Tuesday Afternoon, November 3, 1998

Electronic Materials and Processing Division Room 316 - Session EM+PS+SE-TuA

Plasma Processing of Compound Semiconductors Moderator: C. Eddy, Boston University

2:00pm EM+PS+SE-TuA1 Thermally Induced Improvements on SiN@sub x@:H/InP Devices, E. Redondo, N. Blanco, I. Mártil, G. González Díaz, Universidad Complutense de Madrid, Spain; R. Peláez, S. Dueñas, H. Castán, Universidad de Valladolid, Spain

The electron cyclotron resonance (ECR) plasma technique has been recently proved to be optimum as insulator deposition method in Al/SiN@sub x@:H/InP devices.@footnote 1@ In this communication we present a study of the influence of rapid thermal annealing (RTA) treatments on the interface characteristics of Al/SiN@sub x@:H/InP devices. The insulator was obtained by the ECR plasma method at 200°Cdeposition temperature. The films were deposited in two steps: we deposited first a film with x=1.55 and then another with x=1.43. Total film thickness was 500Å in one set of samples and 200Å in other. RTAs were conducted in Ar atmosphere during 30s in a temperature range between 400 and 800°C. The electrical characteristics of the devices have been obtained by capacitance-voltage (C-V) and deep-level transient spectroscopy (DLTS) measurements. Those films annealed between 400 and 500°C/30s in Ar atmosphere give structures with the minimum interfacial trap density. The interface trap density behavior with the annealing temperature has been observed to show the same trend with both CV and DLTS measurements, reaching lower values in the latest ones. The minimum interfacial trap density value achieved with the best annealing is of 3x10@super 11@ cm@super -2@ eV@super -1@, obtained for 400°C/30s annealing on the thinnest structure (200Å). Besides, DLTS measurements show the presence of features in the spectrum that are characteristic of phosphorus vacancies, V@sub p@, and deep centers. The annealing at 400°C/30s reduces the V@sub p@ content. This suggests that the nitrogen from the insulator is filling these vacancies so InP surface is being passivated. @FootnoteText@ @footnote 1@ S.García, I.Mártil, G.González Díaz, E.Castán, S.Dueñas, M.Fernandez. J.Appl.Phys, 83 (1), 1998, pp 600-603.

2:20pm EM+PS+SE-TuA2 Damage to III-V Devices During Electron Cyclotron Resonance Chemical Vapor Deposition, *F. Ren*, University of Florida, Gainesville; *J.W. Lee, D. Johnson, K. McKenzie*, Plasma-Therm, Inc.; *T. Maeda, C.R. Abernathy, Y-.B. Hahn, S.J. Pearton,* University of Florida, Gainesville; *R.J. Shul,* Sandia National Laboratories

GaAs-based metal semiconductor field effect transistors (MESFETs), heterojunction bipolar transistors (HBTs) and high electron mobility transistors (HEMTs) have been exposed to ECR SiH@sub 4@/N@sub 2@, SiH@sub 4@/N@sub 2@O and SiH@sub 4@/NH@sub 3@ discharges for deposition of SiN@sub x@ or SiO@sub 2@ passivating layers. The effect of source power, rf chuck power, pressure and plasma composition have been investigated. Effects due to both ion damage and hydrogenation of dopants are observed. For both HEMTs and MESFETs there are no conditions where substantial increases in channel sheet resistivity are not observed, due primarily to (Si-H)@super o@ complex formation. In HBTs the carbondoped base layer is the most susceptible layer to hydrogenation. Ion damage in all three devices is minimized at low rf chuck power, moderate ECR source power and high deposition rates.

