## Monday Afternoon, October 2, 2000

#### Semiconductors Room 306 - Session SC+EL+SS-MoA

#### **Reactions on Semiconductors**

Moderator: R.A. Wolkow, National Research Council of Canada

## 2:00pm SC+EL+SS-MoA1 Adsorption of SiH@sub 4@ on Si(001)(2x1) Investigated by Infrared Spectroscopy, *M. Shinohara*, *A. Seyama*, *Y. Kimura*, *M. Niwano*, Tohoku University, Japan

Adsorption of silane molecules, SiH@sub 4@ and Si@sub 2@H@sub 6@, onto Si(001) has so far been investigated extensively, because of the potential of using the silane molecules as the source gas for gas source molecular beam epitaxy (GS-MBE) for the growth of Si. Previous studies on Si deposition using silanes have suggested that during the course of Si crystal growth, silanes dissociatively adsorb on Si surface dangling bonds as trihydride (SiH@sub 3@) and dihydride (SiH@sub 2@) species and then decomposes to surface monohydride species, SiH. However, there has been only a little amount of information about the type of hydride species that are generated during the adsorption of silane on Si surfaces. In this study, we used infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR) to investigate the adsorption of SiH4 on the Si(001)(2x1) surface. IRAS-MIR provides us with valuable information about the hydrogen bonding configurations on semiconductor surfaces. Comparing infrared data with the density functional cluster calculation, we show that the silane molecule dissociatively adsorbs on Si(001)(2x1) to populate a dihydride (SiH@sub 2@) at the bridge site between two adjacent dimers and a monohydride species: the latter is formed by terminating the unsaturated dangling bonds of dimers by hydrogen atoms that are released from the silane molecule. We found that at high surface hydrogen coverage, surface silyl (-SiH@sub 3@) group and monohydride (SiH) species are generated. We interpret that at high hydrogen coverage, silane adsorbs onto a single dimer that has two unsaturated dangling bonds on which a hydrogen atom and a sylil group (-SiH@sub 3@) stick. We also show that a dihydride species that was initially generated by silane adsorption, dissociates even at room temperature and the released hydrogen atoms migrate on the surface to produce more monohydride species.

## 2:20pm SC+EL+SS-MoA2 Si(001):As Gas-source Molecular Beam Epitaxy: As Incorporation and Film Growth Kinetics, *H. Kim*, University of Illinois; *G. Glass*, PTD, Intel Corp.; *J.A.N.T. Soares*, University of Illinois; *P. Desjardins*, Ecole Polytechnique de Montreal; *J.E. Greene*, University of Illinois

Arsenic-doped Si(001) layers with concentrations C@sub As@ up to 5x10@super 18@ cm@super -3@ were grown on Si(001)2x1 at temperatures T@sub s@ = 575 - 900 °C by GS-MBE using Si@sub 2@H@sub 6@ and AsH@sub 3@. At constant flux ratio, C@sub As@ decreases, while the film growth rate R@sub Si:As@ increases, with T@sub s@. TPD measurements show that As segregates strongly to the growth surface and that the observed decrease in C@sub As@ at high T@sub s@ is primarily due to increasingly rapid arsenic desorption from the segregated layer. Decreasing T@sub s@ enhances As incorporation. However, it also results in lower R@sub Si:As@ due to higher steady-state As surface coverages which decrease the total dangling bond coverage and, hence, the Si@sub 2@H@sub 6@ adsorption rate. At constant T@sub s@, C@sub As@ increases, while R@sub Si:As@ decreases, with increasing AsH@sub 3@ flux. All incorporated As resides at substitutional electrically active sites for concentrations up to 3x10@super 18@ cm@super -3@, the highest value yet reported for Si(001):As growth from hydride source gases. D@sub 2@ TPD spectra exhibit @beta@@sub 1@ and @beta@@sub 2@ peaks associated with Si monodeuteride and dideuteride desorption as well as a new peak @beta@@sub 3@ attributed to desorption from Si-As mixed dimers. Steady-state arsenic surface coverages during film growth, and the As segregation enthalphy, were quantitatively determined as a function of C@sub As@ by comparison with As-adsorbed Si(001) reference samples with known As coverages. From AsH@sub 3@ adsorption kinetics and incorporation data, the AsH@sub 3@ reactive sticking probability on Si(001) was determined and As incorporation kinetics were quantitatively modeled. Initial experiments have demonstrated that temperaturemodulated growth can be used to increase both R@sub Si:As@ and C@sub As@ while providing layers which are atomically flat.

