Wednesday Morning, November 4, 1998

Surface Science Division Room 308 - Session SS1-WeM

Physics of Semiconductors Moderator: J. Krim, North Carolina State University

8:20am SS1-WeM1 Medard W. Welch Award Lecture - Optical Spectroscopy of Surfaces and Interfaces: Progress and Opportunities, *D.E. Aspnes*¹, North Carolina State University INVITED

9:00am SS1-WeM3 Chemistry and Intermolecular Interactions of Nitridation and Oxidation Precursors on Si(100)-(2x1), K.T. Queeney, Bell Laboratories, Lucent Technologies; A.B. Gurevich, Columbia University; X. Zhang, E. Garfunkel, Rutgers University; J. Eng, Jr., B.B. Stefanov, K. Raghavachari, Y.J. Chabal, Bell Laboratories, Lucent Technologies

The manner in which various molecules adsorb, dissociate and interact on silicon surfaces can dramatically affect their subsequent incorporation into the silicon substrate and thus the nature of compounds formed at higher temperatures.@footnote 1@ We have studied mechanisms leading to oxidation, nitridation and oxynitridation of silicon via investigations of the structure and reactivity of H@sub 2@O, NO, NH@sub 3@ and N@sub 2@H@sub 4@ on Si(100)-(2x1). Dissociation of these molecules on a single Si-Si dimer yields well-defined structures which are identified using highresolution infrared absorption spectroscopy in a new, sensitive transmission geometry, together with density functional cluster calculations. This powerful combination of theory and experiment also reveals subtle frequency shifts associated with the inter-dimer interactions of surface intermediates. For example, in the case of water adsorption, hydrogen bonding between two hydroxyl groups on neighboring dimers leads to splitting of all the observed vibrations (@nu@(SiO-H), @nu@(Si-H), @delta@(Si-H), @delta@(Si-OH) and @nu@(Si-O)). The magnitude of these splittings (@>=@ 10 cm@super -1@) allows definitive characterization of these interactions with infrared spectroscopy. For instance, two @nu@(OH) peaks corresponding to coupled hydroxyls appear at 3675 and 3660 cm@super -1@, well resolved from the uncoupled O-H stretch at 3684 cm@super -1@; likewise, the two @nu@(Si-O) features of coupled hydroxyl groups are split to 14 cm@super -1@ above and 12 cm@super -1@ below @nu@(Si-O) of the uncoupled species. Similar effects are observed after co-adsorption of water and ammonia. Such interactions provide a natural mechanism for local oxygen and nitrogen agglomeration during the thermal evolution of these surfaces, observed by monitoring changes in @nu@(Si-H) as well as Si-N and Si-O vibrations as atomic nitrogen and oxygen insert into Si backbonds at higher temperatures. @FootnoteText@ @footnote 1@M. K. Weldon, B. B. Stefanov, K. Raghavachari and Y. J. Chabal, Phys. Rev. Lett. 79, 2851 (1997).

9:20am SS1-WeM4 Spectromicroscopy Evidence of Lateral Inhomogeneities for Metal-(III-VI) Semiconductor Interfaces, M. Zacchigna, H. Berger, Ecole Polytechnique Federale, Switzerland; G. Lorusso, F Cerrina, University of Wisconsin, Madison; G. Margaritondo, Ecole Polytechnique Federale, Switzerland

We exploited the very high lateral resolution of the MAXIMUM beamline on ALS to study microscopic lateral variations of semiconductor interface barriers. The capability to analyze the chemical properties with high lateral resolution often reveals unexpected overlayer-substratechemical reactions and links between such reactions and lateral barrier inhomogeneities. The experiment first studied lateral band bending changes in metalsemiconductor junctions for several interfaces between Au or Al and different III-VI compounds. By taking photoemission spectra on a series of microscopic spots along the interface is possible to detect the band bending with high lateral resolution. A novel way to perform this type of measurements, giving the "image" of the band bending, will be presented. The second and more interesting part of our study concerns the search for inhomogeneities in the first steps formation of metal-(III-VI) interfaces. We did discover such inhomogeneities in several prototypical interfaces, expanding and corroborating preliminary data on Au-GaSe interface. Furthermore, for the first time we did establish the sought link between barrier fluctuations and local chemical properties

