

## Surface Science Division Room 308 - Session SS1-TuA

### Semiconductor Surface Chemistry

Moderator: J.A. Yarmoff, University of California, Riverside

2:00pm **SS1-TuA1 The Effect of Phosphorus and Germanium on Silicon Surface Chemistry**, *J.E. Crowell, M.L. Jacobson, G.J. Batinica, M.C. Chiu*, University of California, San Diego

Our studies focus on the deposition surface chemistry of Group IV semiconductors. We have examined the effect that adatoms such as P, Ge, and both P/Ge have on (i) the Si precursor chemisorption behavior and (ii) the hydrogen desorption behavior. Surface phosphorus contains a lone pair of electrons rather than a dangling bond and is thus passive to adsorbing gas molecules, and acts as a site blocker to species diffusing on the surface. In contrast, Ge adatoms contain a dangling bond and behave in a way similar to Si. However, both adatoms modify the surface chemistry of silicon. This presentation will describe TPD, AES, and MIRIRS studies aimed at determining the effect of pre-adsorbed P and Ge on the reactivity of Si(100) and Si(111) surfaces. For example, disilane (Si@sub 2@H@sub 6@) reacts with the Si(100) surface at 300K to form a mixture of SiH@sub x@ species. At higher temperatures, recombination reactions occur which produce silane (SiH@sub 4@) and H@sub 2@ that subsequently desorb. The reactivity of the Si(100) surface decreases with increasing P coverage, as determined by the increase in the selectivity of the Si@sub 2@H@sub 6@ reaction toward SiH@sub 4@ production over H@sub 2@ production. The H@sub 2@ desorption temperature increases with increasing P coverage while the SiH@sub 4@ desorption temperature decreases. A similar increase in H@sub 2@ desorption energy was seen upon H atom exposure of the P/Si surface, whereas Ge pre-adsorption decreases it. These results, a comparison of the (100) and (111) Si surfaces, and the combined effect of P and Ge will be discussed within the framework of electronic and morphological modifications of the surface and ensemble size effects caused by the presence of these pre-adsorbed adatoms.

2:20pm **SS1-TuA2 In situ Boron Doping of Si(100): Effects of Low Boron Concentration on Hydride Surface Reactions**, *B. Gong, D.E. Brown*, University of Texas, Austin; *S.K. Jo*, Kyung Won University, South Korea; *J.G. Ekerdt*, University of Texas, Austin

Hydrogen desorption and hydride adsorption will potentially control film growth rates during in situ doping of Si(100) in chemical vapor deposition processes involving hydride gases. The reactions of hydrogen and disilane with boron-doped Si(100) have been studied with temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS) and low energy electron diffraction (LEED). Recent studies by our group have been conducted in the boron concentration range from 0.001 to 0.05 monolayer (ML) to illustrate the kinetic effects of in situ doping, which has a typical doping level of 10@super 16@-10@super 20@ cm@super -3@. With ~0.001 ML boron, TPD and HREELS show essentially no dihydride formation on the boron doped surface. After H-passivation, the boron doped surface (@theta@@sub B@~0.001 ML) shows a 2x1 reconstruction by LEED, while the H induced reconstruction on a clean surface at the same conditions shows a 3x1 reconstruction. This inability of the H-passivated Si(100) to undergo the 3x1 reconstruction is associated with the subsurface boron-induced silicon dimer vacancy defects. At slightly higher @theta@@sub B@, monohydride starts to be suppressed and decreases with increasing @theta@@sub B@. At @theta@@sub B@= 0.01 ML, monohydride formation decreased 15% and then more slowly with increasing boron coverage due to islanding. A boron electronic effect that deactivates silicon dangling bonds reduces active sites on the surface, which in turn shows less monohydride adsorption with increasing @theta@@sub B@. The saturation coverage of disilane decreases with increasing @theta@@sub B@ due to less dangling bonds as a result of the boron deactivating effect. However, the disilane adsorption rate increases with @theta@@sub B@ while the hydrogen desorption rate is not affected by the addition of boron. We propose that the boron effects on silicon deposition rate is a result of enhanced disilane adsorption rather than enhanced hydrogen desorption.

