Electronic Materials and Processing Division
Room 314/315 - Session EM1-WeA

Si Surface Chemistry

Moderator: M.K. Weldon, Bell Laboratories, Lucent Technologies

2:00pm **EM1-WeA1 Understanding the Evolution of Surface Morphology during Chemical Etching*, M.A. Hines,*** Cornell University*; J. Flidr, Y.-C. Huang, T.A. Newton,* Cornell University, US **INVITED**

In this talk, I will discuss the evolution of surface morphology during the etching of Si(111) by NH@sub 4@F(aq). By combining STM measurements of surface morphology with kinetic Monte Carlo simulations of the etching process, we are able to obtain microscopic information on surface reaction mechanisms. We find that long-range surface roughness can be suppressed by a low density of monolayer-deep etch pits on an otherwise "perfect" surface. On surfaces miscut in the direction, Si(111) etches via a step-flow mechanism that is nucleated by slow etching into the step and then propagated by rapid etching of the nucleated kinks -- the steps "unzip" in a direction parallel to the step. Without terrace etching, individual steps would etch independently, and the long-range surface roughness, which is reflected in the terrace width distribution, would be comparable to that expected of an equilibrium surface. If there is a small probability of terrace etching, the steps repel one another through a kinetic feedback effect that we term dynamic step-step repulsion. This effect is mediated by the anisotropic distribution of terrace pits -- wide terraces have a higher density of pits than narrow terraces. We also find that steps can self-pin during etching. This type of pinning is independent of contamination and is due to the formation of a relatively unreactive structure on the etching step. Once formed, this structure reacts slowly and acts as a self-propagating pinning site to further etching. Self-pinning can drive a morphological transition that leads to chemically induced step facetting. In spite of this pinning, the steps still etch by step-flow.

2:40pm **EM1-WeA3 Structure of a Passivated Ge Surface Prepared from Aqueous Solution*, P.F. Lyman,*** Northwestern University*; D.T. Keane,* Northwestern University and DND CAT*; D.L. Marasco, T.-L. Lee,* Northwestern University*; M.J. Bedzyk,* Northwestern University and Argonne National Lab

We investigated the local structure and order of a aqueously sulfided Ge(001) surface using x-ray standing waves. The adsorption of a group VI element on the Ge(001) surface could satisfy all of the substrate dangling bonds by occupying a bridge site. Such a surface would be expected to be both chemically and electronically passivated, perhaps suppressing surface carrier recombination. In the present study, S/Ge(001) surfaces prepared in aqueous (NH@sub 4@)@sub 2@S solution (diammonium sulfide) exhibited a S coherent position P@sub 004@ of 0.90 ± 0.01, implying that the S adsorption height is 1.27 Å ± 0.01 Å. This closely corresponds to the expected adsorption height for S residing in a bridge site. This finding supports the local geometry inferred for aqueously sulfided Ge(001) by previous workers.@footnote 1@ That study concluded that a single atomic layer of S binds to the surface, residing in the a (1x1) bridge-bonded configuration. However, the present studies showed a low, repeatable value of 0.15 for the coherent fraction. The simplest explanation for these observations is that, in addition to an ordered S monolayer at the interface, a ~5 ML sulfided Ge layer is formed during the chemical passivation treatment. Although this model conflicts with the conclusions of Ref. 1, such an interface is not unlike the native oxide of Si, where several atomic layers of passivating silicon oxide readily form. We are presently conducting other tests of the S/Ge(001) surface to determine the nature of this interface more completely. @FootnoteText@ @footnote 1@G. W. Anderson, et al., Appl. Phys. Lett. 66, 1123 (1995).