9:40am SS1-WeM5 Direct Determination of the Interplay between Gas-Surface Reactivity, Thin Film Strain and Alloy Surface Segregation: Growth of Strained Heteroepitaxial Si@sub 1-x@Ge@sub x@ Thin Films on Si(100), A.M. Lam, Y.J. Zheng, J.R. Engstrom, Cornell University

Silicon-Germanium alloys have attracted attention for more than a decade. The addition of Ge to Si epitaxial films leads to a variety of effects and phenomena, some well understood, some not. Almost untouched are phenomena related to the dissociative adsorption of the relevant thin film precursors on surfaces of the growing alloy. Knowledge of the corresponding sticking coefficients is key to developing relationships between gas phase, surface and sub-surface/bulk compositions. Concerning alloy (Ge) segregation, virtually all work conducted to date has relied on a single in situ experimental probe. We shall present here a comprehensive study of the heteroepitaxial growth of Si@sub 1x@Ge@sub x@ alloys on Si(100) employing no less than 3 complementary in situ probes: supersonic molecular beam scattering, x-ray photoelectron spectroscopy (XPS), and low-energy ion scattering spectrometry (LEISS). Our results for the first time demonstrate the importance of strain in determining gas-surface reactivity in these heteroepitaxial alloys-- the reactivity of the strained Si@sub 1-x@Ge@sub x@ overlayers is not simply an appropriate combination of pure component (bulk, relaxed) reactivities. On the other hand, use of the complementary in situ surface analyses of XPS and LEISS has allowed us to determine both the extent and nature of Ge surface segregation, and its dependence on film growth conditions. In all cases the surface Ge concentration exceeds that found in the bulk (often by an order of magnitude). A two-site model (involving surface and bulk) cannot account for both the XPS and LEISS results, rather a model invoking Ge enrichment in the subsurface layers is required to explain the data.

10:00am SS1-WeM6 Ballistic Electron Emission Microscopy Studies of Tunneling to Surface and Bulk States on Cu (111) Thin Films, W.H. Rippard, M.K. Weilmeier, R.A. Buhrman, Cornell University, US

Thin bilayer films consisting of a thin Au layer and an overlayer of Cu have been grown on the surface of hydrogen passivated Si (111) and Si(100) wafers. UHV STM measurements reveal that these bilayers consist of ~10 nm grains with surfaces that are either atomically flat or transversed by only a few atomic step-edges. X-ray diffraction indicates that these films, for both substrates, consist nearly completely of (111) normal oriented grains. When ballistic electron emission microscopy (BEEM) measurements are made on these systems, a strong contrast is seen between the BEEM current when the STM tip is over a flat surface and when it is positioned at a grain boundary or step edge, with the higher BEEM current occurring in the latter case. This contrast in current can be as much as a factor of three, depending on the sharpness of the STM tip, and occurs for both (100) and (111) oriented substrates. STM spectroscopy measurements indicate the presence of pronounced surface states on the flat areas of the Cu surface and an absence of thes states at grain boundaries and steps. We conclude that the low BEEM current which occurs when the STM tip is positioned over a Cu surface mesa is the result of tunneling predominately to empty surface states, while at grain boundaries and step edges the STM tip is able to tunnel more strongly to the empty bulk states of the Cu, which enhances the BEEM signal. This observation provides a strong demonstration of the role of the metal band structure in determining the amplitude of the BEEM signal, even in the case of the noble metals, and demonstrates a new means by which the degree of coupling between bulk and surface states on the (111) normal surface of Cu, Au and Ag can be determined by BEEM.

