Wednesday Afternoon, November 4, 1998

Surface Science Division Room 309 - Session SS2-WeA

Photochemistry and Deposition

Moderator: C.M. Greenlief, University of Missouri, Columbia

2:00pm SS2-WeA1 Photochemical Routes to Group IV Deposition, G.J. Batinica, J.L. Stepnowski, J.E. Crowell, University of California, San Diego

The fabrication of high-speed electronic devices requires the controlled epitaxial deposition of Si and SiGe thin films. We have explored both thermal and photochemical routes to Si and Ge deposition using disilane (Si@sub 2@H@sub 6@) and digermane (Ge@sub 2@H@sub 6@) as model hydride deposition sources. We have also compared the thermal and photochemical reactivity of Si(100) versus that of Si(111). The deposition reactions have been studied using multiple internal reflection infrared spectroscopy (MIRIRS), temperature programmed desorption (TPD), and Auger electron spectroscopy (AES). Hydrogen and silane (SiH@sub 4@) desorption yields were used to determine the reactivity of disilane on the Si surfaces with and without UV irradiation. Hydrogen and germane desorption yields and relative Ge/Si AES signals were used to determine the reactivity of digermane. UV irradiation during or after dosing of the Si crystal surfaces at 110K greatly enhanced the reactivity of disilane and digermane compared to similar exposures without UV irradiation. Comparison of the reactivity of disilane with Si(100) versus Si(111) show that Si(111) is thermally less reactive than the Si(100) surface. However, both surfaces show similar photo-reactivity to disilane. The photo-induced mechanism of disilane and digermane reactions has been studied using clean, partially deuterated and fully deuterated Si(111) and Si(100) surfaces. Thermally, the reactivity is controlled by the surface dangling bonds; whereas the photo-induced deposition chemistry appears to primarily involve insertion by the photo-generated diradicals, silvlene and germylene. The implication of our results on deposition methodologies will be discussed.

2:20pm SS2-WeA2 Electron Induced Deposition of Germanium on Si(100): TPD, XPS, and HREELS Study, J. Lozano, University of Texas, El Paso, U.S.; J.H. Craig, J.H. Campbell, University of Texas, El Paso

Temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high resolution electron energy loss spectroscopy (HREELS) were used to investigate the effects of an electron beam on Si(100) dosed with digermane at 110 K. At high digermane coverages (>1 ML), three peaks appear on hydrogen TPD traces at 140 K, 575 K, and 740 K. The peak at 140 K corresponds to desorption of hydrogen from molecular overlayers of digermane, as confirmed by the desorption of digermane fragments at 140 K. The TPD features at 575 K and 740 K correspond to hydrogen desorption from surface germanium and from silicon, respectively. The vibrational losses at 820 and 2040 cm@super -1@ in the HREELS data obtained from digermane-covered Si(100) indicate the presence of germanium hydride species on the surface. The formation of the silicon monohydride state is evident by the high-energy broadening of the loss feature at 2040 cm@super -1@. Upon exposure of the highly dosed surface to an electron beam (maximum current density of 9µA/cm@super 2@), the intensity of the low temperature TPD peak at 140 K decreases, while the intensity of the peak at 575 K increases. XPS data show an increase on the relative surface concentration of germanium following electron irradiation of the digermane overlayers. Annealing the surface to 200 K does not decrease the relative concentration of germanium on the electron-irradiated surface. Electron irradiation of digermane/Si(100) at low digermane exposures does not have any detectable effects. These results indicate that the electron beam dissociates the digermane molecular overlayers and deposits germanium on the surface.

2:40pm SS2-WeA3 Photodesorption of Condensed Gases by Lyman-@alpha@, D.A. Bahr, R.A. Baragiola, University of Virginia

We measured the absolute desorption yield of water and carbon dioxide films condensed at low temperatires under irradiation with Lyman-@alpha@ (121.6 nm) photons as a function of sample temperature and irradiation fluence using a double quartz-crystal resonator. We also determined the species desorbed using mass spectrometry. We will discuss the results in terms of basic processes and discuss astrophysical implications. 3:00pm **SS2-WeA4 Photodesorption of Positive Ions from Oxyanion-Containing Inorganic Crystals**, *C. Bandis*, *M.L. Dawes*, *S.C. Langford*, *J.T. Dickinson*, Washington State University

