Surface Science
Room 328 - Session SS1-WeM

Adsorption on Semiconductor Surfaces

Moderator: E.D. Williams, University of Maryland at College Park

8:20am SS1-WeM1 H Transfer and Ge/Si Site Exchange during Germane Adsorption at Si(001), *T. Murata, M. Suemitsu,* Tohoku University, Japan

Germane adsorption at Si(001) is important as an initial elementary step for Ge/Si heteroepitaxy. It also provides an ideal platform to investigate Ge adsorption at Si sites, one of the elementary processes in SiGe epitaxy. Little is known, however, on its details. Among the remaining issues are whether H atoms from germane are transferred to Si atoms or they stay intact at Ge sites and whether a site exchange occurs between Si and Ge during adsorption. To tackle these problems, we have combined TPD and multiple-internal-reflection FTIR, and have investigated the Si(001) surface adsorbed with germane at room temperature. These two methods form a complementary pair since TPD backs up the quantitative aspect of the characterization while FTIR is most powerful in state-resolved analysis. The findings we present here are (1) that almost all the H atoms are transferred from germane to Si atoms and (2) that the site exchange does occur between Si and Ge even at room temperature. The finding (1) is supported by exhaustive dominance of both the SiH-related @beta@@sub 1@ desorption peak in TPD and the SiH-related stretching band in FTIR. Persistence of these SiH-related signatures up to ~1ML of hydrogen coverage is hardly understood without considering a site exchange between substrate Si and adsorbed Ge atoms, leading us to the conclusion (2). Recent ab-initio calculations suggest that the two findings originate from a single event: adatom diffusion. According to Jeong and Oshiyama,[1,2] Si adatom diffusion on Si(001):H surface proceeds via release of the H atom from the adatom to a substrate Si atom, site exchange between the adatom and another substrate Si atom, and capture of the H atom by a "new" adatom. The larger Si-H bonding energy in excess of 30 meV/atom than that of Ge-H may stabilize the Si-H/Ge state once formed. @FootnoteText@ [1] Jeong and Oshiyama: Phys. Rev. B58(1998)12958.[2] Jeong and Oshiyama: Surface Science 436(1999)L666.

8:40am SS1-WeM2 Surface Interaction of SiH@sub 3@ Radicals with Amorphous Silicon: Temperature Dependence of the SiH@sub 3@ Surface Reactivity and the Surface Hydride Composition, *W.M.M. Kessels, J.P.M. Hoefnagels, P.J. Van den Oever, Y. Barrell, A.H.M. Smets, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The growth of hydrogenated amorphous silicon (a-Si:H) thin films from SiH@sub 4@ plasmas is expected to be dominated by SiH@sub 3@ radicals created in the plasma. To obtain insight into the surface reactions of SiH@sub 3@ on the a-Si:H surface, the surface reaction probability of SiH@sub 3@ has been determined by time-resolved cavity ringdown spectroscopy. The experiments have been carried out under nearly pure SiH@sub 3@ conditions for substrate temperatures between 50-450 °C. It has been found that the surface reaction probability of SiH@sub 3@ is 0.30±0.03 independent of the substrate temperature. Information about the chemical state of the a-Si:H surface in terms of surface silicon hydrides has been determined by in situ attenuated total reflection infrared spectroscopy combined with Ar-ion induced desorption experiments. These experiments - carried out in the same temperature range - have revealed that the a-Si:H surface composition changes drastically with increasing substrate temperature from a -SiH@sub 3@ covered surface at low temperatures to a -SiH@sub 2@ and a -SiH covered surface at higher temperatures. From the combination of the experimental results and ab initio calculations and molecular dynamics simulations in the literature, it is concluded that a-Si:H film growth takes place by a two-step reaction mechanism of SiH@sub 3@ in which H abstraction from the surface by SiH@sub 3@ in an Eley-Rideal reaction is the rate-limiting step. This abstraction reaction, which requires nearly zero activation energy, is unaffected by the changing surface silicon-hydride composition and leads to temperature independent growth site creation. SiH@sub 3@ radicals can subsequently stick on the dangling bonds created. Furthermore, some preliminary ideas on an (associated) surface diffusion mechanism will be discussed on the basis of the surface roughness evolution of a-Si:H at different temperatures.