2:40pm SC+EL+SS-MoA3 Scanning Tunneling Microscopy of Impurity Dimers on Hydrogen-Terminated Si(100)-2x1 Surface, S. Matsuura, University of Tokyo, Japan; M. Fujimori, S. Heike, Y. Suwa, H. Kajiyama, T. Onogi, Hitachi, Ltd., Japan; K. Kitazawa, University of Tokyo, Japan; T. Hashizume, Hitachi, Ltd., Japan

We report a new dimer structure on a hydrogen-terminated n-type Si(100)-2x1-H surface found by a scanning tunneling microscopy (STM). The dimer structure is observed almost same as regular surface Si dimers at filled state, at empty state, however, is observed as different structure showing spatial variation of electronic density of states. Similar results were obtained in the case of As-doped surface. The surface density of the structures derived from measurement of the samples with different dopant concentrations was found to be proportional to the dopant density. Electronic structures calculated by first-principles calculations for a phosphorous dimer or an arsenic dimer on the Si(100)-2x1-H surface are in good agreement with the bias dependent STM images of the newly-found structure on the P-doped or As-doped Si(100) surface, respectively. We concluded that the dimer structure represents dopant atoms incorporated on the Si surface and forming a dimer. The calculation also revealed that the surface phosphorous and arsenic atoms are more stable forming dimers than being isolated on the hydrogen-terminated Si surface.

#### 3:00pm SC+EL+SS-MoA4 Adsorption and Reaction of Fluorinated Fullerenes on Silicon, Y. Fujikawa, J.T. Sadowski, Tohoku University, Japan; K.F. Kelly, Pennsylvania State University; K.S. Nakayama, T. Sakurai, Tohoku University, Japan

The adsorption structure of fluorinated fullerene molecules deposited on silicon was studied using scanning tunneling microscopy (STM) and high-resolution electron energy loss spectroscopy (HREELS). The results of HREELS indicated that the fluorine atoms around the molecules were detached from the molecules and chemisorbed to the surface. These fluorine adsorption sites were directly observed around the adsorbed molecules in the STM images. Some of the fluorine-adsorbed sites were found to form thread-like structures, suggesting that the molecules print the fluorine atoms on the terrace due to the rolling movement of the molecules. Annealing produced different degrees of defluorination of the fullerenes and etching of the silicon surface depending on the temperature. By imaging the intermolecular structure of the molecules with the STM, we can directly observe the loss of the fluorine atoms.

#### 3:20pm SC+EL+SS-MoA5 STM Study of Self-Assembled Quantum-Dot Arrays of Sn on Si(111)-(7x7) Surface, *M. Yoon, R.F. Willis,* The Pennsylvania State University

The adsorption and diffusion mechanisms of Sn on the Si(111)-(7x7) at submonolayer coverages have been studied by scanning tunneling microscopy (STM). It is found that the preference of Sn adsorbates on the faultedhalves of the 7x7 unit cell is dependent on adsorbate coverage up to @THETA@ ~ 0.3 monolayer (ML). At higher coverages (~0.3 - 0.5 ML), the tin atoms cluster together on both halves of the 7x7 unit cell, forming a two-dimensional array of self-assembled quantum dots. This is in contrast to the behavior recently reported@footnote 1@ for Tl condensation on Si(111)-(7x7). In this latter case, the element occupies faulted half-cells preferentially and the surface remains metallic. In the present case, the Sn clusters are semiconducting, the surface showing an energy bandgap which increases with increasing coverage. The surface returns to metallic behavior as the number of Sn atoms approaches that of one monolayer of Si. @FootnoteText@ @footnote 1@L. Vitali, M. G. Ramsey, and F. P. Netzer, Phys. Rev. Lett. 83, 316 (1999).

#### 3:40pm SC+EL+SS-MoA6 Evolution of Surface Morphology During Sb Growth on Ge(100), L.H. Chan, E.I. Altman, Yale University

Surfactants such as Sb have been found to promote layer-by-layer growth on metal and semiconductor surfaces. It is known that Sb and Ge intermix only at elevated temperature past 630K. Temperature programmed desorption was performed to study the energetics of Sb adsorption on Ge(100). The results demonstrated a typical high temperature peak that saturated at 1020 K before the appearance of a low temperature sublimation peak below 650 K with increasing Sb exposure. An additional high temperature peak at 1070 K was attributed to bulk incorporation of Sb. On a nominal 1 ML Sb covered Ge(100) surface prepared by deposition at 300K and annealing above the multiplayer desorption peak, scanning tunneling microscopy studies showed three surface layers were exposed. The images displayed bias dependent contrast suggesting the layers were not chemically uniform. To address the reasons for the morphology changes and to identify different components on the surface, a systematic study of Sb growth as a function of coverage and temperature was

