Thursday Morning, October 5, 2000

Semiconductors
Room 306 - Session SC+EL+SS-ThM

Hydrogen On and In Semiconductors

Moderator: J.T. Yates, Jr., University of Pittsburgh

8:20am **SC+EL+SS-ThM1 Step Structures and Energies on Vicinal Si(001) Monohydride Surfaces: Dependence on H Chemical Potential***, **A. Laracuente**, L.J. Whitman,* Naval Research Laboratory

It is well known that foreign adsorbates can alter the equilibrium step structure on surfaces and often have a dramatic effect on film growth. Given that most semiconductor devices are fabricated in hydrogen-rich environments on silicon substrates, a comprehensive understanding of how hydrogen affects Si step energies is essential to the development of accurate models of semiconductor growth and processing. We have determined the equilibrium step structures and step formation energies for the whole range of monohydride-terminated (001)-terrace-plus-step surfaces. Compared with the clean surfaces, hydrogen termination alters the atomic-scale step edge structure and, in many cases, causes large-scale changes in the surface morphology. The structural modifications result directly from a change in the relative energies of the possible single- and double-layer step configurations. On nominal Si(001), the S@sub B@ steps are mostly non-rebonded and rougher after H passivation. A kink distribution analysis reveals that H reduces the nearest neighbor interaction across the S@sub B@ steps by an order of magnitude. Whereas the nearest neighbor interaction strongly depends on H@sub 2@ pressure, i.e. the H chemical potential, the step formation energies do not. On D@sub B@-stepped surfaces, such as Si(1 1 11), a statistical analysis of the steps shows that H lowers the formation energy of non-rebonded D@sub B@ and S@sub B@ steps, making them close in energy to the rebonded D@sub B@ steps. Post annealing a monohydride Si(1 1 11) surface without H significantly changes the n-D@sub B@/r-D@sub B@ ratio, indicating that the D@sub B@ step formation energies strongly depend on H chemical potential.

8:40am **SC+EL+SS-ThM2 Si(100) Surface Roughening and H Atom Absorption: Surface and Bulk Characterizations.***, **S.K. Jo**, J.H. Kang,* Kyung Won University, S. Korea*; X. Yan, J.M. White, J.G. Ekerdt,* University of Texas at Austin*; J. Lee,* Seoul National University, S. Korea*; J.Y. Maeng, S.H. Kim,* Korea Advanced Institute of Science and Technology

Absorption of thermal-energy gaseous hydrogen atoms by Si(100), exceeding by far the dopant and other impurity concentrations, occurs within a narrow substrate temperature (T@sub s@) window centered at ~ 460 K. The absorbed hydrogen persists in the crystalline bulk as highly mobile species before migrating out and desorbing as molecular hydrogen at T@sub s@ as high as 900 K, well above the recombinative desorption temperatures of surface-adsorbed H. Developing and sustaining atomic-scale surface roughness, by H-induced silicon etching, is a prerequisite for H absorption and determines the T@sub s@ window. In support of these conclusions are our TPD, Raman, SIMS, TEM, and STM data for this fundamental and interesting phenomenon of thermal H atom absorption by Si(100).

9:00am **SC+EL+SS-ThM3 Dissociation Pathways of Molecular Hydrogen on Silicon Surfaces@footnote 1@***, **U. Höfer**,* Philipps Universität Marburg, Germany **INVITED**

