# Thursday Afternoon, November 5, 1998

### Electronic Materials and Processing Division Room 316 - Session EM2-ThA

## Non-destructive Testing and In-situ Diagnostics

Moderator: C.J. Palmstrom, University of Minnesota

### 2:00pm EM2-ThA1 In-Situ IR Spectroscopic Study of the Chemical Process of Si-Related CVD Thin Films, *T. Wadayama*, Tohoku University, Japan INVITED

A comprehensive understanding of the molecular process of thin films growing under the chemical vapor deposition (CVD) conditions is quite of importance from a technological point of view. In-situ molecular vibrational study of the dynamic behavior of surface species under such conditions should give us an important clue to the understanding of the process and, further, a useful guide in developing new thin film devices. However, there exist few techniques available for the in-situ observation of the process. The polarization modulation IR spectroscopy (PM-IR), which is based on the difference in absorption intensity of surface species upon the change in the polarization state of the incident IR light, is a powerful tool for detecting signals from surface species over wide ranges of the substrate temperature and gaseous pressure. We have been successful in applying this method to observing in-situ the photo-CVD process of the Si-related thin films as well as the reaction of the films with the metal-organic and the etchant molecules. In the present talk, we will mention (1) the basis of the PM-IR method, the results obtained through the in-situ IR observation of (2) the growing process of the a-Si:H and the a-SiN@sub x@ thin films, and (3) the reaction of the a-Si:H/dimethylaluminum hydride ((CH@sub 3@)@sub 2@AlH) and the a-SiN@sub x@/F@sub 2@. The results suggest that the hydrogen-rich and the Si-rich layers are present on the growing surface of the a-Si:H and the a-SiN@sub x@ film, respectively, illustrating the feasibility of the PM-IR method to the in-situ molecular vibrational study of the chemical process of the CVD thin films.

### 2:40pm EM2-ThA3 Integrated Real-Time Spectroscopic Ellipsometric and Reflectance Difference Measurements on a Commercial OMCVD Reactor, *M. Ebert*, Technical University Berlin, Germany; *K.A. Bell, S.D. Yoo, G.D. Powell, D.E. Aspnes*, North Carolina State University

Comprehensive monitoring of epitaxial growth by organometallic chemical vapor deposition (OMCVD) requires not only near-surface measurements for compositional analysis of the most recently deposited material and bulk measurements for determining layer thicknesses, but also surface analysis for information about growth chemistry. Here, we describe the first unified optical system that meets all 3 needs simultaneously. This system is a multichannel, parallel acquisition and processing, combined reflectancedifference (RD) spectrometer and rotating-polarizer spectroscopic ellipsometer (SE). It is built around a commercial rotating-spindle OMCVD reactor and a state-of-the-art high-speed 16-bit photodiode array (PDA) and allows data to be taken from 200 to 800 nm at a repetition rate of 600 ms to a precision of ±0.0001. These capabilities are realized by the PDA detector, synchronization of the spindle to the polarizer in a 3-to-1 ratio, and a spindle design that allows wobble to be reduced to less than 0.02° during rotation. RD measurements on a test (011) Si wafer, when transformed to normal incidence, are in excellent agreement with normalincidence data. In addition to the diagnostic capabilities of SE, updating complete RD spectra at 0.6 s intervals allows surface reconstructions to be interpreted by pattern recognition as in RHEED.

### 3:00pm EM2-ThA4 Real-Time Optical Control of Ga@sub 1-x@ln@sub x@P Film Growth by P-Polarized Reflectance, *N. Dietz, K. Ito, V. Woods,* North Carolina State University

The engineering of advanced optoelectronic integrated circuits implies the stringent control of thickness and composition. These demands led to the development of surface-sensitive real-time optical sensors that are able to move the control point close to the point where the growth occurs, which in a chemical beam epitaxy process is the surface reaction layer (SRL), built up of physisorbed and chemisorbed precursor fragments between the ambient and film interface. In this contents, we explored the application of p-polarized reflectance spectroscopy (PRS) for real-time monitoring and control of pulsed chemical beam epitaxy (PCBE) during low temperature growth of epitaxial Ga@sub 1-x@ln@sub x@P heterostructures on Si(001) substrates by PCBE. Using a 'reduced order kinetic model' we demonstrate the linkage of the PRS response towards surface reaction chemistry, composition, film growth rate, and film properties. Mathematical control algorithms are introduced and applied that link the PR signals to the

growth process control parameters to control composition and growth rate of epitaxial Ga@sub 1-x@In@sub x@P heterostructures.

