Thursday Morning, November 5, 1998

Electronic Materials and Processing Division
Room 316 - Session EM-ThM

Compound Semiconductor Surface Chemistry

Moderator: R.S. Gold, University of Michigan

8:20am **EM-ThM1 Air-Stable Sulfur-Based Passivation of III-V Compound Semiconductor Surfaces*, C.I.H. Ashby*,** *K.R. Zavadil, A.G. Baca, P.-C. Chang, B.E. Hammons,* Sandia National Laboratories

Although the surface state density can be greatly reduced by sulfur bonding to III-V surfaces, this improvement is transient due to rapid oxidative loss of S from the surface. We have developed a method for stabilizing the improved properties of the semiconductor surface in the presence of S by stabilizing the S against air-oxidation. We employ a two-step process that forms an air-stable metal-S-semiconductor structure. A monolayer of S is applied by UV photodissociation of sulfur vapor. The sulfided surface is then reacted with a metal salt to form an insoluble metal-S overlayer on the semiconductor. XPS characterization of this overlayer shows the presence of the metal, S, and O in the overlayer. Photoluminescence (PL), and Raman spectroscopies have been employed to characterize the effect of the overlayer on surface-recombination-sensitive properties of the interface. For 7x10@super 16@/cm@super 3@ n-GaAs, a 15-fold increase in PL intensity results with the metal-S overlay, which is double the improvement obtained with S-treatment alone. Unlike photosulfidation or the more conventional sufidation with NH@sub 4@S@sub x@, PL intensity following metal-S overlayer deposition does not degrade rapidly in air at room temperature. Passivation of 1.8x10@super 18@/cm@super 3@ n-GaAs produces a 20-30% increase in PL intensity that is retained after more than 10 months in air. In addition, the PL improvements due to the metal-S overlayer are retained following low-temperature deposition of SiNx dielectric coatings. Application of the metal-S passivation layer to GaAs HBTs followed by SiNx encapsulation has produced an increase in dc current gain from 40 to nearly 100 for 2.5x5 µm devices and from 90 to over 100 for large-area (100x100 µm) devices, consistent with a large reduction in surface recombination in these devices. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

8:40am **EM-ThM2 Development of Surface Morphology During H@sub 2@ Plasma Processing of GaAs(001)*, S.W. Robey,*** National Institute of Standards and Technology, US

There is interest in hydrogen plasma etching as a route to low temperature, dry processing for oxide removal from semiconductors. The surface morphology that develops is a determining factor in the success of subsequent device fabrication, making it important to understand surface processes that can influence morphology development during plasma exposure. In situ Auger spectroscopy and RHEED were used in conjunction with ex situ AFM to investigate the development of surface morphology on H@sub 2@ plasma etched GaAs(001) surfaces. Etching of the GaAs, subsequent to the oxide removal, at temperatures above 600 K led to Ga-rich surfaces with a tendency for [11n]-type facet formation. Initial attack on the GaAs surface typically occurred in a localized manner leading to the formation of etch pits. Aligned rows of etch pits are often observed due to preferential etching at mis-cut steps. The preferential attack significantly influences subsequent morphology development. Height-difference correlation functions suggest scaling at small lengths with a roughness exponent in the range of 0.7 - 0.8. A crossover occurs for separations of ~ 30 nm to 60 nm, depending on substrate temperature. The crossover length appears to correlate with typical etch pit dimensions. For larger separations, the slope is much smaller, with some evidence of additional structure in the 100 nm to 200 nm range. Correlations between diffraction and AFM data, connections to continuum models for surface etching including processes such as diffusion, redeposition, etc., and comparison to other experimental work will be discussed.