2:40pm EM+PS+SE-TuA3 Anisotropic Etching of InP using CAIBE (Cl@sub 2@/Ar): Importance of the Sample Temperature Stability and the Reactive Gas Distribution, *B. Lamontagne*, *M. Gagnon*, *J. Stapledon*, *P. Chow-Chong*, *M. Davies*, National Research Council, Canada

Process development has been performed for the dry etching of InP using our Chemically Assisted Ion Beam Etching (CAIBE) system (Ionfab 300 from Oxford Inst.). We studied the etching mechanisms in order to obtain vertical, deep and smooth InP sidewalls. Such etching profiles are essential for optoelectronic discrete devices such as turning mirrors, reflector gratings, deeply etched waveguides, etc. The CAIBE system has a 15 cm diameter R-F driven ion source, the ion beam is usually composed of argon while chlorine is introduced through the gas ring located in front of the heated platen. The sample temperature - a critical parameter when etching InP with chlorine - has been calibrated and monitored using a non-contact sensor: a diffuse reflectance spectrometer (DRS 1000 Thermionics Northwest Inc.). It gives an accurate temperature measurement of the sample itself using the shifting effect of the temperature on the absorption edge position of semiconductors. This diagnostic tool allowed us to monitor the sample temperature increase under ion bombardment (CAIBE process) for various conditions; sample heating and mounting technique, ion beam current and energy. In some extreme process conditions the sample temperature has increased from 20° C to 300° C in less than one minute. Our results point out the need to use a stable process temperature in order to obtain vertical sidewalls. The influence of the reactive gas distribution has also been investigated, for example, by modifying the gas ring design. Etching conditions characterized by vertical (>89°) and long (up to 15 μ m) sidewalls and SiO@sub 2@ mask selectivity of 30 were obtained.

3:00pm EM+PS+SE-TuA4 Hydrogen in Compound Semiconductors, M.D. McCluskev, N.M. Johnson, Xerox Palo Alto Research Center INVITED Hydrogen can be inadvertently introduced at any of several steps in the fabrication of optoelectronic devices. In particular, incorporation of hydrogen can occur during growth, wet chemical processing, or dry etching. The most common consequence of hydrogenation is the passivation of dopant impurities, which leads to a decrease in the electrical conductivity of the material. The most successfully applied experimental technique for directly determining the involvement of hydrogen has been infrared-absorption local vibrational mode (LVM) spectroscopy, which will be illustrated with representative examples. In GaN:Mg grown by metalorganic chemical vapor phase deposition, hydrogen passivates Mg acceptors during the growth. Through experimental and computational studies it has been determined that hydrogen incorporated during growth forms electrically inactive complexes with Mg, and that a furnace anneal dissociates these complexes to activate the acceptor dopant. LVM spectroscopy was essential in the identification of the Mg-H complex. The observed frequency of the hydrogen LVM verified the theoretical prediction that hydrogen attaches to a host nitrogen atom. Recently, large hydrostatic pressures have been applied to compound semiconductors to probe the vibrational properties of hydrogen-related complexes. In GaAs, the pressure dependent shifts of hydrogen stretch modes provide clues about the location of hydrogen in the complexes. In AlSb, pressure was utilized to resolve a mystery as to why the Se-D complex gives rise to one stretch mode peak while the Se-H stretch mode splits into three peaks. This anomalous splitting is explained in terms of a new resonant interaction between the stretch mode and combination modes involving a wag mode harmonic and extended lattice phonons.

3:40pm EM+PS+SE-TuA6 The Interaction of Electrons with Hydrogenated GaN(0001), V.J. Bellitto, B.D. Thoms, Georgia State University; D.D. Koleske, Naval Research Laboratory

Although Group III nitrides have recently been used to produce blue LEDs and laser diodes, many surface properties and processes have yet to be fully understood. One issue important to many applications of these materials is the effect of hydrogen during growth and processing. For example, hydrogen has been reported to significantly affect incorporation of dopants, Group III constituents, and contaminants. We have studied GaN(0001) using low energy electron diffraction (LEED), Auger electron spectroscopy (AES), energy loss spectroscopy (ELS), and high resolution electron energy loss spectroscopy (HREELS). The ELS spectrum of GaN is seen to be particularly sensitive to exposure to atomic hydrogen (produced by a tungsten filament heated to 2073 K). A new peak appears at a loss energy of approximately 12 eV after atomic-hydrogen exposure but is not seen after exposure to molecular hydrogen alone. However, this peak is strongly affected by low energy electron irradiation of the surface. Substantial reduction in the 12 eV peak intensity is observed following exposure to 1.8 microamps of 90 eV electrons for two minutes. After 10 minutes of electron impingement on the hydrogen-atom-exposed surface, ELS spectra appear identical to those taken with no hydrogen atom exposure. Heating to 690 K is also seen to remove the hydrogen-related peak from ELS spectra. Recently, Gillis et al. have shown that simultaneous exposure of GaN to hydrogen atoms and low energy electrons results in anisotropic etching. Implications of these data for both surface science and etching of GaN will be discussed.