3:00pm **EM1-WeA4 Reflectance Difference Spectroscopy of Ge / Si(001)*, V. Zielasek*,** *S.G. Jaloviar, M.G. Lagally,* University of Wisconsin, Madison

Reflectance difference spectroscopy (RDS) has proven to be an easy-to-use tool to monitor semiconductor epitaxy, especially of III-V systems. The origins of the surface optical anisotropy, however, are not yet fully understood. Several calculations for dimerized Si(001) terraces and lately for Ge / Si(001) have been reported and compared with experimental RD spectra from highly vicinal surfaces with the conclusion that steps do not produce an RD signal.@footnote 1@ Recent experiments, however, demonstrate that on vicinal Si(001) with miscut angles even as low as 1° the steps contribute significantly to the RD signal.@footnote 2@ From this, we expect that other morphological features, such as dimer vacancy lines formed during the epitaxy of Ge on Si(001), leave their fingerprint in RD spectra as well. We present a combined RDS and scanning tunneling microscopy (STM) study of Ge / Si(001) using both vicinal and superflat wafers as substrates. STM provides an accurate measure of step density and step structure. A macroscopic anisotropy of the superflat Si(001) surface is obtained by applying uniaxial elastic strain to the sample, leading to step movement and favoring domains with dimer rows oriented in the direction of lowest external compression. We find a shift in energy of RD spectral features with increasing Ge coverage in the sub-monolayer regime. Reversal of the surface stress anisotropy with increasing Ge coverage around 1 monolayer leads to a reversal in sign of the RD signal in the 2 - 4 eV range after applying external strain. For superflat and vicinal Si(001) 4° [110] with similar Ge coverages and annealing temperatures both the RD spectra and the morphologies of the growing films differ. We discuss the relationship of stress induced by Ge adsorption and external strain effects, focussing on their influence on the RD spectra. Supported by NSF, ONR, and Alexander von Humboldt-Stiftung (V.Z.) @FootnoteText@ @footnote 1@J.R. Power et al., Phys. Rev. Lett. 80 (1998) 3133. @footnote 2@S.G. Jaloviar, J.-L. Lin, M.G. Lagally, submitted.

3:20pm **EM1-WeA5 Second Harmonic Study of Ge/Si(100) and Si@sub 1-x@Ge@sub x@(100) Films*, P.S. Parkinson*,** *D.E. Brown, M.C. Downer, J.G. Ekerdt,* University of Texas, Austin

Second harmonic generation (SHG) allows real-time, in-situ measurement of hydrogen coverage on intrinsic silicon. Thus, SHG has been used by this group to perform hydrogen desorption measurements and growth rate calculations on intrinsic silicon.@footnote 1@ Our current challenge is to develop SHG as a tool to study the Si@sub 1-x@Ge@sub x@(100) alloy surface. We present studies of the SiGe/Si(100) and the Ge/Si(100) systems in vacuum around the E@sub 1@ critical point using SHG. In Ge@sub 2@H@sub 6@ atomic layer epitaxy (ALE) on Si(100), the SH intensity increases linearly with Ge coverage; below 5 ALE cycles (approximately 1.5 ML). Further deposition causes a continuous decrease in the signal intensity and a blue shift in the spectra. Hydrogen passivation of the surface leads to substantial quenching of the signal which reveals the sensitivity of the SH response to the near-surface Ge composition. Monitoring the growth of Si@sub 1-x@Ge@sub x@(100) films, with SHG we observed an initial rise in the SH intensity and then a decrease as the films became rougher and thicker. The time constant for the initial rise became shorter with increasing Ge film composition. Spectra of strained smooth SiGe films showed that the SH intensity at the peak maxima increased with increasing Ge film composition. Also, hydrogen saturation of the film surfaces led to an order of magnitude decrease in the SH response, similar to the Ge/Si(100) system. Thus, the initial rise in SH intensity during growth may correspond to the development of the near-surface Ge composition profile at the leading edge of growth. SH intensity decreased with increasing atomic hydrogen coverages on the SiGe/Si(100) surface; the same trend observed on intrinsic Si(100). Therefore, the SH response to hydrogen coverage in the alloy system might be explainable within the framework of models proposed for the H/Si(100) system.@footnote 2@ @FootnoteText@ @footnote 1@ Xu et al., Appl. Phys. Lett., 71, 1376,(1997). @footnote 2@ Dadap et. al., Phys. Rev. B, 56, 1, (1997).