9:00am SS1-WeM3 Interface Structure of an Ultrathin SiO@sub 2@ Film Fabricated by Ozone on Si(100), *K. Nakamura, S. Ichimura,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

Highly concentrated ozone gas is one of the alternative oxidants to fabricate an ultrathin silicon oxide film at low temperature for the microelectronics technology. Our previous study using an HF etching rate of oxide films has implied that, in contrast to a thermally grown oxide film, the thickness of structural transition layers of an ozone-oxide film is so limited within a much thinner region.@footnote 1@ However, direct information on the structure of this interface has not been so far obtained. Thus, we investigated the structure of an ozone-oxide film at the interface on Si(100) by analyzing transverse optical (TO) and longitudinal optical (LO) phonon modes of Si-O-Si asymmetric stretching vibration with Fourier-transformed infrared spectroscopy (FT-IR). The Si-O-Si bond angle in the ozone-oxide film was found to be undistorted even in the region close to the interface. In the case of a thermally grown oxide film, both peaks are known to make a clear red-shift.@footnote 2,3@ However, the position of a TO phonon peak of an ozone-oxide film fabricated at 350 °C kept constant at 1065 cm@super -1@ within <2 nm thickness. Only the LO phonon peak made a red-shift from 1240 to 1200 cm@super -1@. Since the TO phonon frequency is a function of a Si-O-Si bond angle,@footnote 4@ the result shows that the Si-O-Si angle in the thermally grown oxide is distorted close at the interface, but that this bond angle in the ozone-oxide remains unchanged, thus reducing the thickness of structural transition layers compared to that of the thermal oxide. @FootnoteText@ @footnote 1@ K. Nakamura, S. Ichimura, A. Kurokawa, K. Koike, G. Inoue, and T. Fukuda, 17 (1999) 1275.@footnote 2@ S. Miyazaki, H. Nishimura, M. Fukuda, L. Ley, J. Ristein, Appl. Surf. Sci. 113/114 (1997) 585.@footnote 3@ K. T. Queeney, M. K. Weldon, J. P. Chang, Y. J. Chabal, A. B. Gurevich, J. Sapjeta, and R. L. Opila, J. Appl. Phys. 87 (2000) 1322.@footnote 4@ F. L. Galeener, Phys. Rev. B 19 (1979) 4292.

9:20am SS1-WeM4 Application of MIR-FTIR to Multilayered Structures Built on Silicon Substrate: TiCN and Al Deposition and Effects of Hydrogen Diffusion, *S. Bocharov, A.V. Teplyakov,* University of Delaware

A combination of infrared spectroscopy, thermal desorption mass spectrometry, ToF-SIMS and AFM was used to analyze deposition of TiCN and Al from CVD precursors onto a Si(100)-2x1 surface. The TiCN films were easily deposited from tetrakis-(dimethylamino)-titanium (TDMAT) on a clean Si(100)-2x1 surface at slightly elevated temperatures and pressures of 2 microtorr and even lower. Monolayer chemistry does not lead to TiCN deposition. On the other hand, at 593K deposition of TiCN can be easily achieved. The onset of the deposition process coinsides with the thermal decomposition of surface species resulting from the monolayer reactions. The unusual application of MIR-FTIR to study multilayered structures was successfully performed for TiCN and Al deposition onto a TiCN-precovered Si(100). Interestingly, not only surface chemistry of the CVD precursors on TiCN, but also the transformation of the TiCN/Si interface can be followed by such an approach. Hydrogen diffusion from surface decomposition was shown to play a significant role in the formation of the multilayered structure. It was also observed that the diffusion of hydrogen atoms produced by hydrogen dissociation on a hot tungsten filament drives hydrogen towards TiCN/Si interface.

9:40am SS1-WeM5 Indium Phosphide (001)-(2x1): Evidence for a Hydrogen-Stabilized Surface Reconstruction, *G. Chen, D. Cheng, D. Tobin, Y. Sun,* University of California, Los Angeles; *K. Raghavachari,* Indiana University; *R.F. Hicks,* University of California, Los Angeles

Metalorganic vapor-phase epitaxy (MOVPE) is widely used to produce InP-based optoelectronic devices. Deposition of InP (001) films occurs in a large excess of the group V precursors, resulting in the formation of a P-rich (2x1) reconstruction. Scanning tunneling microscopy indicates that the (2x1) is terminated with a complete layer of buckled phosphorus dimers. This structure has been the subject of debate, because it should violate the electron counting model and exhibit partially filled P dangling bonds. In this work, we report on a vibrational study of the (2x1) surface prepared in the MOVPE environment. Infrared spectra collected during deuterium titration reveals the presence of a single sharp P-H stretching mode at 2308 cm^-1. Based on theoretical cluster calculations using density functional theory, this mode results from a single hydrogen atom bonded to one end of the buckled phosphorus dimer. This structure does not violate the electron counting model. In addition, slab calculations by another research group indicate that hydrogen-termination of the P dimers should yield the most stable configuration for the (2x1). Therefore, it may be concluded that

adsorbed hydrogen atoms stabilize the phosphorus-rich surface structure during indium phosphide film growth by MOVPE.

