Surface Science Division
Room 6C - Session SS2+EM-TuA
Semiconductor Surface Chemistry

Moderator: R.M. Feenstra, Carnegie Mellon University

2:00pm **SS2+EM-TuA1 Medard W. Welch Award Address: Halogen Etching of Si with Emphasis on Atomic-Scale Processes***, **J.H. Weaver**[1],* University of Minnesota **INVITED**

Etching is the process of producing a pattern on a surface, and it is central to a great many technologies. Indeed, etching (material removal) plays a complementary role to growth (material addition), and product fabrication includes both etching and growth. This talk will review recent progress made in understanding surface etching of semiconductors. Emphasis will be on atomic-scale changes in surface morphologies for Si(100) etched with halogens, where the parameters that are controlled are the flux and the fluence of the beam and the reaction temperature of the substrate. The kinds of information that can be gained from atomic-resolution scanning tunneling microscopy will be highlighted. Etch morphologies will be linked to site-specific desorption energies, with consideration of terrace pitting and the formation of nanometer-scale patterns. The sequence of events leading to dihalide desorption and the role of vacancies will be described. Comparison of results for F-Si(100) and Cl-Si(100) shows the formation of defects in the second layer for F, a process that results in roughening rather than layer-by-layer etching observed for Cl.

2:40pm **SS2+EM-TuA3 Micrometer-scale "Grooves" and Step Bunching during Extended Oxidation-induced Etching of Si(001) Surfaces***, **J.F. Nielsen,*** The Ohio State University*; M.S. Pettersen,* Otterbein College*; J.P. Pelz,* The Ohio State University

We have used in-situ STM and ex-situ AFM to observe large-scale step rearrangement on Si(001) surfaces that were heated by DC current at ~1000@super o@C for 3-43 hrs in ~10@super -5@ Torr of oxygen. Depending on sample miscut and current direction, these conditions produced either (1) no significant step rearrangement, (2) large scale (5-10µm) step-bunched regions (with separation increasing roughly as t@super 1/2@), or (3) large "grooves", consisting of a highly-ordered sinusoidal step array with in-phase alignment. The grooved and step-bunched phases can coexist on the same wafer, forming neighboring semi-coherent patches extending over hundreds of microns. The interface between the two phases is remarkably sharp. The step-bunching was also observed on surfaces heated in vacuum (no oxygen), and may be similar to electromigration-related behavior reported by Doi et al.@footnote 1@ Regular arrays of "crossing steps" are also seen on the step bunched regions. It is not yet clear whether oxygen is required for the formation of the grooves. The grooves appear to be qualitatively different from the "wavy" steps reported by Tromp and Reuter@footnote 2@ in that they extend coherently over large areas and are not confined to sample regions of extremely low-miscut. We are currently mapping out the precise conditions necessary to produce each surface phase, and are using the wide terraces resulting from step-bunching in on-going studies of spontaneous step creation on ultra-flat Si(001) surfaces. @FootnoteText@ @footnote 1@ T. Doi, M. Ichikawa, and S. Hosoki, Phys. Rev. B. 55, 1864 (1997) @footnote 2@ R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. 68, 820 (1992).

3:00pm **SS2+EM-TuA4 The Structure of Steps on Hydrogen-Passivated Si Surfaces***, **A. Laracuente**, L.J. Whitman,* Naval Research Laboratory

Steps play a critical role during epitaxy, so knowing their structure is crucially important to understanding how films grow. There has been a considerable effort to determine the step structure on Si surfaces oriented near (001).@footnote 1@ On surfaces tilted toward (111), there are four distinct step configurations, single- and double-layer A-type and B-type steps, commonly denoted as S@sub A@, S@sub B@, D@sub A@, and D@sub B@. B-type steps are almost always "rebonded," with two extra atoms per unit cell at the step edge. The extra atoms halve the dangling bond density along each step and thereby make this structure energetically preferred over a non-rebonded configuration. On surfaces tilted more than 3°, only rebonded D@sub B@ steps occur. Because most industrial Si film growth happens in the presence of hydrogen, an accurate picture of such growth requires an understanding of how H affects the Si step structure and dynamics. It was recently predicted theoretically that non-rebonded steps should be energetically more favorable on H-terminated Si.@footnote 2@ We have now verified this prediction experimentally on a range of surfaces oriented from (001) to (114). We find that S@sub B@ steps "unrebond" after H-passivation, as predicted, completely altering the step energetics. Similarly, H passivation splits a large fraction of D@sub B@ steps into S@sub A@+S@sub B@ step combinations. These changes in step structure have a dramatic effect on the step dynamics and the resulting surface morphology, generally leading to much rougher surfaces. We will discuss how these changes can explain a variety of previous observations about the effects of H on Si film growth. @FootnoteText@ @footnote 1@ A. A. Baski, S. C. Erwin, and L. J. Whitman, Surf. Sci. 392, 69 (1997). @footnote 2@ S. Jeong and A. Oshiyama, Phys. Rev. Lett. 81, 5366 (1998).

