepak,* Cornell University

Aqueous silicon etchants play an important role in the fabrication of microelectromechanical systems (MEMS). To improve performance, a reputedly inactive chemical agent -- isopropanol [(CH@sub 3@)@sub 2@CHOH] -- is often added to the etchant. Not only does this simple additive reduce undercutting by up to 75%, it also produces much smoother etched surfaces, in part by suppressing the formation of pyramidal etch hillocks. Using a combination of STM measurements and kinetic Monte Carlo simulations, we will show that these morphological changes have a simple, chemical origin. The site-specific rates of isopropanol reaction on vicinal Si(111) surfaces were studied by kinetic competition with an etchant of known anisotropy and quantified using concentration-dependent changes in the etched surface morphology. The unique properties of isopropanol-enhanced etchants are explained by the relatively high reactivity of the isopropoxide ion. Once formed, the silicon isopropoxy species transiently suppresses etching at specific surface sites and modifies the anisotropy of the etchant.

11:40am **EM-TuM11 Removal of Native Oxide Employing Heated NH@sub 3@/NF@sub 3@ Mixture***, **H. Ogawa,*** The University of Tokyo, Japan*; T. Arai, T. Ichiki,* Toyo University, Japan*; Y. Takamura, Y. Horiike,* The University of Tokyo, Japan

The removal of the native oxide employing a heated NH@sub 3@/NF@sub 3@ mixture was studied using in-situ XPS and FTIR-ATR/RAS. The mixture was heated in an 13 mm diameter Al@sub 2@O@sub 3@ tube whose surface was wound by a resistive heater, then being exposed to a sample set on a stage cooled by a N@sub 2@ gas with room temperature. The chemical oxide was grown in a H@sub 2@SO@sub 4@/H@sub 2@O@sub 2@ solution. The NH@sub 3@/NF@sub 3@ mixture with partial pressure ratio of unity at a pressure of 1 Torr started to remove the oxide from a Al@sub 2@O@sub 3@ tube temperature of 500 °C. For the Si surface after removal of the oxide, new XPS peaks appeared at 103.8 eV in Si2p and 402.2 eV in N1s, respectively. Absorption spectra of Si-H(2100 cm@super -1@), N-H(stretching; 3330 cm@super -1@, bending;1454cmcm@super -1@) and Si-F (783 cm@super -1@) were also observed in the IR measurement. These results exhibit the presence of a (NH@sub 4@)@sub 2@SiF@sub 6@ film deposited on the Si surface after removal of the oxide.@footnote 1@The film desorbed readily at 100 °C in a vacuum and then was terminated by hydrogen. The higher the partial pressure, the faster the oxide removal rate, whereas NH@sub 3@ or NF@sub 3@ alone did not demonstrate any etching reaction. The result that the Al@sub 2@O@sub 3@ tube heated at higher temperature led to the higher etch rate implies generation of the oxide etchant within the tube. Thus, NH@sub 3@ and NF@sub 3@ were introduced separately to two tubes, and when NF@sub 3@ alone was heated, the present reaction was confirmed. The result implies thermally decomposed NF@sub 3@ reacts with NH@sub 3@, generating the oxide etchant. The removal rate ratio of thermal grown SiO@sub 2@ to BPSG (boron phosphorus silicate glass) films was almost unity. It is well known that the usual HF solution produces about ten times higher etch rate for BPSG than for the thermal SiO@sub 2@. Accordingly, this technology allows us to offer a new dry cleaning method of the contact hole surface in ULSI multi-level interconnection process. @FootnoteText@ @footnote 1@M. Hirose, S. Yokoyama and Y. Yamakage: J. Vac. Sci. Technol., B3 (1985)1445.

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