3:40pm **EM1-WeA6 Silicon Epoxide: Fundamental Intermediate in Si(100) Oxidation***, A.B. Gurevich,* Columbia University*; M.K. Weldon,* ***Y.J. Chabal****, B.B. Stefanov, K. Raghavachari,* Bell Laboratories, Lucent Technologies

Understanding the growth and formation of thin oxides is critical to the development of high quality gate oxides. However, obtaining a detailed structural picture of interfacial SiO@sub 2@ poses a formidable scientific challenge due to the lack of long-range order and the critical dependence on processing parameters. We have therefore investigated with infrared absorption spectroscopy the water-induced oxidation of Si(100)-(2x1) under ultra-high vacuum conditions, as a prototypical silicon-oxide system: the water is initially dissociated into H and OH on each surface dimer; as the temperature is increased to 675K, the Si-Si dimer becomes the first target for oxygen insertion into the surface, facilitating in turn the subsequent incorporation of O into the Si backbonds.@footnote 1@ We show here that, upon dehydrogenation at higher temperatures (900K), a surprising structure is formed. The combination of high resoluton IR spectroscopy and density functional cluster calculations can, for the first time, identify this triangular SiOSi sub-unit, termed silicon epoxide, based on subtantially lower Si-O stretch frequencies (780-990 cm@super -1@) and smaller isotopic shifts (20-30 cm@super -1@) compared to those of known oxide structures. These silicon epoxides are similar to COC structures well-known in organic chemistry and characterized by a shorter Si-Si bond (2.4Å). We demonstrate that epoxides are the thermodynamically favored product upon dehydrogenation when three or more oxygen atoms are agglomerated. These epoxide structures are stable at intermediate annealing temperatures (800-1000K) and are observed upon pure oxygen exposure as well. They therefore constitute a metastable intermediate in the growth of thermal gate oxides, and are expected to be preferentially formed both in small molecules and at silica interfaces. @FootnoteText@ @footnote 1@ M.K. Weldon, B.B. Stefanov, K. Raghavachari and Y.J. Chabal, Phys. Rev. Lett. 79, 2851 (1997).

4:00pm **EM1-WeA7 Structure of Ultrathin Silicon Oxide - Silicon Interfaces Studied by Ultraviolet Photoelectron Spectroscopy*, J.W. Keister,*** *J.E. Rowe,* North Carolina State University*; J.J. Kolodziej,* Rutgers University*; H. Niimi,* North Carolina State University*; T.E. Madey,* Rutgers University*; G. Lucovsky,* North Carolina State University

