

# Monday Morning, October 18, 2010

## Surface Science

Room: Santa Ana - Session SS2+EM-MoM

## Semiconductor Surfaces and Interfaces

**Moderator:** J. Millunchick, University of Michigan, Ann Arbor

8:20am **SS2+EM-MoM1 Spontaneous Microfaceting and Pyramid Growth during Si(100) Etching.** *M.F. Faggin, A. Gupta, M.A. Hines,* Cornell University

The spontaneous, etching-induced transformation of an initially flat Si(100) surface to a completely nanofaceted morphology consisting of overlapping pyramidal hillocks has been observed using a combination of morphological and spectroscopic probes and modeled using a fully-atomistic kinetic Monte Carlo (KMC) simulator of Si(100) etching. A novel silicon etchant has been developed that catalyzes the complete chemical transformation of a Si(100) surface into H-terminated Si{111} and Si{110} nanofacets. This finding was confirmed by infrared absorption spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM). The formation of pyramidal hillocks is highly reproducible and occurs on a time scale of several hours, enabling detailed studies of initial hillock formation and subsequent growth. The formation of microfaceted pyramidal hillocks during etching of Si(100) has previously been attributed to local masking on the surface by deposited impurities, etch products or gas bubbles. These mechanisms assume that an adsorbed impurity or gas bubble decorates the apex of every pyramid. Our atomistic simulations uncovered a second mechanism, one that is *intrinsic* to the etchant and that generates dynamically self-propagating pyramidal structures. Attempts to distinguish between these two mechanisms through rational modifications of the etchant chemistry will be described. For example, the kinetics of pyramid growth were followed spectroscopically, enabling quantitative assessment of the effects of chemical additives. These observations are more than an intellectual curiosity, as the silicon solar cell industry is actively searching for inexpensive, environmentally-friendly means of pyramidally texturing Si(100) surfaces to reduce reflection losses. Conversely, in microfabricated devices, suppression of pyramid formation is critical to high-yield manufacturing processes. An understanding of the hillock formation process may lead to the rational design of better etchants.

8:40am **SS2+EM-MoM2 Selective Ablation of Xe on Silicon Surfaces: MD Simulation and Experimental Laser Patterning.** *O. Stein, M. Asscher,* The Hebrew University in Jerusalem, Israel

Laser induced ablation of multilayer Xe on Si has been studied employing molecular dynamics (MD) simulations. 5nsec long laser pulse at  $\lambda=337\text{nm}$  was applied to a Xe slab at thicknesses of 16 32 and 40ML (7744, 15488, 19360 atoms, respectively) adsorbed on top of a 8 layers 5408 atoms Si slab. Evaporative and explosive ablation thresholds were identified at absorbed laser power of 12 and 16MW/cm<sup>2</sup> which corresponds to surface temperature rise of 500 and 658K, respectively. Selective ablation was studied, where only a fraction of the lateral dimension of the computation cell was actually ablated. Extremely strong lateral dissipation among the Xe layers, has led the ablation threshold to shift to higher laser power as the fraction of heated area shrinks. Heated fraction (HF) less than 10% results in practically no ablation at laser power below substrate damage threshold. The MD studies were assessed and verified by experimental laser ablation measurements. A 10nsec Nd:YAG laser pulse operating at  $\lambda=532\text{nm}$  was employed. It was found that for 80 and 160ML Xe layer thickness, full ablation was reached at laser power of 6.9 and 8.4MW/cm<sup>2</sup> which corresponds to surface temperature rise of 180 and 220K respectively. Line-edge profile resulting from fractional laser induce desorption- coverage grating formation followed by metallic lift-off experiments were compared to the MD simulations of selective ablation, revealing a remarkable similarity.

Key words: Molecular Dynamics Simulations, Laser Ablation, adsorbed Xe on Si, Coverage Grating.