### 3:20pm EM2-ThA5 Electron Cyclotron Resonance Induced Surface and Subsurface Defects in GaAs Exposed to a Chlorine/Ar Plasma, O.J. Glembocki, R.T. Holm, W.E. Carlos, D. Leonhardt, Naval Research Laboratory; C.R. Eddy, Boston University; K.K. Ko, S.W. Pang, University of Michigan; D.S. Katzer, Naval Research Laboratory

The detection and control of dry etched induced electronic damage is critical to the formation of high quality semiconductor devices. In order to avoid ambient contamination, we have used in-situ photoreflectance (PR) to study the behavior the surface electric fields and surface photovoltage in both n-type and p-type GaAs exposed to a chlorine/Ar plasma generated by an electron resonance cyclotron source. By monitoring the desorption of the Ga and As chlorides, we find that the removal of Ga is the rate limiting step. This leads to a surface that is Ga rich and decorated by Ga vacancies which change the surface pinning position in both n- and p-GaAs. In addition, the etched surfaces show a decreased surface photovoltage. By using in-situ chemical etching/passivation with chlorine, we are able to uncover subsurface damage and show that it is distinctly different from the Ga vacancies formed on the surface. We find that the bulk etch damage has an exponential profile and that it is amphoteric, behaving as a very deep donor in n-GaAs and a deep acceptor in p-GaAs. Our experiments further indicate that both states of this defect lie below midgap. Possible candidates are point defects such as interstitials. Spin resonance results will be used in discussing the nature of the defects.

## 3:40pm EM2-ThA6 Reciprocal-Space Analysis of Optical Spectra, S.D. Yoo, N.V. Edwards, D.E. Aspnes, North Carolina State University

Reciprocal-space analysis of optical spectra yields significant improvements in determining critical point energies in comparison to conventional realspace analysis. Enhanced diagnostic power is realized because, among other aspects, baseline effects, spectral information, and noise are localized in the low, middle, and high Fourier coefficients, respectively, allowing information to be extracted largely independent of baseline and noise artifacts. We use reciprocal-space analysis to address several issues regarding spectroscopy of electronic materials, both in real-time and offline applications. Among these are the determination of optimal slit widths and numbers of data points that allow data to be taken at the fastest rate for a given signal-to-noise ratio and a simple analytic expression that describes the apparent shift of apparent critical point energies with overlayer thickness. We apply reciprocal-space analysis to various problems in electronic materials. The binding energies of the A. B. and C excitons of various GaN layers epitaxially grown on sapphire and SiC substrates have been determined to within 1 meV from low temperature reflectance data, which allows the in-plane strain and upper valence band parameters to be determined to similar accuracy. Apparent bulk critical point energies and broadening parameters of (110) Ge samples with and without a thin (~30 Å) Ni overlayer show substantial (~10 meV) differences, providing further evidence of photon-induced localization of optically excited electron and hole states. Finally, analysis of photoluminescence and photoluminescence excitation (PLE) spectra of GaAs/AlGaAs single quantum wells shows that exciton energies can be obtained independent of baseline artifacts to a wavelength uncertainty of 0.1 Å, which is particularly important for PLE where baselines cannot be determined unambiguously.