10:20am SS1-WeM7 Current-Voltage Measurements of Ultrathin Metal-Si(111) Sensors, H. Nienhaus, H.S. Bergh, B. Gergen, University of California, Santa Barbara; A. Majumdar, University of California, Berkeley; E.W. McFarland, W.H. Weinberg, University of California, Santa Barbara A novel microfabricated Si-based device structure was developed in order to characterize the transport properties of thin metal films on Si(111) ranging from 10 Å to 150 Å. Metals were evaporated onto the device under ultrahigh vacuum conditions. The evaporation temperature was varied between 130 and 180 K. The design of the device allowed zero-force electrical contacts to the very thin metal films on silicon for current-voltage (I/V) measurements. The resulting I/V curves were analysed within the thermionic emission theory. The change of Schottky-barrier height, ideality factor and serial resistance was monitored as a function of film thickness and temperature. Cu, Ag and Fe films were investigated on Si(111). Generally, an improvement of the rectifying properties was observed with increasing thickness. To study the temperature dependence, Cu films of about 60 Å were annealed to room temperature. This treatment led to a significant increase of the barrier height from 0.45 to 0.65 eV and a

¹ Medard W. Welch Award Winner Wednesday Morning, November 4, 1998

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decrease of the ideality factor from about 2.5 to values close to 1. Subsequent cooling of the annealed samples conserved the excellent rectifying properties. This finding indicates that annealing of low-temperature deposited films reduces the inhomogeneity of the contact barrier height. Further evaporation of Cu onto annealed diodes led again to lower barrier heights and larger ideality factors. First results suggest that the devices are suitable sensors for detecting hot charge carriers created by gas-surface reactions.

10:40am SS1-WeM8 Electroless Deposition of Au onto H-Si(111), I. Suni, R. Srinivasan, Clarkson University

Electroless deposition of Au from aqueous HF onto p-type H-Si(111) has been studied by electrochemical methods, atomic force microscopy (AFM), Rutherford backscattering (RBS), and surface second harmonic generation (SHG). The H-terminated Si(111) surface is prepared by HF etching prior to Au deposition. We have found evidence that Au deposition occurs by a two-step process, where initial deposition of AuCN is rate-limited by diffusion, while subsequent reduction of Au is rate-limited by surface reaction involving a fluoride-containing species. The growth of Au nanoclusters can be monitored by SHG through the development of the surface plasmon resonance, which occurs above a threshold cluster size of about 2 nm. The SH signal goes through a temporal maximum and then declines again due to interdiffusion of Au and Si. Surface kinetics can then be analyzed by manipulating the solution phase equilibria and following the effects on Au reduction by SHG. This analysis reveals that HF, not HF@sub 2@@super -@, is the mechanistically important species and that Au reduction is half-order in HF.

11:00am SS1-WeM9 Growth of Si@sub 1-x@Ge@sub x@ on Si(011): Kinetics, Surface Structure, and Morphological Evolution, N. Taylor, H. Kim, T. Spila, P. Desjardins, J.E. Greene, University of Illinois, Urbana-Champaign

Strained Si@sub 1-x@Ge@sub x@/Si(011) heterostructures provide additional degrees of freedom over the more common Si@sub 1x@Ge@sub x@/Si(001) system for bandgap engineering. The maximum film/substrate conduction band offset is predicted to be substantially larger, the optical bandgap decreases more rapidly with increasing x, and optical selection rules allow hole-intersubband transitions to be excited by light parallel to multiple quantum well layers. In this investigation, Si@sub 1-x@Ge@sub x@ layers with x @<=@ 0.35 were grown on Si(011) by gassource molecular beam epitaxy (GS-MBE) using Si@sub 2@H@sub 6@ and Ge@sub 2@H@sub 6@ at T = 400-950 °C. The growth kinetics are a function of the following complex surface reconstructions: $16x^2$ at x < x@sub c@ and 2x8 at x > x@sub c@. The critical Ge concentration x@sub c@ ranges from 0.10 at T = 475 °C to 0.06 at T = 650 °C. As the temperature is raised from 650 to 725 °C, the surface gradually transforms to a 1x1 reconstruction for all x. Temperature-programmed desorption (TPD) measurements show that the 16x2 unit cell consists of 16 adatoms and 8 pi-bonded dimers, resulting in 32 dangling bonds compared to 64 for the 1x1 surface. In the surface-reaction-limited growth mode at T < 500 $^{\circ}$ C. the rate-limiting growth step is hydrogen desorption from the Si and/or Ge monohydride. The surface structure consists of uniformly-sized terraces, according to atomic force microscopy (AFM) measurements. In the fluxlimited regime at T = 500-650 °C, the growth rate is limited by the surfacedependent reactive sticking coefficient and the morphology is characterized by extensive faceted pitting. At T > 650 °C, the growth rate rises with temperature as the dangling bond coverage increases with the surface transformation to a 1x1 reconstruction. At these high temperatures, the surface morphology consists of long ridges oriented along the [100] direction.