9:00am **EM-ThM3 Thermal Chemistry and Photochemistry of Organothiols Chemisorbed on GaAs(110)*, N. Camillone, III,*** *K.A. Khan, R.M. Osgood, Jr.,* Columbia University

Self-assembled monolayers of organothiols and related compounds hold promise for use in the semiconductor industry as ultrathin electron beam resists, atomic-layer-epitaxy precursor layers, and monolayer adhesives. We have recently begun fundamental studies of the surface chemistry and photophysics of small organothiols [CH@sub 3@SH, (CH@sub 3@S)@sub 2@ and CH@sub 3@SCH@sub 3@] on GaAs. Temperature programmed desorption measurements indicate that each of these species interact strongly with the GaAs surface. The first monolayer of CH@sub 3@SH desorbs near 300 K, compared to approximately 100 K for the second layer, indicating a chemical interaction between the thiol and the surface, despite the fact that the molecule predominantly appears to desorb intact. The behavior of (CH@sub 3@S)@sub 2@ is quite different; the disulfide decomposes upon adsorption (or during the TPD temperature ramp) and desorbs predominantly as CH@sub 3@SCH@sub3@ at approximately 500 K, perhaps as the result of a concerted associative/dissociative desorption process which leaves sulfur at the surface. In addition, we will report on UV photoreaction cross section measurements and photoreaction products for these thiol, sulfide and disulfide compounds. For example, the measured cross section for photodissociation of an annealed (CH@sub 3@S)@sub 2@ monolayer at 193 nm is orders of magnitude smaller than that for CH@sub 3@SH.

9:20am **EM-ThM4 The Surface Structures of In@sub x@Ga@sub 1-x@As@sub y@P@sub 1-y@ (001) Films Grown by Metalorganic Vapor-Phase Epitaxy*, L. Li,*** University of California, Los Angeles*; B.-K. Han, M.J. Bergarney,* University of California, Los Angeles, US*; D. Law, Q. Fu, R.F. Hicks,* University of California, Los Angeles

Strained films of In@sub x@Ga@sub 1-x@As@sub y@P@sub 1-y@ were grown on GaAs and InP (001) substrates by metalorganic vapor-phase epitaxy (MOVPE). The film thickness and composition, and the degree of strain were determined by analysis of high-resolution x-ray diffraction spectra. In addition, the large-scale morphology, the atomic structure and the composition of the film surfaces were characterized after growth by low-energy electron diffraction, x-ray photoelectron spectroscopy, infra spectroscopy of adsorbed hydrogen, and scanning tunneling microscopy. All the surfaces immediately following MOVPE are composed of atomically flat terraces that are separated by double height steps. The steps exhibit smooth, gradual undulations along the terrace edges. Close-up images of the terraces reveal a disordered (2x1) or c(4x4) structure, which arises from a random mixture of group V atoms and alkyl groups adsorbed on top of the surface. Annealing in vacuum desorbs the alkyl groups and then the group V atoms, generating a variety of reconstructions at progressively higher group III coverages. Many new reconstructions are observed on these films, including (2x3), (3x2) and other (nx2) unit cells, where n is an odd integer. Evidently, these surfaces do not obey the electron counting scheme that holds for unstrained GaAs (001), and therefore, they may be positively or negatively charged. The structure and properties of some of these new surfaces will be described at the meeting.

9:40am **EM-ThM5 Low Induced Damages Dry Etching of III-V Materials for HBT Applications using ICP in Chlorinated Plasma*, J.J. Etrillard,*** *J.F. Bresse, C. Daguet, M. Riet, J. Mba,* CNET, France Telecom, France

Etching of InGaAs and InP in ICP using SiCl4 was studied for HBT application. Low sample temperature was used to minimize the etching isotropy and to reduce the element V desorption. The low ion energy etching process results in a damaged layer thickness of a few angströms. AES results on InP demonstrate a very thin layer of non-stoichiometric material. The nature of the etching mask impacts on the surface contamination: local contamination effects due to sputtering are observed. For such low ion energy processes, the sample preparation before ICP etching is shown to be very important for the surface roughness, as observed by AFM. Various preparation shemes have been investigated, before ICP etching, aiming at a reduction of the surface degradation resulting from ICP etching. It is shown that the best results in terms of roughness and etch-rate are obtained with a silicon nitride mask and a surface oxidation before a wet desoxidation immediatly preceding the ICP etching. An ICP process was used successfully for partly etching the base mesa of HBT structures. No significant difference was observed in terms of induced damages and HBT current gain.