#### 4:00pm EM2-ThA7 Observation of Adsorption and Reaction of NH@sub 3@ on Al@sub 2@O@sub 3@, AIN and AION Under Steady-State Conditions Using IRRAS, V.M. Bermudez, Naval Research Laboratory

The surface chemistry of Al@sub 2@O@sub 3@, AlN and Al oxynitride ("AION") with NH@sub 3@ is important in the MOCVD growth of GaN on these substrates. Thin films of Al@sub 2@O@sub 3@, AlN and AlON have been grown by reacting a NiAl(111) surface with O@sub 2@, NH@sub 3@ or NO, respectively.@footnote 1@ The resulting buried-metal-layer structures have then been employed as substrates for studies of NH@sub 3@ adsorption under steady-state conditions, at 300 K and up to 200 Torr. using polarization-modulated fourier-transform infrared reflection absorption spectroscopy. For Al@sub 2@O@sub 3@ evidence is seen, in the form of a change in the LO phonon, for incorporation of N into the surface to form a dilute "AION-like" phase. The @delta@@sub s@ symmetric deformation mode of adsorbed NH@sub 3@ is easily detected under high (@>=@25 Torr) static pressures. For AIN, no evidence of adsorbed NH@sub 3@ is seen in a 200 Torr ambient. For AlON, distinct surface and volume LO phonon modes are seen, with the former responding reversibly to chemisorbed NH@sub 3@. The @delta@@sub s@

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frequency indicates a lesser degree of Lewis acidity on AlON vs. Al@sub 2@O@sub 3@ surfaces, which may favor 2D GaN growth on AlON by increasing the surface mobility of NH@sub x@ species. For each of the three materials, IRRAS also provides useful information about the structural quality of the films prior to NH@sub 3@ exposure. @FootnoteText@ @footnote 1@Franchy et al., Appl. Phys. A 65 (1997) 551.

### 4:20pm EM2-ThA8 Time of Flight Mass Spectroscopy of Recoiled Ions Comparative Studies of Gallium Nitride Thin Film Deposition By Various Molecular Beam Epitaxial Methods, E. Kim, I.E. Berishev, A. Bensaoula, University of Houston; K.L. Waters, J.A. Schultz, Ionwerks

GaN thin films were successfully grown by electron cyclotron resonance molecular beam epitaxy (ECR-MBE), gas source MBE (GSMBE), and chemical beam epitaxy (CBE). Time of flight mass spectroscopy of recoiled ions (TOF-MSRI) and RHEED were used in-situ to determine the surface composition, the crystalline structure, and the growth mode of GaN thin films deposited by the three MBE methods. The substrate nitridation and the buffer layers were characterized by TOF-MSRI and RHEED. In GSMBE, the Ga/N ratio is found to correlate well with ex-situ optical properties. In the case of CBE, the carbon incorporation determines the surface morphology, the crystalline quality and the optical activity of the epilayers. In the case of CBE, no nucleation was possible until a combination of ECR nitrogen and TEG was used for the low temperature buffer. The carbon and oxygen levels were found to depend greatly on the TeGA flow and substrate temperature. A model describing the main experimental observations will be presented. The model explains both the chemical dissociation of ammonia at low temperatures and the Ga to N TOF-MSRI peak ratio for various Ga and ammonia fluxes. Our study shows that under optimized conditions crystalline epilayers with good optical and surface morphologies can be obtained with all three methods. 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.

### 4:40pm EM2-ThA9 Near-Surface Variation of Gallium Nitride Cathodoluminescence with Annealing, *T. Levin, J. Schöfer, A.P. Young, L.J. Brillson,* The Ohio State University; *J.D. MacKenzie, C.R. Abernathy,* University of Florida, Gainesville