Device-grade ultrathin (9-18 Å) films of silicon dioxide, prepared from crystalline silicon by remote-plasma oxidation, are studied by the surface-sensitive method of ultraviolet photoelectron spectroscopy. The 2p core-level spectra for silicon (at ~100 eV binding energy) show evidence of five distinct states of Si. These peaks are attributed to the five oxidation states of silicon between 0 (the Si substrate) and +4 (the thin SiO@sub 2@ film), although the precise configuration has recently been called into question.@footnote 1@ We find that the peaks for Si@super 1+@ through Si@super 4+@ are shifted relative to the Si@super 0@ bulk peak to higher binding energy by 0.92 eV, 1.90 eV, 2.51 eV and 3.86 eV. The relatively weaker signal found for the three intermediate states (+1, +2, and +3) is attributed to silicon atoms at the interface between these two materials. Estimates of the interface thickness from the intermediate valence signal agree with the value reported earlier of 3-5 Å (~ 2 ML).@footnote 2,3@ In this work, the position and intensity of the five peaks are measured as a function of post-growth annealing temperature (700 - 900 °C), crystal orientation, and incorporation of N@sub 2@ in the reactant gas flow. One result we have found is that annealing produces more abrupt interfaces, but never more abrupt than about one or two monolayers. This comes from the observation of a sudden drop in the interface thickness (in particular the Si@super 2+@ peak intensity) upon reaching 800-900 °C annealing temperature. A more complete and quantitative analysis will be presented which explores the effects of the other sample parameters and takes advantage of nonlinear least-squares fitting routines. @FootnoteText@ @footnote 1@McFeely, Zhang, Banaszak-Holl, Lee, Bender J. Vac. Sci. Tech. B 14(4), 2824-2831 (1996). @footnote 2@Himpsel, McFeely, Taleb-Ibrahimi, Yarmoff, Hollinger, Phys. Rev. B 38, 6084-6096 (1988). @footnote 3@Himpsel, Meyerson, McFeely, Morar, Taleb-Ibrahimi, Yarmoff Core Level Spectroscopy at Silicon Surfaces and Interfaces, in Campagna and Rosei, eds. Photoemission and Absorption of Solids and Interfaces with Syncrotron Radiation (Proceedings of the International School of Physics "Enrico Fermi", Course CVIII, Varenna, Italy. 1988.) North-Holland/Elsevier Science Publishers: 1990, pp. 203-236.

4:20pm **EM1-WeA8 Influence of Rapid Thermal Annealing on Vicinal Si(111)/SiO@sub 2@ Interfaces Investigated by Optical Second Harmonic Generation.*, J.F.T. Wang,*** *G.D. Powell, D.J. Stephens, R.S. Johnson, B.R. Solazzo, Y. Wu, D.E. Aspnes, G. Lucovsky,* North Carolina State University

We have studied optical Second Harmonic Generation, SHG, from Si/SiO@sub 2@ interfaces formed by 800°C thermal oxidation of vicinal Si(111) surfaces off-cut approximately 5 degrees in the 112bar direction. Changes in the rotational anisotropy of the SHG were observed when interfaces were annealed at temperatures between about 800 and 1000°C. We have analyzed the rotational anisotropy by including harmonic functions that reflect the C@sub 1v@ and C@sub 3v@ symmetry of the vicinal Si(111) surface corresponding respectively to steps and terraces of the vicinal surfaces. The relative phase difference, @phi@@sub 13@, between the C@sub 1v@ and C@sub 3v@ harmonic contributions is strongly influenced by the Rapid Thermal Annealing, RTA, temperature. In this paper we compare our results with an incident wavelength of 800 nm (or 1.55 eV) from a Ti:sapphire laser to previous reported work with incident wavelength of 1053 nm (or 1.17eV) using a Nd:YLF laser. The largest change in @delta@@phi@@sub 13@, ~72 degrees, using the 1.55 eV laser source is between 800°C and 900°C which is consistent with the previously reported studies using the Nd:YLF laser.@footnote 1@ However, @delta@@phi@@sub 13@ is larger for a pump beam of 800 nm compared to that of 1053 nm, ~72° compared to ~38°. These results are consistent with the anharmonic oscillator model if the laser energy is less than about one-half of the resonance energy of the anharmonic oscillator.@footnote 2@ Finally, it is important to note that annealing at 900°C has been shown to reduce sub-oxide interfacial bonding introduced at the Si/SiO@sub 2@ interface during thermal and plasma-assisted oxidation processes@footnote 3@ suggesting that changes in @delta@@phi@@sub 13@ between 800 and 900°C anneals in the SHG response are associated with changes in interface bonding that include a reduction of the extent of transition regions with the sub-oxide bonding arrangements. @FootnoteText@ @footnote 1@C. H. Bjorkman, C. E. Shearon, Jr., Y. Ma, T. Yasuda, G. Lucovsky, U. Emmerichs, C. Meyer, K. Leo, and H. Kurz, J. Vac. Sci. Technol. A11(4), 964 (1993) @footnote 2@Y. R. Shen, The Principles of Nonlinear Optics (John Willey & Sons, New York, 1984) @footnote 3@G. Lucovsky, A. Banerjee, B. Hinds, C. Claflin, K. Koh and H. Yang, J. Vac. Sci. Technol. B15, 1074 (1997), and references therein.