10:00am **EM-ThM6 Variable Substrate Temperature for Precise Growth of II-VI Interfaces*, Y. Luo,*** *M. Han, J.E. Moryl, R.M. Osgood, Jr.,* Columbia University

This paper describes the use of variable substrate temperature for the controlled growth of compound semiconductor hetero-interfaces. The investigation uses UHV surface probes to show that choice of surface temperature and temperature ramping during each half of bilayer growth, can lead to a precisely controlled interface composition. The emphasis on the investigation thus far is controlled interface abruptness, composition and crystallinity. The experiment uses sequential dosing of a ZnSe(100) substrate with dimethylcadmium and H@sub 2@S, respectively, in a UHV system. The substrate temperature is controlled by a temperature controller system and may be raised from 100K to 700K at 4K/sec. In situ surface analysis is accomplished with TPD, AES, LEIS and LEED. The experiments showed that, when DMCd was dosed onto a well ordered c(2x2) ZnSe substrate, the composition of surface growth varied dramatically with the substrate temperature. AES and TPD measurements show that this variation is directly dependent on the chemical interaction of the organic ligands at the surface at differing substrate temperatures. For example, within the temperature range from 250 K to 370 K, the Cd growth mode can change from a simple 0.5 monolayer Cd insertion, to a self-terminating one monolayer deposition or even a thick multilayer of Cd with significant Zn depletion near the interface. In the presence of a hydrogen sulfide flux the percentage of sulfur growth at the surface is directly dependent on the surface-coverage of existing methyl groups due to previous dosing of DMCd. Finally we have found that by selection of dosing temperature and the following temperature ramping one can accurately manipulate the interface compsition on a monolayer scale, e.g. a mixture of a half monolayer Zn and a half monolayer Cd, or an abrupt full monolayer of Cd or intermediate layers of Zn@sub 1-x@Cd@sub x@Se@sub 1-y@S@sub y@.

10:20am **EM-ThM7 Effect of Surface Interactions on Band Offsets at Buried Semiconductor-Insulator Interfaces***, **B.R. Schroeder**, S. Meng, M.A. Leskovar, M.A. Olmstead,* University of Washington

Once an interface between two materials is buried, it is generally assumed to be stable. However, when a CaF@sub 2@/Si film is exposed to atmosphere, the interface spacing increases by 1.7 Å and the band offset decreases by 0.5 eV. The mechanism for this modification of a buried interface is not understood. We have investigated the effect of surface exposure on the band offset at a buried CaF@sub 2@/Si(111) interface. Thin films (4-6 monolayers) of CaF@sub 2@, grown by molecular beam epitaxy on Si(111) substrates, were exposed to atmospheric pressure of various atmospheric constituents and the change in band offset was measured by core level photoemission spectroscopy. Exposure to nitrogen had a negligible effect, while exposure to water vapour (+ nitrogen) had the same result as atmosphere. Exposure to oxygen also reduced the band offset, but by a smaller amount. The decrease in band offset was partially reversible upon annealing at 450 °C. Besides the decrease in band offset, exposure to water or atmosphere also leads to the disappearance of the interface photoemission satellite. This may indicate a structural change in bonding at the interface, which in turn would alter the interface dipole. The magnitude of the band offset and decay of the interface satellite scale roughly with the amount of oxygen present in the film. To test this correlation, silicon was deposited at room temperature on (unexposed) CaF@sub 2@/Si(111). The band offset at the lower interface again decreased by about 0.5 eV, but in this case no additional oxygen was observed. This indicates that oxygen is sufficient to change the band offset but not necessary.

10:40am **EM-ThM8 Comparison of Morphology and Interfacial Composition of Pd Ultra-thin Films on 6H- and 4H-SiC at Different Annealing Temperatures***, **W.J. Lu**, D.T. Shi, E. Bryant, A. Burger, W.E. Collins,* Fisk University

