

# Monday Morning, October 15, 2007

## Surface Science

Room: 611 - Session SS2-MoM

### Surface Structure, Growth, and Etching of Silicon and Germanium

Moderator: S. Chiang, University of California, Davis

8:00am **SS2-MoM1 Combined Scanning Tunnelling Microscopy and Stress Measurements to Elucidate the Origins of Surface Forces During the Oxidation of Si(111)-7x7**, *N.T. Kinahan, D.E. Meehan*, Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) & Trinity College Dublin, Ireland, *T. Narushima, K. Miki*, National Institutes of Natural Sciences, Japan, *J.J. Boland*, CRANN & Trinity College Dublin, Ireland

The oxidation of silicon surfaces has been widely studied due to its scientific and technological importance. However, despite extensive experimental and theoretical studies, the details of the oxidation reaction are not yet fully understood. It has recently been suggested that surface stress measurements may prove useful in elucidating this and related issues. In the case of adsorption on solid-state surfaces, stress arises primarily from differences in atomic size and electronegativity, in addition to unit cell expansion due to the incorporation of atoms into the substrate. Here, we study the surface stress evolution encountered during oxidation of the Si(111)-7x7 surface using a novel system combining both surface stress measurement and scanning tunnelling microscopy (STM) capabilities.<sup>1,2</sup> The former measurement is based on the displacement of a large silicon cantilever sample, while the latter measurement permits direct observation of the atomic structure of the same cantilever sample. We show that the initial oxidation of the Si(111)-7x7 surface at room temperature involves two compressive stress stages with different growth signatures. The atomic scale origins of the measured surface stress evolution will be discussed and supported via complementary STM data. In particular, we demonstrate that the initial rapid rise in compressive stress is associated with selective oxidation of the faulted-half units of the 7x7 reconstruction.

<sup>1</sup> T. Narushima, N.T. Kinahan, J. J. Boland, *Rev. Sci. Instrum.* 76 095113 (2005).

<sup>2</sup> T. Narushima, N.T. Kinahan, J. J. Boland, *Rev. Sci. Instrum.* 78 053903 (2007).

8:20am **SS2-MoM2 Kinetic Monte Carlo Simulation of Oxide Island Formation and Step Pinning during Etching by Oxygen of Vicinal Si(100)**, *M. Albao*, National Sun Yat-Sen University, Taiwan, *J.W. Evans*, Iowa State University, *F. Chuang*, National Sun Yat-Sen University, Taiwan

A lattice-gas model was developed incorporating a recently observed oxide island shape transformation from linear to two-dimensional<sup>1</sup> during initial stages of oxidation of Si(001). Kinetic Monte Carlo (KMC) simulations of such a model offers clues as to the nature of the pinning of steps and their subsequent transformation into finger-like structures<sup>2,3</sup> during prolonged etching of vicinal Si(100) by exposure to molecular oxygen. KMC results suggest that the initial linear shape of oxide clusters might allow them to protect slightly wider sections of the steps against erosion than would a similar 2D island of the same number of atoms. This proposal follows from comparison of the width of the "fingers" that subsequently evolved from the pinning by these two cluster types. Thus, the initial shape of the islands as much as their size appears to be key in stabilization and long-term survival of fingers. Additionally, the same model was used to uncover potential mechanisms for boosting oxide cluster nucleation and thus cluster populations at step edges. In turn, this increased concentration of oxide clusters at the steps sets the stage for increased chances of pinning.

<sup>1</sup> H. Togashi, H. Asaoka, T. Yamazaki, M. Suemitsu, *Jpn. J. App. Phys.* 44 (2005) 1377.

<sup>2</sup> J.V. Seiple and J. Pelz, *Phys. Rev. Lett.* 73 (1994) 999.

<sup>3</sup> M.A. Albao, D.-J. Liu, M.S. Gordon, and J.W. Evans, *Phys. Rev. B* 72 (2005) 195420.