Surfaces of inorganic, ionic crystals with complex oxyanions can be dramatically altered by UV and electron irradiation. Previous work has shown that such irradiation desorbs XO@sub n@ and O@sub 2@, where X = N, P, C, and possibly S. This electronic decomposition produces cation defect complexes from which intense positive ion emission can be photoinduced. We describe two-beam experiments where either two laser beams or a laser and an electron beam are cofocused. One beam (UV laser or electron) is used to generate defects, and the second beam (laser) is used to photodesorb ions. We report metal and metal-containing ion emission accompanying nanosecond laser pulses at 248 and 1064 nm from alkali nitrates and calcium phosphates. The resulting ion kinetic energies can exceed the photon energy by factors of ten. The effect of time delay between two pulsed beams will also be presented. The critical role of radiation induced chemistry and the ion emission mechanism will be discussed. This work is supported by the Department of Energy under Contract DE-FG06-92ER14252.

3:20pm SS2-WeA5 Direct Observation of Synchrotron-Radiation-Stimulated Decomposition of SiO@sub 2@ Thin Films on Si(111) Surfaces using Scanning Tunneling Microscopy, T. Miyamae, T. Urisu, S. Hirano, Institute for Molecular Science, Japan; H. Uchida, T. Yagi, Toyohashi University of Technology, Japan; I. Munro, Institute for Molecular Science, Japan

Synchrotron radiation (SR) stimulated decomposition of silicon dioxide thin films on Si(111) surfaces were observed by using a ultrahigh vacuum scanning tunneling microscopy (UHV-STM) and Low energy electron diffraction (LEED). SiO@sub 2@ films were shown to be almost removable by SR irradiation. Si(111)-(7 by 7) reconstructed structure were observed by LEED after two hours SR irradiation at surface temperatures as low as 650 C°. In spite of the observation of clear 7 by 7 LEED pattern, the STM images did not show clean and flat surface at this temperature. The clean (7 by 7) reconstructed surface temperature of 700 C°. Analysis of the evolution in the clean region suggests that the desorption mechanism may be different between thermal and SR stimulated desorption processes. The results show that the feasibility of this technique for low-temperature cleaning of silicone surface is demonstrated.

3:40pm SS2-WeA6 Surface Decomposition Reaction of Trisdimethylaminoantimony on GaSb(100)-(3x1), K. Yong, P.D. Kirsch, J.G. Ekerdt, University of Texas, Austin

Trisdimethylaminoantimony (TDMASb) is a novel Sb-precursor for the deposition of Sb-containing alloys by organometallic vapor phase epitaxy. Deposition using TDMASb can lower the growth temperature and also minimize carbon incorporation in the layers. The decomposition of TDMASb on GaSb(100)-(3x1) was studied using temperature programmed desorption, temperature programmed static secondary ion mass spectroscopy, low energy electron diffraction, and X-ray photoelectron spectroscopy. TDMASb decomposes on the surface at temperatures below 200 K and dimethylamine was desorbed through two reaction pathways. Homolysis of the antimony-nitrogen bond resulted in desorption of the dimethylamine radical at 380 K. Methylmethyleneimine was formed and desorbed from the surface through hydrogen elimination at 480 K. Deposition of Sb from 5 monolayers of TDMASb on GaSb(100) induced the change of surface structure from (3x1) to (1x1). We propose that surface Sb atoms are the reactive sites for the decomposition of TDMASb.

4:00pm SS2-WeA7 Interaction of Ethylene with the Ge(100)-2x1 Surface: Coverage and Time-Dependent Behavior, *A.V. Teplyakov*, Stanford University; *P. Lal, Y. Noah, M.J. Kong*, New York University; *S.F. Bent*, Stanford University

Chemical modification of semiconductor surfaces has been a subject of thorough investigations for decades because of its relevance to the fabrication of electrical and optical devices. Despite these efforts, very little is known about the chemical properties of germanium surfaces. Here we present studies of the adsorption and thermal chemistry of ethylene on Ge(100)-2x1. Ethylene has been studied in detail on Si(100)-2x1, and provides a good reference system for comparing silicon and germanium reactivity. The results of multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy and temperature programmed desorption (TPD) studies suggest that ethylene chemisorbs on the Ge(100)-(2x1) surface at room temperature. IR spectroscopy gives evidence for only one adsorbate structure on this surface at room temperature. However,

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TPD measurements show two molecular desorption features, indicating that at least two adsorption configuration can exist. Complex temperature-, time-, and coverage dependent behavior of ethylene adsorption on Ge(100)-2x1 will be presented and analyzed.