# Monday Afternoon, October 2, 2000

conducted. At room temperature, Sb adsorbs as tetramers and pairs of dimers. Several Sb@sub 4@ adsorption states are identified. Subsequent island growth leads to a poorly ordered surface with short strands of Sb dimer rows. The growth of longer dimer rows was interrupted by the growth of other nearby dimer rows randomly distributed on the Ge surface. Antimony incorporated into the top layer on either annealing or deposition at 600 K. Annealing gave well-structured dimer rows across the surface in all layers. However, intermixing of Sb and Ge at elevated temperature created ad-dimer clusters, vacancy islands, and reattachment of Sb and Ge ad-dimers on the top layer to the step edges. The implications of these results on surfactant-mediated growth will be discussed.

#### 4:00pm SC+EL+SS-MoA7 Effects of Exposure on GaSe Passivated Si(111), J.A. Adams, A. Bostwick, S. Meng, B.R. Schroeder, M.A. Olmstead, F.S. Ohuchi, University of Washington

GaSe growth on Si(111) 7x7 between 500°C and 550°C results in the formation of a bilayer, which passivates the substrate dangling bonds and serves as the interface for further film growth. Ga sits directly atop surface Si, and the resultant interface bonding leaves Se lone-pair states on the surface, similar to Si(111):As. This makes the Si(111):GaSe surface resistant to contamination, and additional GaSe does not stick for T@sub substrate@@>=@500°C. We have studied the effects of exp osure to various atmospheric constituents on the electronic states and surface structure of the bilayer-passivated silicon surface using x-ray photoelectron spectroscopy and diffraction (XPS/XPD), low-energy electron diffraction (LEED) and ultraviolet photoelectron spectroscopy (UPS). We find that exposure to N@sub 2@ at atmospheric pressure has no apparent effect on the atomic or electronic structure and no N@sub 2@ is found to stick on the surface. However, we find that exposure to atmosphere for 5 minutes does change the surface states as observed from UPS, although LEED shows that the atomic structure of the GaSe bilayer does not change. The surface states can be almost completely recovered upon annealing at 500°C for 1 minute. Exposure to other atmospheric constituents such as O@sub 2@ and H@sub 2@O were also studied.

4:20pm SC+EL+SS-MoA8 Temporal Changes of Photoemission Spectra of the Alkali-metal-induced Ge(111) 3x1 Surface, G. Lee, Korea Research Institute of Standards and Science, Korea; C. Hwang, Korea Research Institute of Standards and Science; Y. Park, S. Cho, Korea Research Institute of Standards and Science; Korea; H. Lee, Korea Research Institute of Standards and Science; E. Cho, Chonnam National University, Korea

We investigated the temporal changes of the core-level photoemission spectra of the Ge(111)3x1 reconstructed surface induced by alkali metals (Li and Na) in UHV chamber. It is found that while the spectra from the Ge(111)3x1-Na surface is hardly affected, those from the Ge(111)3x1-Li surface change significantly in time. We identify that the changes of the core-level spectra from the Ge(111)3x1-Li surface are due to the contamination by residual oxygen gas in the chamber. The contamination rate of the Ge(111)3x1-Li surface is even higher than that of the clean surface, contradicting the expectation that alkali-metal-induced 3x1 reconstruction passivates the surface against oxidation. We discuss the difference in the contamination rate between the Ge(111)3x1 surfaces induced by different alkali-metal adsorbates.

## 4:40pm SC+EL+SS-MoA9 Role of Excited Electronic States in Reactions on Si(100), J.S. Hess, D.J. Doren, University of Delaware

Low-lying excited electronic states of the Si(100) surface can play a role in activated adsorption reactions. The nature of the lowest surface excited state and its coupling to the surface ground state will be described. Density functional theory calculations on cluster models of Si(100) have been used to predict the minimum energy difference between the optimized ground state and first excited state levels. The minimum energy crossing point between the two states was explicitly calculated, as was the spin-orbit coupling between them. The energy needed to reach the excited state surface is low enough, and the coupling between the states is strong enough, that crossing between the two states will be facile. The two states will be in thermal equilibrium and a significant population of the excited state is expected at typical reaction temperatures. The role of the excited state in selected reactions will also be discussed.