3:20pm **SS2+EM-TuA5 Microscopy of Si(001) Surface Defects Produced by keV He Ion Irradiation at Low Temperatures***, K. Kyuno, **D.G. Cahill**, R.S. Averback,* University of Illinois, Urbana-Champaign*; J. Tarus, K. Nordlund,* University of Helsinki, Finland

The interactions of bulk point defects (interstitials and vacancies) with silicon surfaces influences microstructures and dopant profiles created by low-energy ion implantation. To gain insight on the migration of ion-induced defects and their interactions with surfaces, we use variable temperature scanning tunneling microscopy (STM) to measure the areal density of surface defects created by 5 keV He ion irradiation of Si(001) at low temperatures. Samples are irradiated to a dose of 1.7 and 3.4x10@super 13@ ions cm@super -2@ at 80, 130, 180, and 294 K, and imaged at the same temperature. Because of the background density of surface vacancies, we focus our analysis of the STM images on the densities of adatoms, dimers, and clusters formed by the ion bombardment. The density of these protrusions at 80 and 130 K is approximately linear in dose, independent of temperature, and in reasonable agreement with our molecular dynamics calculations of surface defect concentrations. At 180 K, the measured density of protrusions is enhanced by a factor of ~3; we interpret this result in terms of the onset of bulk defect migration. Surprisingly, the Si(001) surface appears to be a relatively inefficient trap for bulk defects under our experimental conditions; our results can be explained by the migration and trapping of defects formed within less than 1 nm of the surface.

3:40pm **SS2+EM-TuA6 A Variable Temperature Scanning Tunnelling Microscopy Study of Si(100) Etching Dynamics***, **C.F. Herrmann**, J.J. Boland,* University of North Carolina

The etching behavior of bromine on the Si(100) surface was investigated using variable temperature scanning tunneling microscopy (VT-STM). The clean Si(100) was initially dosed with bromine to passivate the surface. The passivated surface was then heated slowly and imaged simultaneously with no additional bromine exposure. STM images were taken at several temperatures from 600K to 750K to study the etching dynamics of Si(100) with bromine. The initial distribution of vacancies peaked at a single dimer unit and decayed monotonically to higher lengths. After further heating, repartitioning was observed and dimer vacancies of odd lengths were preferentially formed. The motion of single dimer vacancies was also observed in addition to a novel etching structure. The implications for chemical etching are discussed.

4:00pm **SS2+EM-TuA7 Dissociative Adsorption and Recombinative Desorption of H2 on Si(100)-2x1***, **F.M. Zimmermann**, X. Pan,* Rutgers University

The interaction of hydrogen with Si(100) is of considerable technological importance since hydrogen desorption is the rate-limiting step in low-temperature chemical vapor deposition of Si. Furthermore, this system is intriguing from a fundamental point of view, due to a multitude of unusual and remarkable experimental observations, such as desorption kinetics intermediate between first order and second order, and the so-called 'barrier puzzle': A large barrier to adsorption is seen in adsorption experiments, whereas in desorption dynamics experiments the desorbing molecules paradoxically show no signs of having traversed such a barrier. Using surface second harmonic generation, we have measured the adsorption and desorption kinetics as a function of surface temperature, H coverage, and exposure pressure. These measurements reveal more highly unusual kinetic behavior. Contrary to what is expected from Langmuirian site-blocking considerations, the sticking probability increases markedly with coverage, indicating a self-catalyzed adsorption mechanism. In addition, the sticking probability exhibits a pronounced dependence on exposure pressure, ruling out most 'simple' adsorption mechanisms. The observations are interpreted in terms of a self-catalyzed, barrier-less, inter-

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[1] **Medard W. Welch Award Winner**

dimer adsorption mechanism (observed with the STM by Biedermann, Knoesel, Hu, and Heinz, submitted to Phys. Rev.). Our model quantitatively explains the measured adsorption and desorption kinetics (temperature, coverage, and pressure dependence), and provides a natural explanation of the vexing barrier puzzle. Fitted model parameters are in very good agreement with independently obtained experimental and theoretical values.