8:40am **SS2-MoM3 Etching of Si(100) Surfaces in H<sub>2</sub>O**, *I.T. Clark, B.S. Aldinger, A. Gupta, M.A. Hines*, Cornell University

An etchant that produces atomically flat or near-atomically flat Si(100) surfaces has long been sought by the microelectronics industry. While a number of aqueous bases are known to produce atomically flat Si(111) surfaces, a comparable etchant for the commercially important Si(100) surface has not been demonstrated. We will present the results of a combined chemical and morphological investigation into the etching of Si(100) surfaces by room-temperature deoxygenated water. Over the course of several hours of etching, the surface develops a surprisingly homogeneous 4-fold symmetric cross-hatch motif dominated by orthogonal

"stripes" running along {110} directions. Simultaneous spectroscopic investigations demonstrate the development of a microfaceted H-terminated surface, consisting of Si{111}, Si{110} and Si{100} planes. A simple model for the development of highly homogeneous surfaces during H<sub>2</sub>O etching will be discussed

9:00am **SS2-MoM4 Super-Saturation Etching on Si(100)-(2x1) via Cl Insertion: A New Reaction Pathway**, *A. Agrawal, R.E. Butera, J.H. Weaver*, University of Illinois at Urbana-Champaign

We use scanning tunneling microscopy to show that Cl<sub>2</sub> dosing of Cl-saturated Si(100)-(2x1) at elevated temperature leads to uptake beyond "saturation". The surface then evolves along a new etching pathway that involves insertion of extra Cl, denoted Cl(i), in Si-Si dimer bonds or back-bonds, diffusion of Cl(i) to form the volatile precursor, and pairwise desorption of SiCl<sub>2</sub>. Insertion is made possible by chemisorption that is mediated by dangling bond sites. Upon dissociation, one Cl atom adsorbs at the dangling bond while the other inserts with ~10% probability. The dangling bonds required for insertion are produced by phonon-activated electron-stimulated desorption of atomic Cl from the surface. These studies establish a novel form of Cl<sub>2</sub> dissociative chemisorption, and this should stimulate further investigations into surface dynamics.

9:20am **SS2-MoM5 The Growth and Evolution of Ag on Ge(111) Studied by LEEM**, *J.A. Giacomo, S. Chiang*, University of California, Davis

The clean Ge(111) surface has a c(2x8) reconstruction at room temperature. When Ag is dosed onto the surface two main structures are found, a low coverage (4x4) and a higher coverage ( $\sqrt{3}\times\sqrt{3}$ )R30° phase. We have used the real-space imaging capabilities of a low energy electron microscope (LEEM) to investigate the growth, phase transitions, and dynamics of these phases. The (4x4) phase begins to form at temperatures above 200°C and coverages above 0.1ML. LEEM videos show the (4x4) phase grows with a high dependency on surface steps. This dependency on steps has been attributed to the high diffusivity of Ag adatoms along the step edges<sup>1</sup>. The growth of the (4x4) phase also produces faceting of the surface which is shown in the LEEM images as the (4x4) phase grows from the steps. At higher coverages the (4x4) phase transitions into a ( $\sqrt{3}\times\sqrt{3}$ )R30° phase. LEEM data of the growth of this phase shows little dependence on the steps with the phase propagating over the terraces. This growth pattern is attributed to the higher diffusivity of Ag adatoms across the (4x4) layer<sup>1</sup> reducing the advantage of diffusion along the steps. Near the desorption temperature, we have found an interesting phase transition as domains of ( $\sqrt{3}\times\sqrt{3}$ )R30° abruptly transform to the lower coverage (4x4) and then to a disordered phase. The disordered phase produces no contrast in the LEEM images but if the condensed phases are allowed to completely disappear and the sample is then immediately cooled the (4x4) and ( $\sqrt{3}\times\sqrt{3}$ )R30° phases recondense on the surface. This indicates that the Ag has not completely desorbed and is still present on the surface in a disordered phase.