Er-doped GaN with its promising luminescence yield is of considerable importance for optical communications. However, interfaces can induce significant changes in Er efficiency for optical pumping. Here we report on low energy cathodoluminescence spectroscopy (CLS) to probe the emission of GaN:Er as a function of distance from the semiconductor surface. CLS reveals order-of-magnitude emission variations of Er dopants and related Er-defect complexes vs. depth. Variable incident beam energies (0.5 - 5 keV) provided a strongly depth-dependent excitation from ca. 4 to 40 nm. GaN was grown by metal-organic molecular beam epitaxy at 925°C and doped to 3 x 10@super 18@ cm@super -3@. The primary spectral feature observed was the 0.8 eV (1554 nm) Er emission, which increases by over an order of magnitude with increasing excitation depth. Relative to the broad 'yellow' luminescence between 1.5 and 2.5 eV, which exhibits little or no increase away from the GaN surface, the variation in 0.8 eV emission suggests a depletion of Er within the outer 10 nm. The CLS also reveals three sharp spectral lines at 1.8, 2.2, and 2.3 eV which have been associated with Er 4f transitions from excitation spectroscopy.@footnote 1@ However, the intensities of these features do not scale directly with the 0.8 eV line as a function of depth or processing, but reflect the sensitivity of these additional transitions to near-surface defects and impurities. Annealing the GaN:Er to 500°C for 5 min extends the otherwise bulk emission from these levels to a more uniform distribution extending to within 10 nm of the surface. Further annealing to 700°C promotes even stronger near-surface as well as bulk emission from these lines. However, it produces no significant change in the depth distribution of the 0.8 eV emission but enhances its yield by over a factor of two. Overall, the contrast in intensity variation of specific Er 3+ emission lines with depth reveals the sensitivity of dopant intra-shell transition strengths to nearsurface defects. @FootnoteText@ @footnote 1@M. Thaik, U. Hommerich, R.N.Schwartz, R.G.Wilson, and J.M.Zavada, Appl. Phys. Lett. 71, 2641 (1997).

5:00pm EM2-ThA10 In-situ Formation, Reactions, and Electrical Characterization of MBE Grown Metal/Semiconductor Interfaces, *L.C. Chen*, *D.A. Caldwell*, University of Minnesota; *T.G. Finstad*, University of Oslo, Norway; *C.J. Palmstrom*, University of Minnesota

An in-situ probe station is used for the determination of the electronic properties of interfaces being modified in an MBE system. After MBE growth of the semiconductor structures, contacts were formed by metal deposition through a removable molybdenum shadow mask. An abrupt change in doping profile serves as a marker layer to allow doping density versus depth profile measurements obtained from capacitance-voltage (C-V) to be used to measure the position of the electrical metal/semiconductor interface relative to the marker laver, allowing metal/semiconductor reaction kinetics to be determined electrically in-situ. C-V measurements on n/n@super +@ GaAs structures were used to monitor the Ni/GaAs reaction and subsequent GaAs regrowth. The measurements indicated that 500Å of Ni consumes 700Å of GaAs during Ni@sub 3@GaAs formation, which is in excellent agreement with RBS and cross-sectional TEM measurements. Exposure of Ni@sub 3@GaAs to As@sub 4@ at 300°C results in the formation of NiAs at the surface and epitaxially regrown GaAs at the Ni@sub 3@GaAs/GaAs interface. The doping profiles indicated the complete regrowth of the 700Å GaAs beneath the contact. In-situ current-voltage (I-V) measurements of the NiAs/regrown-GaAs interfaces showed good Schottky behavior (V@sub bn@=0.87 V, n=1.08). C-V measurements showed further that the net electrically active donor density 2000Å beneath the contact changed during the different stages of reaction; it was 9.0x10@super 16@ (after Ni deposition), 6.5x10@super 16@ (after complete Ni@sub 3@GaAs formation), 5.0x10@super 16@ (after subsequent GaAs regrowth), and 9.0xl0@super 16@ (after an additional 585°C anneal). This results from the formation of point defects in the underlying GaAs during the reactions, which are eliminated by a 585°C anneal. In-situ electrical measurements on MBE-grown epitaxial metallic compound/Ga@sub 1-x@Al@sub x@As heterostructures grown on various surface terminations before and after annealing with emphasis on Sc@sub x@Er@sub 1-x@As structures will also be presented.

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