9:00am **SS2+EM-MoM3 Tuning Properties of Thin Films by Aminofunctionalization.** *A.V. Teplakov,* University of Delaware

9:20am **SS2+EM-MoM4 Helium Atom Diffraction Measurements of the Surface Structure and Vibrational Dynamics of CH<sub>3</sub>-Si(111) and CD<sub>3</sub>-Si(111) Surfaces.** *J.S. Becker, R.D. Brown,* University of Chicago, *E. Johansson, N.S. Lewis,* California Institute of Technology, *S.J. Sibener,* University of Chicago

The surface structure and vibrational dynamics of CH<sub>3</sub>-Si(111) and CD<sub>3</sub>-Si(111) surfaces were measured using helium atom diffraction. The elastic diffraction patterns exhibited a lattice constant of 3.82 Å, in accordance with the spacing of the silicon underlayer. The high quality of the observed diffraction patterns indicates a high degree of long-range ordering for this novel interface. The vibrational dynamics were investigated by measurement of the Debye-Waller decay of the elastic diffraction peaks as the surface temperature was increased. The angular dependence of the specular ( $\theta_i = \theta_f$ ) decay revealed perpendicular mean-square displacements and He-surface well depths of  $1.0 \cdot 10^{-5} \text{ Å}^2 \text{ K}^{-1}$  and 7.5 meV for the CH<sub>3</sub>-Si(111) surface and  $1.2 \cdot 10^{-5} \text{ Å}^2 \text{ K}^{-1}$  and 6.0 meV for the CD<sub>3</sub>-Si(111) surface. Effective surface Debye temperatures of 983 K for CH<sub>3</sub> and 824 K for CD<sub>3</sub> were calculated. These unusually large Debye temperatures suggest that collisional energy accommodation at the surface occurs primarily through Si-C local mode. The parallel mean-square displacements were  $4.3 \cdot 10^{-4} \text{ Å}^2 \text{ K}^{-1}$  and  $4.5 \cdot 10^{-4} \text{ Å}^2 \text{ K}^{-1}$  for CH<sub>3</sub>- and CD<sub>3</sub>-Si(111) surfaces, respectively. The increase in thermal motion is consistent with interaction between the helium atoms and Si-CH<sub>3</sub> bending modes. These experiments yield new information on the dynamical properties of these robust and technologically interesting semiconductor interfaces.

9:40am **SS2+EM-MoM5 Comprehensive Descriptions of Surface Atomic Structure.** *J.C. Thomas, J. Mirecki Millunchick,* The University of Michigan, Ann Arbor, *N.A. Modine,* Sandia National Laboratories, *A. Van der Ven,* The University of Michigan, Ann Arbor

**INVITED**

Comprehensive descriptions of surface atomic structure have been developed over the years for a wide range of metals and covalent crystals, but this understanding has typically been obtained only after extensive trial and error. Unfortunately, experimental and theoretical characterization of surfaces is complicated significantly in systems that can exhibit metastable surface reconstructions or in alloy systems, where atomic size mismatch and lattice mismatch strains play an important role and can give rise to phase coexistence. Clearly, a systematic and rigorous approach to determining surface structure is needed in order to explore surface phenomena in alloy systems or away from equilibrium. We have developed an approach that uses prior knowledge about the surface atomic structure of a pure system, along with first principles energy calculations and statistical mechanical methods, to systematically and efficiently explore new ground-state and near-stable surface reconstructions, finite temperature behavior, and alloying effects. We describe the automated generation of III-V (001) surface reconstruction candidates in the group V-rich regime and discuss how our approach is used to study the complex surface structure of the In<sub>x</sub>Ga<sub>1-x</sub>As (001) alloy, which exhibits nanoscale coexistence domains and where an unexplained ( $n \times 3$ ) reconstruction is observed over a wide range of conditions.