4:40pm **EM1-WeA9 The Initial Stages of Si(100) Oxynitridation by NO: An Infrared Study*, J. Eng, Jr.,*** *K.T. Queeney, Y.J. Chabal, B.B. Stefanov, K. Raghavachari,* Bell Laboratories, Lucent Technologies*; X. Zhang, E. Garfunkel,* Rutgers University

The oxynitridation of Si(100) by N@sub 2@O has been studied extensively because the electrical properties of thin silicon oxynitride films are superior to those of silicon oxide films with the same thickness. Although the oxynitridation mechanism is not completely understood, it is generally believed that N@sub 2@O decomposes to form NO under industrial processing conditions, and that NO is the species ultimately responsible for oxynitridation. On this basis, we have chosen to study the initial reaction of NO with clean Si(100) by using infrared spectroscopy, Auger electron spectroscopy, and low energy electron diffraction. We conclusively show that NO dissociatively adsorbs on Si(100) at room temperature, thereby resolving an existing debate in the literature.@footnote 1@ Heating the NO/Si(100) surface to 650 @degree@C causes the formation of SiO@sub x@N@sub y@ structures which have strong characteristic modes at 858, 989, and 1057 cm@super -1@. These modes have been assigned based on isotopic labeling studies involving @super 15@N@super 16@O and @super 14@N@super 18@O, as well as ab-initio density functional calculations. Auger studies show that heating to 850 @degree@C removes oxygen, but the nitrogen 379 eV KLL feature is not attenuated. However, the Si-H vibrational features observed in H atom post-dosing experiments designed to probe the surface after heating to 850 @degree@C are similar to those obtained by exposing clean Si(100) to H atoms, indicating that the N atoms reside in subsurface sites. Additional information about the Si-N modes is obtained by studying the adsorption and thermal decomposition of ammonia on Si(100) surfaces. @FootnoteText@ @footnote 1@ Y. Taguchi, M. Fujisawa, and M. Nishijima, Surf. Sci. Lett., 233 (1990) L251-252

5:00pm **EM1-WeA10 Growth and Analyses of Silicon Nitride Thin Films on Si(111) and Si(100)*, X.-S. Wang,*** Hong Kong University of Science & Technology, China*; N. Cue,* Hong Kong University of Science & Technology, China, Hong Kong, China

Silicon nitride is attractive for applications as dielectric and wide bandgap semiconductor materials. Using LEED, SPM, AES and XPS, we have analyzed geometric, thermodynamic and electronic properties of silicon nitride thin films grown on Si(111) and Si(100) substrates. The nitride films are prepared in two ways: (a) nitridation of Si substrates, i.e., by exposing clean Si samples to NH@sub 3@ or NO of various dosage and at substrate temperatures about 1150 K; (b) Si deposition under a flux of NH@sub 3@ or NO. In the second method, the substrate temperature can be kept significantly lower than 1150 K. On Si(111), the nitride thin films show a clear 8/3x8/3 superstructure. On nitrided Si(100), LEED shows a weak 1x2 + 2x1 pattern sometimes. Analysis of lattice structure of Si@sub 3@N@sub 4@ indicates that crystalline Si@sub 3@N@sub 4@ film epitaxy on Si(111) is feasible, while on Si(100) this is much more difficult. The nitride films show a remarkable thermal stability in comparison with silicon oxide films. Desorption of oxide films starts at about 1075 K, whereas the nitride films remain stable at a substrate temperature as high as 1350 K. Furthermore, surface crystalline order of the nitride films is preserved after air exposure and even after going through system baking. The implication of these results on application of nitride, oxide and oxynitride thin films in microelectronics will be discussed.

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