2:40pm **SS1-TuA3 Chemical Modification of Semiconductor Surfaces: Functionalization Using Cycloaddition Reactions**, *S.F. Bent*, New York University

Due to the increasing importance of organic-based electronic and optical devices, there is much interest in developing attachment chemistries to

join organic structures with inorganic semiconductor substrates. In this presentation, the use of unsaturated hydrocarbons to form the initial organic layer by direct bonding to silicon and germanium surfaces in vacuum will be discussed. A series of unsaturated molecules, both cyclic and non-cyclic, have been investigated using various methods including multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy, near-edge X-ray absorption fine structure (NEXAFS), and temperature-programmed reaction/desorption (TPR/D). Conjugated dienes such as butadiene can undergo Diels-Alder-like [4+2] cycloaddition reactions on both Si(100)-2x1 and Ge(100)-2x1 surfaces, whereas non-conjugated dienes and alkenes react by direct [2+2] addition. The relative reactivity of Si(100)-2x1 and Ge(100)-2x1 toward unsaturated molecules will be compared. An overview of the bonding and thermal reactivity of the different compounds will be presented, and the potential for these types of cycloaddition reactions in future applications will be discussed.

3:20pm **SS1-TuA5 Cycloaddition Reactions at Germanium Surfaces**, *S.W. Lee, L.M. Nelen*, University of Missouri, Columbia; *H. Ihm*, University of Texas; *C.M. Greenlief*, University of Missouri, Columbia

The adsorption and reaction of a number of cyclic unsaturated hydrocarbons with the Ge(100) surface is investigated. It is shown that well-defined ordered organic layers can be formed on semiconductor surfaces. On semiconductor surfaces the majority of the reactions with hydrocarbons occur at or near the dangling bonds of the reconstructed surface. The dangling bonds on a Ge(100)-(2x1) surface are arranged in surface dimers. This arrangement of dangling bonds means that it is possible to form a molecularly ordered thin film that is covalently bound to the surface, provided that one can have the reaction occur at the dangling bond sites. In this paper we present an investigation of the structure and chemical bonding of the organic film/semiconductor interface. Data are obtained for a number of different starting precursor molecules using photoelectron spectroscopy, high resolution electron energy loss spectroscopy and temperature programmed desorption. The molecules investigated include 1,3-cyclohexadiene, 1,4-cyclohexadiene, and cyclohexene. The possibility of a surface Diels-Alder [4+2] cycloaddition, as well as, a [2+2] cycloaddition reaction are explored. Either cycloaddition reaction leads to an organic layer that is ordered with respect to the germanium surface.

3:40pm **SS1-TuA6 Binding Energies of Hydrogen on Flat and Vicinal Silicon Surfaces**, *M.B. Raschke, U. Höfer*, Max-Planck-Institut für Quantenoptik, Germany

Despite the importance of hydrogen interaction with silicon in many technological applications and its role as a model system for chemisorption on semiconductor surfaces, the binding energy of hydrogen on silicon surfaces is not well known. In a novel experimental approach, a bakeable UHV-quartz apparatus was used to establish thermal equilibrium between molecular hydrogen and well-defined Si(111) and Si(001) surfaces at gas pressures of 10@super -5@ 1 mbar and temperatures of 770 - 980 K. Under these conditions, continuous dissociative adsorption and recombinative desorption of H@sub 2@ lead to an equilibrium hydrogen coverage on the surfaces which is measured sensitively using optical second-harmonic generation (SHG). The resulting adsorption isotherms allow for the accurate determination of the hydrogen binding energies and their dependence on surface coverage. In the case of H/Si(111)7x7, the binding energy increases from 2.9 eV to 3.1 eV in the investigated coverage range between 0.05 ML and 0.3 ML. The Si-H bond is thus found to be considerably weaker than hydrogen bonding in silanes (3.7-3.9 eV). The values are compatible with a large barrier (0.9 eV) for phonon-assisted sticking of H<sub>2</sub>/Si.<sup>1</sup> They are in good agreement with theoretically predicted Si-H bond strengths at the adatoms and restatoms of this surface.<sup>2</sup> Exploiting substantial differences in reactivity between the step and terrace sites towards molecular hydrogen, equilibrium and non-equilibrium hydrogen coverages on vicinal Si(001) could also be investigated. From measurements for various surface temperatures on samples with different angles of miscut it is inferred that the steps are thermodynamically favored by approximately 0.2 eV.<sup>1</sup> <sup>2</sup> Bratu and U. Höfer, Phys. Rev. Lett. 74 (1995) 1625. <sup>2</sup> H. Lim, K. Cho, I. Park, J. D. Joannopoulos, and E. Kaxiras, Phys. Rev. B 52 (1995) 17231