10:40am **SS2+EM-MoM8 The Structure of Metal-Rich (001) Surfaces of InAs and InSb.** *J.J. Kolodziej,* Jagiellonian University, Poland

11:00am **SS2+EM-MoM9 Monolayer Passivation of Ge(100) Surface via Nitridation and Oxidation.** *J.S. Lee, S. Bishop, T. Kaufman-Osborn, A.C. Kummel,* University of California at San Diego

The monolayer passivation of Ge(100) surface via formation of Ge-N and Ge-O surface species was studied using scanning tunneling microscopy (STM) and density functional theory (DFT) to develop a process of minimizing interface defect density between Ge and a high-k dielectric layer in a highly scaled device. Direct nitridation was performed on a Ge(100) surface using an electron cyclotron resonance (ECR) plasma source with pure N<sub>2</sub> gas. It was hypothesized that plasma nitridation at elevated temperature (500°C) would form an ordered nitride structure that would combine the low defect density of GeO<sub>2</sub> with the higher thermal stability of GeON via formation of a Ge-N ordered structure. Experimental and theoretical modeling showed that bandgap states are produced from the ordered nitride structure resulting in Fermi level pinning of the surface; however, it is predicted that H-passivation on the nitride structure would unpin the Fermi level by reducing the dangling bonds and the bond strain. The best method to passivate a Ge(100) surface is to form a layer of GeO<sub>2</sub> which is free of suboxides. However, this process is difficult to scale using

thermal oxidation by  $O_2$ , so alternative oxidants,  $H_2O$  and  $GeO_2$ , were studied. At room temperature, the  $H_2O$ -dosed Ge surface showed Ge-OH sites with very few Ge adatoms, while the e-beam deposition of  $GeO_2$  formed semi-ordered Ge-O structures and Ge ad-species. It is likely the  $H_2O$  dosing produces an ideal passivation layer since it displaces few surface Ge atoms. Nevertheless, annealing above  $300^\circ C$  converts the surface oxides into suboxide rows on both  $H_2O$  and  $GeO_2$  dosed Ge surfaces due to the reactivity of  $GeO_2$  with Ge. Scanning tunneling spectroscopy (STS) shows that the Fermi level of the  $n$ -type Ge surfaces covered by suboxides is near the valence band edge, consistent with formation of Ge suboxide rows likely causing Fermi level pinning. The atomic layer deposition (ALD) of  $GeON$  and  $SiO_2$  are being studied to form a monolayer or bilayer of passivation with a minimum defect density and the improved thermal stability.

11:20am **SS2+EM-MoM10 Formation of Titanium Sub-Oxide from  $TiO_2$  ALD Films on Si and Ge Substrates after Vacuum Anneal**, *R.M. Methaapanon, P. Ardalan, S.F. Bent*, Stanford University

11:40am **SS2+EM-MoM11 Interfacial Effects of Near-surface Dopant Diffusion and Electrical Activation in Silicon**, *P. Gorai, Y. Kondratenko, E.G. Seebauer*, University of Illinois at Urbana-Champaign

Defect behavior in silicon can be controlled by manipulating the chemical state of nearby surfaces and solid-solid interfaces, with important implications for transistor fabrication by ion implantation and annealing. Silicon interstitials formed during the ion implantation step are responsible for unwanted transient enhanced diffusion (TED) of dopants, and affect the degree of dopant activation as well. Earlier work in our laboratory has shown that certain chemical treatments of surfaces and interfaces changes its ability to act as sinks for interstitials. The fundamental kinetic quantity describing "sink" behavior can be described by an annihilation probability ( $S$ ). Yet surfaces and interfaces also support electrically charged defects, which create local strong electric fields that influence the local motion of interstitials that are charged. The degree of charge buildup can be quantified by an electric potential ( $V_i$ ). The combined effects of  $S$  and  $V_i$  not only influence the annihilation of interstitials, but lead under some conditions to the pile up of electrically active dopant near the surface or interface. However, up to now, the precise nature of the interplay, including the most relevant time scales during annealing, has never been quantified. Through continuum modeling on the nanometer length scale, the present work provides such quantification. Differential equations describing the diffusion and reaction of silicon and boron interstitials are solved to yield the time evolution of boron profiles that are compared in important cases to experiment.

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