4:00pm EM+PS+SE-TuA7 III-V Surface Plasma Nitridation: A Challenge for III-Nitride Epigrowth, G. Bruno, M. Losurdo, P. Capezzuto, MITER-CNR, Italy; E.A. Irene, University of North Carolina, Chapel Hill

A challenge in the growth and processing of III-V nitrides is the control and optimization of the substrate/epilayer interface. It has been reported that high quality epilayers of GaN and related materials can be obtained by nitridation of the sapphire and GaAs substrates before the film growth. Substrate nitridation allows to accomodate the lattice mismatch between substrates and GaN epilayers and crucially affects the cristalline quality and

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structure of both the buffer and epitaxial GaN layers. In this contribution, the focus is on the nitridation process of GaAs and GaP (100) substrates to form GaN layers and of (0001) sapphire surfaces to form thin AIN. In order to elucidate the chemistry and kinetics of these solid state anion exchange reactions, the nitridation of (100) InP is also investigated. Nitridations are performed in a remote radiofrequency plasma metalorganic chemical vapor deposition (MOCVD) apparatus by exposing surfaces to the downstream flow of N@sub 2@ and N@sub 2@-H@sub 2@ plasmas, taking the advantages of low process temperatures and minimal surface damage. In situ optical diagnostics such as optical emission spectroscopy (OES) and spectroscopic ellipsometry (SE) are used to fingerprint in real time the gas phase and surface modifications, respectively. Thus, the chemistry and kinetics of the plasma-surface interactions are described toghether with the surface/interface composition and morphology. AFM analysis has been used to measure the surface roughness and to validate the effectiveness of plasma nitridation with respect to the conventional thermal nitridation by NH@sub 3@. Transmission electron microscopy (TEM) is used to highlight the different structural aspects of the nitride layers obtained by N@sub 2@ and N@sub 2@-H@sub 2@ mixtures. Optimizing the surface temperature and the N@sub 2@/H@sub 2@ ratio the formation of an interfacial As-rich layer in the GaAs/GaN growth is minimized, the nitridation depth is increased up to 15nm and compact and chemically stable GaN layers are obtained.

4:20pm EM+PS+SE-TuA8 III-Nitride Dry Etching - Comparison of Inductively Coupled Plasma Chemistries, H. Cho, Y-.B. Hahn, D.C. Hays, C.R. Abernathy, S.M. Donovan, J.D. MacKenzie, S.J. Pearton, University of Florida, Gainesville; J. Han, R.J. Shul, Sandia National Laboratories

A detailed comparison of etch rates, etch yields, surface morphology and sidewall anisotropy has been performed for GaN, InN and AlN etched in Inductively Coupled Plasma discharges of BCl@sub 3@, Bl@sub 3@, BBr@sub 3@, ICl and IBr. Etch selectivities of 100:1 for InN over GaN and AlN are obtained in Bl@sub 3@ due to the relatively high volatility of the Inl@sub x@ products and the lower bond strength of InN. The selectivities are much lower in the other chemistries. The etched surfaces of the nitrides are smooth over a broad range of source and chuck powers, pressures and discharge compositions, and there is typically a slight deficiency of N@sub 2@ in the near-surface (@<=@ 100Å) region. The etch yields for all of the chemistries are relatively low (@<=@ 2), indicating that the high ion flux in the ICP tool is a critical factor in obtaining practical etch rates for the nitrides.