Pd/SiC has been applied as a chemical sensor for hydrogen and hydrocarbon gases at high temperatures. The diffusion and interfacial reaction between the thin film and SiC substrate alter the electrical properties of the device. In this work, the morphology and interfacial composition of Pd ultra-thin films on 6H- and 4H-SiC substrates are studied at different annealing temperatures using atomic force microscopy and X-ray photoelectron spectroscopy. The Pd ultra-thin films were deposited by RF sputtering with about 3 nm thickness. The SiC substrates are 3.5° titled, Si-face and n-type 6Hand 4H-SiC, and the Pd thin film deposition and annealing conditions are the same for both samples. The samples were annealed at 100 to 400°C for 30 minutes in air. The Pd ultra-thin films on both SiC substrates have a good uniformity. The morphology of the Pd ultra-thin films on 6H- and 4H-SiC are very similar for unannealed and annealed samples at 100 and 200°C, and the Pd diffusion on SiC has occurred at 200 °C. As the annealing temperature increases, the surface of the Pd film becomes rougher. At 300°C, the Pd islands, 40 to 70 nm in diameter, are found on 4H-SiC substrate by atomic force microscopy. The diameter of Pd islands on 6H-SiC are about 20-40 nm. At 400°C, the irregular shaped holes on the Pd ultra-thin film are formed on 4H-SiC substrate, while the morphology of the Pd thin film on 6H-SiC is unchanged. Using XPS measurements, at 300°C, more Pd on 4H-SiC has reacted with the SiC substrate to form Pd silicates than on 6H-SiC, thus 4H-SiC is more reactive with Pd than 6H-SiC. No significant changes in Schottky barrier height were found for both Pd/6H-SiC and Pd/4H-SiC samples. The relationships between the structural factor in SiC and the behavior of Pd diffusion and reaction on 6H- and 4H-SiC will be presented Keywords: Pd thin film, SiC, atomic force microscopy, X-ray photoelectron spectroscopy.

11:00am **EM-ThM9 Field Emission Studies of BN Overlayers on Various Substrates***, **N. Badi**, A. Tempez, D. Starikov, A. Bensaoula,* University of Houston*; V.P. Ageev, S.V. Garnov, M.V. Ugarov, S.M. Klimentov, E. Loubnin, V.N. Tokarev,* General Physics Institute, Russia*; K.L. Waters, A. Shultz,* Ionwerks

We have studied electron field emission from BN films deposited on various substrates (flat and tip shaped) by End Hall ion source and electron cyclotron resonance plasma source-assisted physical vapor deposition. The chemical bonding states of B, C, N and the valence band structures were investigated by x-ray photoelectron spectroscopy XPS. Post-growth annealing, thermal processing and surface laser modification effects on the field emission properties were investigated. Thin carbon doped BN films exhibited a turn-on voltage as low as 30 V and a maximum current density of 1A/cm@super 2@. The ield emission nature was verified using Fowler-Nordheim plot studies. A significant difference between the initial I (E)-behavior and that measured during subsequent cycles, with a noticeable stepwise jump of the emission current by orders of magnitude, was observed. Similarly, features in the peak current variation with applied voltage were measured and are probably due to a resonance tunneling emission effect. To that end, the valence band distribution of both the acceptor and donor's energy levels in these BN thin films were investigated under a variety of excitations. In addition, the field emission and conductivity properties of the BN surfaces have been performed using scanning tunneling emission microscopy (STFEM). The total spatial resolution of this technique was as high as a few nm. The experiments were conducted in the emission mode under negative and positive bias. The 3-D surface topography mapping and its correlation to the field emission properties were investigated and the results will be presented and discussed. This work was supported by funds from a NASA cooperative agreement #NCC8-127 to SVEC, a Texas Advanced Research Program Grant # 1-1-27764, and a Texas Advanced Technology Program Grant # 1-1-32061. This material is also based upon work supported by the U.S. Civilian Research and Development Foundation under Award No. REI-247

11:20am **EM-ThM10 Influence of Ammonia Surface Reactions in GaN Chemical Vapor Deposition***, **M.E. Bartram**,* Sandia National Laboratories