The dissociative adsorption of H@sub 2@ on Si(001) has emerged as a prototype for activated chemical reactions on semiconductor surfaces. One of the most distinctive features of this basic reaction is the low sticking probability for dissociative adsorption (< 10@super -11@) and the fact that thermally induced distortions of the Si lattice enhance the reactivity by many orders of magnitude. In order to reveal the atomic-scale motion responsible for "phonon assisted sticking" we have performed a series of experiments employing optical second-harmonic generation (SHG), supersonic molecular beam dosing, and scanning tunnelling microscopy (STM). It will be demonstrated that, similar to thermally activated dynamical distortions, the reactivity can be enhanced by static distortions of the surface by precoverage with atomic hydrogen or by steps. The barriers to adsorption at these well-defined sites were determined. They revealed systematic trends that could be reproduced by density functional calculations and traced back to the interplay between electronic structure and local distortions of the Si surface. We find that hydrogen adsorption proceeds via inter-dimer reaction pathways in all cases. Whenever the energy splitting between the reactive dangling-bond states of adjacent dimers may be reduced by low-energy displacements of Si atoms, the adsorption barrier is found to be low. @FootnoteText@ @footnote 1@ Work performed in collaboration with W. Brenig, A. Biedermann, M. Dürr, T. F. Heinz, M. Hilf, Z. Hu, P. Kratzer, E. Pehlke, M. B. Raschke and M. Scheffler.

9:40am **SC+EL+SS-ThM5 Hydrogen Bonding on Compound Semiconductor Surfaces***, **R.F. Hicks**, Q. Fu,* University of California, Los Angeles*; L. Li,* University of Wisconsin, Milwaukee*; C.H. Li,* University of California, Los Angeles

Hydrogen adsorption on gallium arsenide and indium phosphide (001) surfaces has been studied by scanning-tunneling microscopy and internal-reflection infrared spectroscopy combined with ab initio molecular cluster calculations. The calculations are based on a series of clusters that accurately simulate the group III and V dimer termination of the surface. Good agreement has been achieved between the vibrational frequencies predicted by the theory and those observed in the experiments. On the anion-rich surfaces, hydrogen adsorbs on arsenic (or phosphorous) dimers to form isolated and coupled monohydrogen bonds and dihydrogen bonds. Conversely, on the cation-rich surface, hydrogen adsorbs on gallium (or indium) dimers to form terminal and bridged metal hydrides. The latter species occur in isolated or coupled structures involving two or three metal atoms. The implications of these results for the surface science of compound semiconductors will be discussed at the meeting.

10:00am **SC+EL+SS-ThM6 Scanning Tunneling Microscopy of Low Temperature Adsorption H2 on GaAs(001)***, **H. Xu**,* National University of Singapore, Singapore*; Y. Lee, J. Lee, A. Lee,* National University of Singapore

The variable temperature scanning tunneling microscope (VT-STM) has been used to study in-situ the transition of 2x6 reconstruction of GaAs (001) at low temperature. High resolution STM images show that the metastable As dimers rows of 2x6 reconstruction in GaAs (001) becomes unstable under the attack of the dissociated adsorption H@sub2@. As dimers were broken firstly due to the formation of double atom lines structure by the attacking of hydrogen on As dimers atoms. Furthermore, the opened As atoms rows on the top of this surface were twisted gradually up to coalesce together with a width of 3 As dimers. Unexpectedly, these compressed As atoms suddenly extend along the original As dimers rows direction(-110) gives rise to form a metastable trimer As rows.

10:20am **SC+EL+SS-ThM7 Theoretical Approaches for Predicting SiGe Heteroepitaxy***, **C. Mui**, S.F. Bent, C.B. Musgrave,* Stanford University

The demand for silicon-germanium devices has been growing in recent years due to potential applications in areas such as infrared photodetection, wireless communications and quantum nanostructures. The need for improved SiGe processing has motivated efforts to better understand the detailed reaction mechanisms of SiGe heteroepitaxy, including the adsorption of gas phase precursors and the removal of hydrogen from SiGe surfaces. We have used Becke3LYP density functional theory to study the effect of Ge alloying on the energetics and kinetics of H2 desorption from SiGe surfaces. We have investigated H2 desorption from the Si-Si homodimer, the Si-Ge heterodimer and the Ge-Ge homodimer sites. We found that in the transition state the two desorbing hydrogen atoms are localized above one surface atom, such that the structure resembles a dihydride species. The transition states on all three types of dimers have similar geometries, independent of the identity of the surface dimer atoms. Furthermore, the activation barriers depend only on the identity of the dimer atom not bonded to the desorbing hydrogens. For example, the activation barrier for H2 desorption from the Si site of a Si-Ge heterodimer is lower than that from a Si-Si homodimer by 10.6 kcal/mol. However, the barrier for desorption from the Ge-Ge homodimer is the same as that from the Si site of a Si-Ge heterodimer. We also found that the activation barrier for H2 desorption is only affected by surface Ge, and not Ge in the bulk. Calculations on a three dimer cluster showed that the activation barriers are dependent on cluster size, indicating that charge transfer and surface strain play a role in the desorption process. Finally, we will present results concerning additional surface reactions including the adsorption of germane on SiGe surface dimers.