4:00pm **SS1-TuA7 The Reactions of Trimethylgallium and Ammonia on GaN(0001)**, *H.-T. Lam, J.M. Vohs*, University of Pennsylvania

The reactions of trimethylgallium and ammonia on MOVPE-grown GaN(0001) were studied using temperature programmed desorption, high-resolution electron energy loss spectroscopy, Auger electron spectroscopy,

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and Rutherford backscattering spectrometry. The results of this study show that TMGa dissociates on GaN(0001) to form monomethylgallium (MMGa) and/or dimethylgallium (DMGa) and surface methyl groups at temperatures above 250 K. The MMGa/DMGa species either desorb between 250 and 450 K or undergo further dissociation forming adsorbed methyl groups and Ga atoms. For low TMGa coverages, surface methyl groups desorb near 600 K producing gaseous methyl radicals. At higher coverages a fraction of the methyl groups undergo dehydrogenation producing methane at 590 K and surface carbon atoms. The reaction of ammonia on GaN(0001) was found to proceed via dissociation to form surface NH<sub>x</sub> species and atomic hydrogen above 300 K.

**4:20pm SS1-TuA8 An Investigation of the Surface Reaction Mechanisms of Alternating-Grown Ordered Layers: CdS on ZnSe(100), M. Han, Y. Luo, J.E. Moryl, R.M. Osgood, Jr., Columbia University**

In previous experiments we have found that ordered layers of CdS on ZnSe(100) substrate were formed by a binary surface reaction sequence using gas-phase dosing of the substrate with CH<sub>3</sub>Cd and with H<sub>2</sub>S. This system provides a prototypical example of the interplay between reaction and desorption in such a binary sequence. In this talk we report a careful investigation of the surface chemistry using TPD. The experiments were performed in a UHV chamber, which is also equipped with AES, LEIS and LEED. Analysis of the TPD spectra show clearly that adsorbed DMCd irreversibly dissociates on ZnSe(100)-c(2x2) surface, and that the previously reported self-limiting reaction results from a methyl-termination of the surface. At ~ 370K, DMZn desorbs from this surface due to a methyl exchange reaction. This desorption temperature is independent of coverage, indicating a first-order reaction. In addition, at high DMCd exposures, the adsorption and desorption process leads to replacement of surface Zn by Cd. The experiments have also examined the reaction of the methyl-terminated surface with H<sub>2</sub>S. This reaction is also self-limiting, yielding desorbed CH<sub>4</sub> and forming a sulfur-hydride-terminated surface. Studies of surfaces formed by more than one binary reaction sequence showed that the alternating growth surfaces are also terminated with either methyl group or sulfur-hydride. The methyl-passivated surface above the first layer preferentially desorbs methyl radicals at ~390K instead of metal-alkyl species. For the sulfur-hydride-terminated surface the recombinative reaction of HS species causes desorption of H<sub>2</sub>S at 480K. In this case, the symmetric peak shape and its shift to lower temperature with increasing the coverage suggest a second-order reaction mechanism. In more general terms the above results indicate that the relative strengths of bonding energy for methyl-metal(II) and metal-VI element play an important role in the surface reactions.