<sup>1</sup> E. Suliga and M. Henzler, *Journal of Physics C-Solid State Physics* 16, 1543 (1983).

9:40am **SS2-MoM6 Chemical Vapor Deposition of Boron Carbide as a Passivation Film for Ge Surfaces**, *P.R. Fitzpatrick, J.G. Ekerdt*, The University of Texas at Austin

As electronic device dimensions are scaled down Ge is receiving considerable attention as an alternative to Si. The primary motivation is the higher charge carrier mobility in Ge compared to Si. However, the Ge/GeO<sub>x</sub> interface is chemically and electrically unstable. This work investigates the ability of boron carbide (BCN) films to passivate single crystal Ge surfaces and Ge nanowires. The BCN films are deposited by thermal chemical vapor deposition (CVD) using dimethylamine borane with NH<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> coreactants. Adjustments to the gas composition during CVD make it possible to tune the BCN stoichiometric composition, constituent bonding, and dielectric constant. Ion scattering spectroscopy (ISS) and x-ray photoelectron spectroscopy (XPS) were used to determine the minimum thickness of BCN resulting in a continuous film on Si(100) and Ge(100) substrates. Si(100) was chosen to develop the experimental protocol because of its well-documented surface chemistry. To determine film continuity using ISS, the ratio of the post-BCN substrate signal (either Si or Ge) to the predeposition bare substrate signal was plotted as a function of BCN thickness (determined by XPS peak attenuation for Si and spectroscopic ellipsometry for Ge). Due to the high surface sensitivity of ISS, a continuous BCN film should result in complete attenuation of the substrate signal. BCN becomes continuous at ~2.5nm when grown on Si(100) and ~3.5nm when grown on Ge(100). Differences in the BCN/Si and BCN/Ge interface were examined by depth profiling to understand how interface reactions affect film nucleation. A series of ISS scans gradually sputters the BCN, and XPS scans following each ISS scan track the atomic

composition of BCN until the Si or Ge substrate is reached. In both cases the film composition at the substrate interface drastically differs from the bulk composition ( $\text{BC}_{0.7}\text{N}_{0.1}$ ), with N dominating the B and C contributions at the interface. Nitrogen accumulation is much more pronounced on Si. The BCN film at the BCN/Si interface is comprised of ~70% N whereas the film at the BCN/Ge interface is only ~40% N. XPS was used to determine BCN-coated Ge's ability to withstand oxidation by monitoring changes in the Ge 2p and Ge 3d oxidation states with increasing ambient exposure time. A discontinuous 2.0nm BCN film slows, but does not prevent, Ge oxidation. A continuous 3.5nm BCN film shows no oxidation of Ge following 2 weeks ambient exposure.

10:20am **SS2-MoM8 Novel Superstructure of Thin Pb Film on Si(111) Induced by the Interplay of Quantum Well States and Interfacial Adsorbates**, A.A. *Khajetoorians*, H. *Eisele*, S.Y. *Qin*, C.-K. *Shih*, The University of Texas at Austin

Epitaxial thin Pb films on Si(111) are well known to exhibit pronounced QSE manifested by the phase matching of the Fermi wavelength and the layer thickness, giving rise to bilayer oscillation as well as a re-entrant quantum beats of longer periodicity. Such quantum oscillation phenomena have been observed in preferred film thickness, the location of quantum well states, as well as superconductivity. This work reveals yet another intriguing phenomenon manifested by the QSE: Formation of a novel superstructure resulting from the interplay of the quantum well state of the metal film and the cesium adsorbates at the interface of Si(111) substrate and Pb thin film overlayers. The superstructure consists of a periodicity of about 8 nm, incommensurate with the Si(111) 7x7 periodicity. Moreover, there is a dependence of the actual periodicity and orientation on the film thickness. This work is supported by: IGERT-NSF: DGE-054917; FRG: (DMR-0306239, DMR-0606485), Alexander von Humboldt Foundation.