4:40pm EM+PS+SE-TuA9 Photoenhanced RIE of III-V Nitrides in BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@ Plasmas, A. Tempez, N. Medelci, N. Badi, I. Berichev, D. Starikov, A. Bensaoula, University of Houston; A. Chourasia, Texas A&M University

Boron nitride (BN) and gallium nitride (GaN) are known as superior semiconductor materials for UV optoelectronic and high power, high temperature applications. As a consequence of their high molecular bond strength, these materials are extremely difficult to etch. In order to address the device processing issue, reactive ion etching (RIE) tests were performed on BN and GaN thin films. Our experiments show that optimum etching occurs using BCl@sub 3@/Cl@sub 2@/Ar chemistries for GaN and Cl@sub 2@/Ar for BN. In the case of GaN, the BCl@sub 3@/Cl@sub 2@/Ar mixture results in the highest reported RIE GaN etch rates.@footnote 1@ Auger and x-ray photoelectron spectroscopy analyses of the etched surfaces always show a depletion of the surface nitrogen atomic composition which increases with the dc bias (rf power). The impurity incorporation, C and Cl also shows the same trend. In order to improve the etch rates at lower powers, a photoenhanced RIE process was investigated. A BCl@sub 3@/Cl@sub 2@/Ar/N@sub 2@ plasma in combination with a xenon arc lamp was utilized. Preliminary results show a 33% increase in GaN etch rates for a -220 V dc bias (100 W rf power). The dependence of etch rates, surface composition and chemistry, and surface morphology on dc bias (rf power) and photo-irradiation flux will be presented. In addition, the energy and angle distribution of the reaction species from nitride materials exposed to well characterized reactive beams were investigated. The results will be compared to those from RIE and Photo-RIE data and a model for the possible surface etch reactions will be 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. @FootnoteText@ @footnote 1@N. Medelci, A. Tempez, E. Kim, N. Badi, I. Berichev, D. Starikov and A. Bensaoula, 1998 MRS Spring Meeting (in print).

5:00pm EM+PS+SE-TuA10 Characteristics of Cl@sub 2@ -based Inductively Coupled Plasmas during the GaN Etching, *H.S. Kim, J.W. Jang, Y.H. Lee, G.Y. Yeom,* Sungkyunkwan University, Korea; *J.W. Lee, T.I. Kim,* Samsung Advanced Institute of Technology, Korea

Planar inductively coupled Cl@sub 2@-based plasmas have been used to etch GaN and etch properties having smooth and nearly vertical etch profiles with the etch rates close to 850 nm/min could be obtained with Cl@sub 2@-rich gas combinations. To understand the effects of plasma conditions on the GaN etch properties, The quarupole mass spectrometry(QMS), optical emission spectroscopy(OES), and an electrostatic probe have been used. Especially, the quadrupole mass spectrometer system we used in the analysis of the plasmas was configured with ion optics, energy filter, and integral electron impact ion source for plasma diagnostics. Therefore, not only the radical densities but also positive and negative ion densities and their energy distributions were also measured. As process conditions used to study the effects of plasma characteristics on the GaN etch properties, Cl@sub 2@ was used as the main etch gas and Ar, BCl@sub 3@, and CH@sub 4@ were used as additive gases. Operational pressures were varied from 5mTorr to 30mTorr while other conditions such as inductive power, bias voltage, and substrate temperature were fixed at 600 watts, -120 volts, and 70 centigrade, respectively. The relative amounts of reactive ions (Cl@super +@, Cl@sub 2@@super +@, Cl@super -@, etc.), Ga-containing etch products(GaCl, GaCl@sub 2@, and GaCl@sub 3@ for Cl@sub 2@ plasma), and nitrogencontaining etch products (N, N@sub 2@, NH@sub 3@, etc.) were estimated by the plasma mass spectrometric measurements. The results showed that the enhancement of GaN etch rate was related to the increase of Cl radical and reactive ion such as Cl@super +@, Cl@sub 2@@super +@, etc. measured by the QMS and OES during the Cl@sub 2@-based inductively coupled plasma etching. Therefore, chemical reactions between Ga in GaN and Cl and Cl@sub 2@@super +@ from Cl@sub 2@, under the sufficient ion bombardments to break GaN bonds, appear to be important in the GaN etching. More detailed analysis of plasmas and their relation to GaN etching will be given in the presentation.

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