UHV thermal desorption mass spectroscopy measurements of N@super 15@H@sub 3@ chemisorbed on GaN(0001) have demonstrated that ammonia undergoes both reversible and irreversible decomposition on the surface. Overall, N@super 15@H@sub n@ fragments and surface hydrogen from ammonia dissociation either (I) recombined to liberate N@super 15@H@sub 3@ or (II) decomposed further to enrich the surface with nitrogen. This was accompanied by the desorption of N@super 15@@sub 3@, N@super 15@N@super 14@, N@super 14@@sub 2@, and H@sub 2@ at a temperature below that required for congruent GaN sublimation. These reactions are the "crossroads" for the other important reaction avenues on the surface. Considering case I, production of surface hydrogen from ammonia decomposition suggests that this rate may be sensitive to hydrogen coverage and hence be influenced by the H@sub 2@ carrier gas used commonly in GaN CVD. Case II suggests that in addition to supplying the nitrogen for GaN growth, ammonia decomposition can also lead to the extraction of nitrogen from the surface when the nitrogen coverages are sufficiently high. This catalytic removal of surface nitrogen in the form of N@super 15@N@super 14@ and not N@super 14@H@sub 3@ indicates further that N-H bond formation as an initial step in potential hydrogen etching reactions can be overwhelmed by the tremendous driving force of the NN bond energy (226 kcal/mol). Therefore, while the nitrogen feed to the surface in the form of ammonia is necessary to compensate for congruent GaN sublimation and also contribute to GaN growth, it can also provide a low energy reaction pathway for the removal of nitrogen from a nitrogen enriched surface. This suggests that the overall nitrogen incorporation rate must be well-matched to the Ga deposition rate to maintain the proper stoichiometry and a reproducible overall growth rate. We have also observed that ammonia lowers the temperature for the desorption of TMG from surface defects. This decrease in the TMG-surface bond energy which can also lower the TMG residence time on the surface, suggests ammonia surface reactions have the potential to inhibit TMG reactions during GaN CVD. (Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the USDOE under DE-AC04-94AL85000.)

11:40am **EM-ThM11 Optimization of the Nitridation of Sapphire Substrates Using a Fractional Factorial Designed Experiment***, **T.J. Kropewnicki**, P.A. Kohl,* Georgia Institute of Technology

Future advances in the performance of wide bandgap microelectronic devices depend on further improvements in the quality of the materials from which these devices are fabricated. Nitridation of the substrate is an important step that promotes the growth of high quality Group III nitride semiconductors; however, very few systematic studies of the nitridation process have been done. Herein, we report on a fractional factorial designed experiment to optimize the nitridation of sapphire substrates for the subsequent growth of GaN by plasma assisted molecular beam epitaxy (MBE). The sapphire substrates were nitridated with hydrazine using a process described elsewhere.@footnote 1,2@ Single replicates of a 2@super4-1@ fractional factorial design were performed. The investigated factors were the pretreatment of the sapphire substrate with a 3H@sub 2@SO@sub 4@ : H@sub 3@PO@sub 4@ etch prior to introduction into the reactor, an in situ H@sub 2@ cleaning step prior to nitridation, the substrate temperature, and the nitridation time. Four center points were included in the design to test for nonlinearity and to yield an estimate of the experimental error. The material properties used to assess the quality of the nitridated surfaces were the nitrogen content of the surface (as measured by x-ray photoelectron spectroscopy) and the surface roughness (as measured by atomic force microscopy). Bulk GaN films were then grown on each of the nitridated sapphire substrates by r.f. plasma assisted MBE. The bulk growth conditions were determined with a separate designed experiment,@footnote 3@ and these conditions were held constant for each of the growths. The influence of the nitridated surfaces on the quality of the bulk GaN films was studied by photoluminescence and x-ray diffraction. The results of this fractional factorial designed experiment as well as their impact on the growth of GaN on sapphire substrates will be discussed. @FootnoteText@ @footnote 1@T. Kropewnicki and P. Kohl, "Hydrazine Cyanurate as a Nitrogen Source for Thin Nitride Film Growth," Journal of Vacuum Science and Technology A, 16 (1), 139 (1998). @footnote 2@T. Kropewnicki and P. Kohl, "Nitridation of Substrates with Hydrazine Cyanurate for the Growth of GaN," Proceedings of the 1998 Spring MRS Meeting, San Francisco, CA, April 1998. @footnote 3@K. Lee and G. May, unpublished.

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