10:40am **SS2-MoM9 Controlled Selforganization of Atom Vacancies in Monatomic Gallium Layers**, P.C. *Snijders*, Delft University of Technology, The Netherlands (now at ORNL), E.J. *Moon*, University of Tennessee, Knoxville, C. *Gonzalez*, J. *Ortega*, F. *Flores*, Universidad Autonoma, Madrid, Spain, H.H. *Weitering*, University of Tennessee, Knoxville, and Oak Ridge National Laboratory

Ga adsorption on the Si(112) surface results in the formation of pseudomorphic Ga atom chains. Compressive strain in these atom chains is relieved via creation of adatom vacancies.<sup>1</sup> These vacancies selforganize into meandering vacancy lines (VLs) similar to the well-known nx2 superstructures for Ge on Si(100).<sup>2</sup> We show that the average spacing between these line defects can be experimentally controlled continuously, within limits, by adjusting the chemical potential  $\mu$  of the Ga adatoms. The small VL spacings in this system result in significant VL correlations that cannot be captured within a mean field analysis of the VLs.<sup>2</sup> We derive a conceptually new lattice model that quantitatively connects Density Functional Theory (DFT) calculations for perfectly ordered structures, with the fluctuating disorder seen in experiment and the experimental control parameter  $\mu$  for this correlated VL system. Applying this model to statistical data from large scale STM images, we calculate the (repulsive) VL interaction energy and the kink energy. This hybrid approach of lattice modeling and DFT can be applied to other examples of line defects in hetero-epitaxy, especially in cases where correlation effects are significant and a mean field approach is not valid.<sup>3</sup>

<sup>1</sup> C. Gonzalez, P.C. Snijders, J. Ortega, R. Perez, F. Flores, S. Rogge, and H.H. Weitering, Phys. Rev. Lett. 96, 126106 (2004), P.C. Snijders, S. Rogge, C. Gonzalez, R. Perez, J. Ortega, F. Flores, and H.H. Weitering, Phys. Rev. B 72, 125343 (2005).

<sup>2</sup> X. Chen, F. Wu, Z. Zhang, and M.G. Lagally, Phys. Rev. Lett. 73, 850 (1994).

<sup>3</sup> Part of this work (HHW) was supported by the US DOE Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, through Oak Ridge National Laboratory which is managed by UT-Battelle, LLC.

11:00am **SS2-MoM10 Gold Nanowire Formation on Si(110) Studied by SPM**, M. *Yoshimura*, M. *Tanaka*, K. *Ueda*, Toyota Technological Institute, Japan

Recently, nanostructures such as quantum dots and wires have been focused because of their exotic properties originated from the confinement of electrons, such as Coulomb blockade, charge density waves, spin density waves, etc. Several chain structures have been observed for Au/Si systems such as Au/Si(557).<sup>1</sup> For the Au/Si(110) system, Yamamoto reported a variety of surface phases using reflection high-energy electron diffraction (RHEED),<sup>2</sup> and only one phase, 2x5 structure, has been investigated in real space by scanning tunneling microscopy (STM).<sup>3</sup> In this study, we aim to clarify the relationship between several surface phases of Au/Si(110) by high-resolution STM and atomic force microscopy (AFM). On the basis of high-resolution SPM images, we propose structural models for the phases and discuss the mechanism of nanowire formation. At 0.2-0.3 ML coverage, up-and-down structure of the clean Si(110) surface is destroyed, and 1x2 structure was clearly confirmed by FFT analysis, corresponding to

nucleation of the nanowire. It is suggested that (110) facets develop in the Si(110) surface. The density of the nanowires increases with Au coverage to 0.25 ML. The spacing between the wires varies from 5a to 10a (a: unit length along the [-110] direction of Si(110)). At the coverage of 0.30 ML, it becomes constant at 5a, showing 2x5 surface phase. The nanowire consists of double rows with fluctuation character. The detailed atomistic processes of nanowire formation, as well as possible atomic structure models, are discussed.