**4:40pm SS1-TuA9 Competition Between Passivating and Etching in Halogen Reactions with III-V Semiconductor Surfaces, W.K. Wang, University of California, Riverside; W.C. Simpson, Pacific Northwest National Laboratory; J.A. Yarmoff, University of California, Riverside**

Halogen adsorption on III-V semiconductor surfaces with certain reconstructions leads to the formation of an ordered overlayer, while other III-V surfaces become disordered and etch. It has been suggested that the initial atomic structure and stoichiometry play important roles in determining whether a surface passivates or etches. A single crystal face of a given III-V material can have many surface reconstructions, each of which has a slightly different stoichiometry in the outermost few atomic layers. In this study, a direct comparison is made of the adsorption of halogens on different reconstructions of the same material. From the results, the microscopic mechanism underlying the predilection for ordering or disordering can be ascertained. Synchrotron-based soft x-ray photoelectron spectroscopy and low energy electron diffraction were employed to investigate surfaces following reaction. These techniques provide information about the chemical bonding and ordering on the surface. For example, for I<sub>2</sub> reaction with the In-terminated InAs(100)-c(8x2) surface, a well-ordered (1x1) structure forms and all of the iodine attaches to In. The As-terminated InAs(100)-c(2x8) surface, on the other hand, becomes disordered and iodine attaches to both In and As atoms. This can be explained by a preference for iodine to initially bond with the electron-deficient group III In atoms. In contrast, I<sub>2</sub> reaction produces ordered structures on both the Ga-terminated and As-terminated GaAs(100) surfaces. Cl<sub>2</sub> reactions almost always lead to etching after sufficient exposures, no matter what the initial surface structure, although following small exposures some ordered structures may form. In this presentation, the microscopic mechanisms underlying this behavior will be discussed.

**5:00pm SS1-TuA10 A Scanning Tunneling Microscopy Study of [(t-butyl)GaS]<sub>4</sub> Adsorption on GaAs, R.I. Pelzel, University of California, Santa Barbara, U. S. A.; B.Z. Noshov, University of California, Santa Barbara; B. Firmland, Norwegian University of Science and Technology, Norway; W.H. Weinberg, University of California, Santa Barbara**

Gallium sulfide layers grown using the single-source molecular precursor [(t-butyl)GaS]<sub>4</sub> have shown promise in providing long-term chemical and electrical surface passivation for GaAs. With this in mind, we have conducted an ultrahigh vacuum investigation of the initial stages of [(t-butyl)GaS]<sub>4</sub> adsorption on GaAs(100)-(2x4) and (4x2). Adsorbing [(t-butyl)GaS]<sub>4</sub> at elevated surface temperatures (> 650 K) results in carbon-free adsorption as judged by Auger electron spectroscopy. For low coverages on both reconstructions, low energy electron diffraction (LEED) data indicate that both the (2x4) and the (4x2) surface reconstructions remain intact. Scanning tunneling microscopy (STM) images show that the adsorption of submonolayer coverages of [(t-butyl)GaS]<sub>4</sub> disorders the surface reconstructions. Subsequent deposition results in further disordering until a coverage of approximately 1 ML where a weak (2x1) LEED pattern is observed. The (2x1) surface order is not observable in STM prior to annealing to a temperature of approximately 780 K. The (2x1) surface observed using STM following annealing is well-ordered, and images will be presented. Possible models of GaS growth achieved using [(t-butyl)GaS]<sub>4</sub> will be discussed. @FootnoteText@ @footnote 1@ P. P. Jenkins, A. N. MacInnes, M. Tabib-Azar, and A. R. Barron, Science 263, 1751 (1994); A. N. MacInnes, M. B. Power, A. R. Barron, P. P. Jenkins, and A. F. Hepp, Appl. Phys. Lett. 62, 771 (1993); M. Tabib-Azar, S. Kang, A. N. MacInnes, M. B. Power, A. R. Barron, P. P. Jenkins, and A. F. Hepp, Appl. Phys. Lett. 63, 625 (1993).

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