10:40am **SC+EL+SS-ThM8 Real-time Monitoring of H@sub 2@ Adsorption on C(001) at High Temperature by Ultraviolet Photoelectron Spectroscopy***, **Y. Takakuwa**, M. Asano,* Tohoku University, Japan

The hydrogen-terminated diamond surface has attracted much attention not only as a high efficiency electron emitter because of its electron affinity being negative (NEA) but also as a p-type conductive surface for fieldeffect-transistor devices. On the other hand, H@sub 2@ desorption on the hydrogen-terminated diamond surface occurs appreciably at higher temperature than 900@super o@C. This suggests that during the synthesis of diamond thin films by chemical vapor deposition using hydrocarbon gases such as methane the diamond-growing surface could be terminated by hydrogen and therefore NEA, even though the growth temperature is as high as 800-1000@super o@C. In this study, the electron affinity, secondary electron emission and pinning position of the Fermi level during exposing a diamond C(001) surface to H@sub 2@ at 700@super o@C and 1x10@super -5@ Torr were investigated by a real-time monitoring method of ultraviolet photoelectron spectroscopy. It was observed that (1) molecular hydrogen not activated by a hot tungsten filament absorbs dissociatively on the C(001) surface, wile it takes about 120 min to cover wholly the surface with hydrogen; (2) the electron affinity decreases from +0.4 eV for the clean surface to a negative value when the hydrogen coverage is about 90%; (3) the Fermi level is positioned at 0.61 eV above the valence band maximum just when the diamond surface changes to NEA; (4) the secondary electron yield increase with the hydrogen exposure time even after the complete termination of the surface with hydrogen. On the basis of the observed results, the time evolution of the surface electronic state during the hydrogen adsorption on the C(001) surface is discussed.

11:00am **SC+EL+SS-ThM9 Infrared Studies of Hydrogen on Diamond (100)***,* ***J.N. Russell, Jr.,*** Naval Research Laboratory*; J. Hovis, R.J. Hamers,* University of Wisconsin*; G.T. Wang, S.F. Bent,* Stanford University*; M.P. D'Evelyn,* General Electric CRD*; J.E. Butler,* Naval Research Laboratory

Hydrogen atoms play a critical role in the chemical vapor deposition of diamond thin films. Currently, hydrogen plasmas are used to produce reproducible, clean, smooth, diamond (100) single-crystal surfaces. The use of diamond films for microelectronic or surface acoustic wave devices requires a fundamental understanding of the diamond surface termination and its interaction with adsorbed species. The hydrogen terminated diamond (100) surface is comprised of two 2x1 domains of monohydride surface dimers. Using s- and p-polarized multiple internal reflection infrared spectroscopy, the symmetric and asymmetric stretches of the HCCH surface dimer are easily resolved and are compared to ab initio calculations of the frequencies. The thermal dependence of the CH stretches is monitored as a function of the anneal temperature. When the hydrogen terminated surface is covered with a condensed layer of physisorbed molecules, the surface CH vibrational frequency is significantly influenced. We discuss the implications of these observations.