<sup>1</sup> H. W. Yeom et al., Phys. Rev. B 72, 035323 (2005).

<sup>2</sup> Y. Yamamoto, Surf. Sci. 271, 407 (1992).

<sup>3</sup> J. L. McChesney et al., Phys. Rev. B 72, 035446 (2005).

11:20am **SS2-MoM11 Faceting and Band-Flattening Induced by Sb-Indiffusion into Si(5 5 12)-2x1**, H. *Li*, H. *Kim*, J.M. *Seo*, Chonbuk National University, Korea

Initial stages of antimony (Sb) adsorption on the Si(5 5 12)-2x1 surface have been studied by STM/STS in order to understand interfacial reaction between adsorbed Sb atoms and the Si template with one-dimensional (1-D) symmetry. It has been found that there are two distinct steps, Sb indiffusion and preferential adsorption, at the initial Sb adsorption on Si(5 5 12)-2x1 held at 600 C. Initially, deposited Sb atoms (up to 0.15 ML) diffuse into the subsurface and cause indirect Si deposition. As a result a  $\pi$ -bonded Si chain is firstly formed on dimer/adatom row like homoepitaxy, and the surface reconstruction gradually changes from a (5 5 12) terrace to (337) terraces with (113) steps. The band is flattened by 0.2 eV by subsurface doping with indiffused Sb atoms. As soon as the subsurface Sb sites are saturated by indiffused Sb atoms, additionally deposited Sb atoms are preferentially adsorbed along the upper (113)-step edges and form 1-D Sb wires with a spacing of about 10 nm which corresponds to two periodic lengths of the original (5 5 12) surface. Once Sb-adsorption sites, (113) steps, are saturated, deposited Sb atoms cluster for themselves and do not contribute to nanowire fabrication. From the present studies, it has been found that both Sb indiffusion and preferential adsorption stabilize the high-index surface through relieving surface strain by way of either inserting or attaching Sb atoms, but once such surface strain is relieved, the 1-D growth mode also terminates.

11:40am **SS2-MoM12 Surface Reconstructions Induced by Calcium Fluoride Growth on Si(001)**, Y. *Cui*, J. *Nogami*, University of Toronto, Canada

The growth of Calcium Fluoride ( $\text{CaF}_2$ ) on Silicon has been widely studied since it grows epitaxially on Si with small lattice mismatch (0.6% at room temperature). There is an extensive literature on  $\text{CaF}_2$  growth on Si(111) where a natural epitaxial relationship results in flat thin films with low defect density. However, very little work has been reported for  $\text{CaF}_2$  on Si(001). It is known that  $\text{CaF}_2$  grown on Si(001) forms either compact islands or long ridges in the Stranski-Krastanow mode.<sup>1,2</sup> STM images of the wetting layer show an inhomogeneous row like structure.<sup>3</sup> In this STM study, 2x3 or 2x4 periodicities were identified in the first layer depending on  $\text{CaF}_2$  coverage and growth temperature. The LEED pattern shows an unusual combination of spots and streaks with variable line width and intensity. The configuration of the pattern is caused by the alignment of surface unit cells and phase disorder. The nucleation of  $\text{CaF}_2$  small areas is also seen and paves a way to further studies on 3D insulator nanowires. Finally the parallels between these results and the ones obtained for growth of  $\text{CaF}_2$  on Si(111) is discussed.

<sup>1</sup> Loretto, D.; Ross, F.M.; Lucas, C.A.: Applied Physics Letters, v 68, n 17, 22 April 1996, p 2363-5

<sup>2</sup> Pasquali, L.; D'Addato, S.; Selevaggi, G.; Nannarone, S.; Sokolov, N.S.; Suturin, S.M.; Zogg, H.: Nanotechnology, v 12, n 4, Dec. 2001, p 403-8

<sup>3</sup> Sumiya, T.; Miura, T.; Fujinuma, H.; Tanaka, S.: Surface Science, v 376, n 1-3, 10 April 1997, p 192-204.

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