4:20pm SS2-WeA8 Interaction of Amines with Hydrogen on Al(111), J.N. Russell, Jr., C.S. Kim, Naval Research Laboratory

High quality AIN films, for optoelectronic devices, high power electronics and sensors, are generally produced via MOCVD of NR@sub 3@ and R@sub 3@Al (R = H, CH@sub 3@, or C@sub 2@H@sub 5@). We explored the chemical interaction of ammonia, methylamine, and ethylamine with clean and hydrogenated Al(111) in an UHV environment using temperature programmed desorption and/or infrared reflection absorption spectroscopy. On clean Al(111), the compounds adsorb molecularly and desorb by 200 K. In contrast, on the H-covered surface, a new desorption state (ß) is seen at about 250 K for each reactant. The ß-state coverage of each compound tracks that of H. Infrared spectroscopy shows that NH@sub 3@ preferentially adsorbs via a Lewis acid-base interaction at monohydride sites with the Al-N bond inclined away from the surface normal. While NH@sub 3@ does not dissociate nor exchange H atoms with the H-precovered surface, the alkylamines dissociate. New HD desorption features, at 240 and 270 K, are observed for perdeutero-alkylamines on H/Al(111). In addition, hydrocarbon desorption is observed at about 600 K for the alkylamines when coadsorbed with hydrogen. We discuss the implications of this work on the MOCVD of AIN films.

4:40pm SS2-WeA9 Adsorption and Reaction of Chlorine on Low Index Diamond Single Crystal Surfaces, S. Hadenfeldt, C. Benndorf, University of Hamburg, Germany

The lowering of the substrate temperature achieved by the low pressure diamond deposition from halogenated precursors is believed to involve surface processes, including halogen adsorption, desorption and reaction with H(ad). In this work we studied the adsorption of chlorine on the low index diamond (100), (111) and (110) single crystal surfaces as well as on polycrystalline diamond CVD films in UHV using thermal desorption spectroscopy (TDS), Augerelectron spectroscopy (AES), low energy electron diffraction (LEED) and photoelectron spectroscopy (UPS / XPS). Elemental halogen was dosed by solid state electrolysis of silverchloride at elevated temperatures or direct dosing of chlorine gas through a heated oxide ceramics tube. The single crystals were regularely cleaned by pretreatment in a hydrogen plasma and showed clear reflexes in LEED. The CVD films were studied as received from the CVD process. In AES upon successive halogen dosing a linear increase of the intensity of the halogen Auger signal and a simultaneous decrease in intensity of the 272 eV carbon signal can be seen at first. No LEED overstructures could be observed upon adsorption on either surface. Depending on the sample preparation and history, in general two different desorption behaviours are observed in TDS. From the hydrogen rich, plasma prepared surface chlorine is desorbed continuously with a maximum around 600 K. Around 850 K chlorine is completely removed. On a hydrogen depleted surface, where less halogen adsorbs at a given exposure, two regions of chlorine desorption can be observed. Up to 730 K a steady decrease of chlorine is noted, which levels off, until finally all chlorine is desorbed around 950 K. Halogen uptake of the diamond surface can be increased either by thermally activating the surface or by dosing of atomic hydrogen prior to halogen adsorption.

5:00pm SS2-WeA10 Desorption Kinetics of Hydrogen and Deuterium from Diamond (111)x(1x1) via Helium Atom Scattering, S.A. Safron, J.G. Skofronick, Florida State University; A. Glebov, J.P. Toennies, S. Vollmer, Max Planck Institut fuer Stroemungsforschung, Germany

The rate constants for the isothermal desorption of hydrogen and deuterium from diamond (111)-H(1x1) and -D(1x1) surfaces, respectively, have been measured over the temperature range 990 K to 1080 K by monitoring the helium atom Bragg diffraction beam intensities as a function of time. The rate behavior for both H and D followed first order reaction kinetics and a distinct isotope effect was observed in the desorption rates. The temperature dependence of the rate constants could be represented by an Arrhenius law. In fitting the data to determine the Arrhenius activation energies, the pre-exponential (or frequency) factors were taken to be the previously reported diamond (111)-(1x1) C-H or C-D stretching mode (S-mode) frequencies, 8.5x10@super13@ s@super-1@ for H and 6.4x10@super13@ s@super-1@ for D. The respective activation energies were then determined to be 2.69 eV (62.0 kcal/mol) and 2.74 eV (63.2 kcal/mol).@footnote1@ @FootnoteText@ @footnote1@ Work supported in part by US DOE grant no. DE-FG02-97ER45635 and NATO grant no. GRC.961145.

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