11:20am **SC+EL+SS-ThM10 Fundamental Connection Between the ESD of H/D at Silicon Surfaces and at Oxide/Silicon Interfaces***,* ***K. Cheng****, J. Lee, Z. Chen, J.-P. Leburton, E. Rosenbaum, K. Hess, J.W. Lyding,* University of Illinois, Urbana-Champaign

Parallels can be drawn between electron stimulated desorption (ESD) of hydrogen at silicon surfaces in UHV and the ESD of hydrogen at the oxide/silicon interface in CMOS transistors. In particular, the multiple carrier vibrational heating mechanism for ESD, and the giant hydrogen/deuterium isotope effect play important roles in interface degradation. In this paper we will present results demonstrating the primary role of channel hot carriers in the degradation of the oxide/silicon interface of transistors. Experiments performed on p-channel MOSFET's show essentially no isotope effect for the creation of interface traps when carriers are injected into the oxide. However, a large isotope effect, consistent with vibrational heating, is observed when carriers flow along the oxide/silicon interface. One key difference between a H-passivated silicon surface and a H-passivated oxide/silicon interface is that there is a distribution of Si-H bond strengths at the interface due to variations in the amorphous oxide matrix. Experimental results will be presented which directly measure this distribution as well as show its ramifications in terms of rapid interface trap creation. The significance of this study comes from the fact that it is still a widely held view that the dominant transistor degradation mechanisms arise from carrier injection into the oxide, and therefore will be scaled away as industry trends progress. However, by performing new experiments and using basic surface science as a setting for their interpretation, we are able to show that there are fundamental problems with this view. Our results are supported by the fact that even state-of-the-art 0.18mm, 1.5 V CMOS chips show hundreds times lifetime improvement when hydrogen is substituted by deuterium.

11:40am **SC+EL+SS-ThM11 Depth-Resolved Determination of the Hydrogen Concentration at Buried SiO@sub 2@/Si(100) Interfaces by Resonant Nuclear Reaction Analysis***,* ***M. Wilde****, M. Matsumoto, K. Fukutani,* University of Tokyo, Japan*; Z. Liu, Y. Kawashima,* NEC Corp., Japan

Hydrogen at the SiO@sub 2@/Si interface has been discussed to affect the electronic performance of MOS diodes by influencing the density of states at the interface. Drastic improvements of the reverse current resistance were reported after H@sub 2@-annealing of such devices.@footnote 1@ In this study the hydrogen concentration at the SiO@sub 2@/Si interface is measured directly by a Nuclear Reaction Analysis (NRA, based on the @sup 1@H(@sup 15@N, @alpha@@gamma@)@sup 12@C reaction), and the influence of H@sub 2@-annealing is investigated. Oxidized Si(100) samples with SiO@sub 2@ films of (19.0 - 41.5 nm) thickness were studied. In the as-oxidized condition, H near the SiO@sub 2@/Si interface is identified at a concentration lower than 4x10@sup 19@ cm@sup -3@. In the NRA depth profiles of all samples the center of the near-interface H-distribution appears at a depth (5±1) nm shallower than the interface location determined by ellipsometry. While no H is found in the silicon substrate, hydrogen is accumulated in a several nm wide layer within the oxide film adjacent to the interface. This result supports the idea of a transition region between the mere interface and the SiO@sub 2@ material, where stoichiometry and strain-induced defects may act as local bonding sites for hydrogen. In-situ annealing of the oxidized wafers in ambient H@sub 2@ gas causes a substantial increase of the H-concentration near the SiO@sub 2@/Si(100) interface, whereas the width of the H-distribution and its position within the oxide film remain unchanged. The H-distribution is thermally stable below the annealing temperature of 400@deg@C. On heating to higher temperatures in vacuum depletion of H from the interface layer occurs to a concentration level below the as-oxidized condition. Hydrogen can be replenished at the interface by repeating the H@sub 2@-annealing procedure. @FootnoteText@ @footnote 1@ S. Fujieda, H. Nobusawa, M. Hamada, T. Tanigawa, J. Appl. Phys. 84 (1998) 2732.

Author Index

Bold page numbers indicate presenter