11:20am SS1-WeM10 Surface Structural Study of Ultra-Thin Si (111) on SiO@sub 2@, M. Noh, University of Tennessee and ORNL; A.P. Baddorf, Oak Ridge National Laboratory; H.H. Weitering, University of Tennessee and ORNL

Si on insulator (SOI) material is important for extension of metal-oxide silicon (MOS) technology development in the next generation of microelectronics. Technological requirements have led to interest in very thin SOI layers. The surface structure of ultra-thin layers of (111) oriented SOI has been investigated for the first time, using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). SOI samples were prepared using the Separation by Implanted Oxygen (SIMOX) method, then characterized by Rutherford backscattering spectrometry (RBS) to determine the thickness and quality of the Si overlayer. LEED observations from a 2000 Å thick Si layer on 5000 Å SiO@sub 2@ reveal a sharp 7x7 diffraction pattern, well known for bulk Si (111) surfaces. STM images of

the same surface show nearly defect free 7x7 surface reconstructions with terrace lengths exceeding 1000 Å. These observations reveal that the surface of a thin Si (111) film on SiO@sub 2@ can be fabricated with a comparable degree of structural perfection as the (111) surface of bulk Si. The quality of the (111) SOI surface was monitored as a function of Si top layer thickness after thinning by dry oxidation and stripping. Results are compared to previous images of (100) SOI surfaces.@footnote 1,2@ @FootnoteText@ @footnote 1@K.C. Lin, O.W. Holland, L.C. Feldman, and H.H Weitering, Appl. Phys. Lett. 72 (1998) 2313. @footnote 2@Oak Ridge National Laboratory (ORNL) is managed by Lockheed Martin Energy Research Corp. for the U. S. DOE under contract number DE-AC05-96OR22464.

11:40am SS1-WeM11 Reconstructed Oxide Structures Stable in Air: Monolayer Silicate on Hexagonal SiC Surfaces, U. Starke, J. Schardt, J. Bernhardt, K. Heinz, University of Erlangen-Nuernberg, Germany

Ultrathin oxide layers on hexagonal SiC surfaces were studied using lowenergy electron diffraction (LEED) and Auger electron spectroscopy (AES). SiC(0001) and SiC(000-1) samples were ex situ prepared using thermal hydrogen etching or microwave powered hydrogen plasma treatment. A well ordered (@sr@3x@sr@3)R30° reconstructed surface is observed by LEED immediately upon introduction into vacuum. The samples contain oxygen of approximately one layer equivalent bonded to Si atoms as indicated by AES. By a full dynamical LEED structure analysis carried out for the SiC(000-1) surface the crystallographic structure is determined: The silicon oxide is arranged as a silicate (Si@sub 2@O@sub 3@) layer ontop of the SiC substrate forming rings of the (@sr@3x@sr@3)R30° periodicity with twofold coordinated oxygen atoms in the topmost position. The oxygen incorporation into the surface is presumably caused by a rapid oxidation in air of the well ordered topmost substrate bilayer. The extreme stability of the resulting surface reconstruction is caused by the absence of dangling bonds in the surface terminating silicate layer. Similar results are indicated for the SiC(0001) surface by preliminary LEED calculations.

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