10:00am SS1-WeM6 Chemically Resolved STM Imaging of Al on Al$_{0.1}$Ga$_{0.9}$As(001)-c(2x8)/(2x4), *M.J. Hale, D.L. Winn, A.C. Kummel,* University of California, San Diego

It has been proposed that growing an oxide/AlGaAs/GaAs stack will prevent interface roughness from interfering with carrier mobility within the channel when attempting to create a GaAs-based MOSFET. Before attempting to grow an oxide/AlGaAs interface, one must first characterize the AlGaAs(001) surface. We will present STM images of the AlGaAs(001) surface in which Al and Ga can be distinguished. Al atoms in the second layer of Al$_{0.1}$Ga$_{0.9}$As(001)-c(2x8)/(2x4) cause the adjacent As atoms in layer one to be brighter than As atoms bonded to Ga atoms in STM images. Al is a stronger charge donor than Ga, which makes the As atoms in layer one bonded to Al atoms in layer two to have a greater charge density than As atoms bonded to Ga. This affect was only seen for p-type AlGaAs grown on a p-type GaAs substrate. Scanning tunneling spectroscopy (STS) measurements show that the excess charge transferred to the first layer As atoms from the second layer Al atoms causes electrical inversion to occur on the surface. For n-type Al$_{0.1}$Ga$_{0.9}$As(001)-c(2x8)/(2x4) grown on an n-type GaAs substrate, the ability to differentiate Al from Ga atoms in STM images is not possible. STS spectra show that the Fermi level resides near the conduction band, typical of a non-inverted n-type sample. This result is consistent with our model of a strong charge donation by Al since excess charge would not affect the position of the surface Fermi level in n-type material. The ability to differentiate between second layer Al and Ga atoms on p-type AlGaAs(001) with STM will enable further studies to understand the oxide/AlGaAs(001) interface.

10:20am SS1-WeM7 Atomistic Mechanisms of Fermi-level Pinning at the Oxide-Semiconductor Interface, *J.Z. Sexton, M.J. Hale, D.L. Winn,* University of California, San Diego*; M. Passlack, A.A. Demkov,* Motorola Inc.*; A.C. Kummel,* University of California, San Diego

Understanding the mechanism of Fermi-level pinning is critical in the development of an electronically passive oxide - III/V semiconductor interface. This insulator-semiconductor interface is important in the development of a practical of III / V MOSFET technology. We have observed Fermi-level pinning and un-pinning in STM and STS at the GaAs(001)-2x4 surface in three cases, upon sub-monolayer a) deposition of oxygen atoms, b) vapor deposition of Ga$_2$O and c) vapor deposition of In$_2$O. We have seen that the oxide layer formed upon atomic oxygen exposure forms a pinned interface. However, when a vapor deposited gallium oxide layer is formed, the surface remains unpinned. When In$_2$O is vapor deposited on the GaAs-2x4 surface, several bonding structures are formed, ultimately leading to a pinned interface. We have identified the bonding structures using first-principles calculations and have identified the mechanism for Fermi-level pinning for all the cases listed above. The Fermi-level pinning in case a) is due to a deep-level state, caused by significant charge withdrawal from the gallium atoms by oxygen. The Fermi-level unpinning in case b) is due to the bonding configuration resulting in a geometrically favorable and charge balanced structure. The Fermi-level pinning in case c) is dependent on the specific structure observed in STM. We have done calculations to elucidate the bonding and electronic structure of the observed bonding configurations and have observed that some structures are pinned and some are unpinned. We have seen two types of Fermi-level pinning: 1) deep level pinning caused by a fixed interface atomic state in the band-gap region and 2) a dipole-like pinning that is distributed over the covalent bonding network which induces states on the valence and conduction band edges. In summary, the bonding structure at the interface determines the existence and type of Fermi-level pinning.

10:40am SS1-WeM8 Coupling Reactions of Trifluoroethyl Iodide on GaAs(100), *N.T. Kemp, N. Paris,* **N.K. Singh,** The University of New South Wales, Australia

Alkyl coupling reactions studied to date have been restricted to gold, silver and copper surfaces, where the only coupling product formed has always been the corresponding higher alkane. In this paper we report, the coupling reactions of trifluoroethyl iodide on GaAs(100) which forms, not only the higher alkane, but a higher alkene as well. In this respect the alkyl coupling reactions on the GaAs surface differ from those on transition metal surfaces. Additionally, the ability of a semiconductor surface to catalyse carbon-carbon bond formation has not been reported previously by other researchers. The techniques of X-ray photoelectron spectroscopy and thermal desorption spectroscopy have been used to study the surface reactions of 2-iodo-1,1,1-trifluoroethane (CF_3CH_2I) on GaAs(100). Our results show that coupling of surface CF_3CH_2 species, generated via the dissociative adsorption of CF_3CH_2I, yields both $CF_3CH_2CH_2CF_3$ and $CF_3CH_2CH=CF_2$. The coupling pathway competes with the disproportionation reactions of CF_3CH_2, to form $CF_2=CH_2$ as the major product of this pathway. In addition, we observe the formation of volatile etch products IF_x, GaI, AsI, GaF, AsF and As$_2$I. This paper will discuss the mechanisms by which these products form from the adsorbed CF_3CH_2 and I species, and the role that the GaAs surface plays in the reaction pathways proposed.

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