# 5:00pm SC+EL+SS-MoA10 Dynamics of Photo-induced Reaction on a Chlorinated Si(111) Surface, S. Haraichi, F. Sasaki, Electrotechnical Laboratory, Japan

In order to study photo-induced reaction of Si/Cl in the low fluence region, which is an influential candidate for low-damage manufacturing at the atomic level, the reaction mechanism was examined in terms of the photo-

excitation dynamics using femtosecond second-harmonic generation (SHG). SH signals on a clean 7x7 surface show a rapid dip induced by the pump beam, which is finished within several 100 fs. It is ascribed to charge transfer from the bulk Si to the 7x7 surface and subsequent surface recombination of photo-produced carriers through surface dangling bond states. The rapid dip is not seen on the chlorinated surface, because the surface dangling bond states are disappeared. With the increase of the pump beam power the decay profile of SH signals drastically changes and an upward peak clearly appears on the chlorinated surface. The upward peak is due to the precursor of surface reaction on the Si/Cl system. Though we observed both of photo-excitation SH dynamics on an n-type and a p-type Si surface, the difference was not found. The band bending near the chlorinated surface does not contribute to the reaction dynamics, because it is most likely that the photo-produced carriers immediately flatten the bands. We also observed the reaction dynamics dependence on the pump photon energy. The threshold pump power of the reaction induced by a 1.55 eV pump peam and a 3.1 eV pump beam were 45 mW and 4 mW, respectively. This difference is not only due to an absorption coefficient but also the excitation levels and the relaxation paths, because the upward peak position of SH dynamics was different in two pump photon energy.

#### **Author Index**

-A-Adams, J.A.: SC+EL+SS-MoA7, 2 Altman, E.I.: SC+EL+SS-MoA6, 1 — B — Bostwick, A.: SC+EL+SS-MoA7, 2 - C -Chan, L.H.: SC+EL+SS-MoA6, 1 Cho, E.: SC+EL+SS-MoA8, 2 Cho, S.: SC+EL+SS-MoA8, 2 — D — Desjardins, P.: SC+EL+SS-MoA2, 1 Doren, D.J.: SC+EL+SS-MoA9, 2 — F — Fujikawa, Y.: SC+EL+SS-MoA4, 1 Fujimori, M.: SC+EL+SS-MoA3, 1 — G — Glass, G.: SC+EL+SS-MoA2, 1 Greene, J.E.: SC+EL+SS-MoA2, 1 -H-Haraichi, S.: SC+EL+SS-MoA10, 2

### Bold page numbers indicate presenter

Hashizume, T.: SC+EL+SS-MoA3, 1 Heike, S.: SC+EL+SS-MoA3, 1 Hess, J.S.: SC+EL+SS-MoA9, 2 Hwang, C.: SC+EL+SS-MoA8, 2 — K — Kajiyama, H.: SC+EL+SS-MoA3, 1 Kelly, K.F.: SC+EL+SS-MoA4, 1 Kim, H.: SC+EL+SS-MoA2, 1 Kimura, Y.: SC+EL+SS-MoA1, 1 Kitazawa, K.: SC+EL+SS-MoA3, 1 -L-Lee, G.: SC+EL+SS-MoA8, 2 Lee, H.: SC+EL+SS-MoA8, 2 -M-Matsuura, S.: SC+EL+SS-MoA3, 1 Meng, S.: SC+EL+SS-MoA7, 2 -N-Nakayama, K.S.: SC+EL+SS-MoA4, 1 Niwano, M.: SC+EL+SS-MoA1, 1

-0-Ohuchi, F.S.: SC+EL+SS-MoA7, 2 Olmstead, M.A.: SC+EL+SS-MoA7, 2 Onogi, T.: SC+EL+SS-MoA3, 1 — P — Park, Y.: SC+EL+SS-MoA8, 2 — S — Sadowski, J.T.: SC+EL+SS-MoA4, 1 Sakurai, T.: SC+EL+SS-MoA4, 1 Sasaki, F.: SC+EL+SS-MoA10, 2 Schroeder, B.R.: SC+EL+SS-MoA7, 2 Seyama, A.: SC+EL+SS-MoA1, 1 Shinohara, M.: SC+EL+SS-MoA1, 1 Soares, J.A.N.T.: SC+EL+SS-MoA2, 1 Suwa, Y.: SC+EL+SS-MoA3, 1 -w-Willis, R.F.: SC+EL+SS-MoA5, 1 — Y — Yoon, M.: SC+EL+SS-MoA5, 1