4:20pm **SS2+EM-TuA8 Novel Mechanisms for Plasma Etch Front and CVD (Chemical Vapor Deposition) Growth Front Roughening***, **Y.-P. Zhao**[1], J.T. Drotar, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

Plasma etching and chemical vapor deposition (CVD) are major tools for thin film processing in microelectronic industry. Although kinetic roughening of thin films has attracted considerable attention in recent years, very little work has been focused on the study of surface roughening mechanisms during plasma etching and chemical vapor deposition. Here, we report a novel etch front roughening phenomenon during the plasma etching of Si(100) substrates. The surface power spectrum shows an obvious wavelength selection which does not occur in conventional noise-induced roughening. The average local surface slope is almost invariant while the vertical roughness grows as a power law in time, w ~ t^@beta@, with a growth exponent @beta@ = 0.91 ± 0.03. We develop a general non-local model to describe the roughening process in plasma etching based on the gas transport kinetics for a large Knudsen number. The flux of the reactive particles redistributes according to the re-emission mechanisms that are influenced by the surrounding morphology. Our extensive numerical calculations and Monte Carlo simulations for various re-emission modes show that @alpha@ (roughness exponent) ~ @beta@ ~ z ~ 1 for plasma etching, which is consistent with our experimental results. Our calculations demonstrate that the proposed model is universal in describing the roughening of plasma etching. In addition, the reverse of this model can be used to describe CVD growth. Our Monte Carlo simulations show that @alpha@ ~ @beta@ ~ 0, z ~ 2 for CVD growth. Detailed comparisons between local and non-local dynamic growth models, as well as the growth and etching processes will also be presented. @FootnoteText@ Work supported by NSF.

4:40pm **SS2+EM-TuA9 Resonance-Enhanced Multiphoton Ionization Studies of the Etching of Silicon by Molecular Chlorine***, **T.A. Barckholtz**, L. McDonough, S.R. Leone,* University of Colorado, Boulder

Laser ionization time-of-flight mass spectrometry is a powerful technique for characterizing the neutral products of the etching of semiconductor materials. We previously showed that single photon ionization (SPI), which uses the 9th harmonic of a Nd:YAG laser, provides excellent characterization of the neutral products of the etching of silicon by molecular chlorine, both thermally@footnote 1@ and during ion-enhanced etching.@footnote 2@ Two drawbacks of using the SPI technique are the low laser power available (ca. 10 µJ/pulse) and the lack of resolution of the state distributions (electronic, vibrational, rotational) of the products. To address these deficiencies, we recently implemented a Nd:YAG-pumped dye laser on an etching apparatus that enables resonant electronic multiphoton ionization (REMPI) schemes for the detection of the neutral species. Because of the greater laser power available (several mJ/pulse), the detection sensitivity has been dramatically increased. For example, the REMPI signal intensity of neutral atomic Si during thermal etching is approximately 200 times greater than the SPI intensity. Furthermore, complete state resolution of the Si spin-orbit (@super 3@P@sub 2@, @super 3@P@sub 1@, and @super 3@P@sub 0@) and metastable (@super 1@D@sub 2@) states is obtained. For SiCl, due to its broad rotational and vibrational distributions, the detection sensitivity is increased by a smaller factor, and only partially resolved state distributions are possible. We plan to use the enhanced sensitivity and partial state resolution to investigate the mechanism for the ion-enhanced etching of silicon by chlorine in greater detail than was possible with the SPI technique. The results of these studies will be compared with the predictions of published molecular dynamics simulations. @FootnoteText@ @footnote 1@Materer, N.; Goodman, R. S.; Leone, S. R. JVST A 1997, 15, 2134-2142. @footnote 2@Goodman, R. S.; Materer, N.; Leone, S. R. JVST A, submitted for publication.

5:00pm **SS2+EM-TuA10 Femtosecond Photo-induced Dynamics on a Cleaned and a Chlorinated Si(111) Surfaces***, **S. Haraichi**, F. Sasaki,* Electrotechnical Laboratory, Japan

A photo-induced chemical etching of Si is considered as a powerful candidate of the next-generation device fabrication thechnology from the view point of extremely low damage. However the atomic and/or dynamic mechanisms of the photo-induced reaction of Si/halogen systems have not been well understood. We have investigated photo-induced dynamics on a cleaned and a chlorinated Si(111) surfaces using femtosecond second-harmonic generation (SHG). For the pump-probe measurements, Ti-sapphire laser at 1300nm and 800nm with a 100fs pulse width were used as the probe and the pump beams, respectively. With the wavelength at 1300nm, a contribution of absorption is negligible and the surface specific information can be obtained. SHG intensities from a cleaned 7x7 surface decay rapidly just after the pump beam coincides with the probe beam and increase with a rapid and a slow time constants of around 1ps and more than several tens ps. These results were probably due to an immediate photo-excitation and two kinds of relaxation of 7x7 surface states. On the other hand, SHG intensities from a chlorinated Si surface increase rapidly just after the pump beam irradiation and decay with a time constant of around several ps, based on Si-Cl bonding states. On both a cleaned and a chlorinated Si surfaces, the time constants show no significant dependence on the pump beam fluency under the critical fluency of the etching reaction.

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[1] **Morton S. Traum Award Finalist**

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