Carrier concentration and surface electron accumulation in indium nitride layers grown by high pressure chemical vapor deposition

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Electronic and structural properties of InN layer grown by high pressure chemical vapor deposition have been studied by high-resolution electron energy loss spectroscopy (HREELS) and room temperature infrared reflection measurements. HREEL spectra after atomic hydrogen cleaning exhibit N–H bending and stretching vibrations with no indications of an indium overlayer or droplet formation. Broad conduction band plasmon excitations are observed centered at 3100–4200 cm^{-1} at various locations across the surface in HREEL spectra acquired with 25 eV incident electron energy. The plasmon excitations are shifted about 300 cm^{-1} higher in spectra acquired using 7 eV electrons due to higher plasma frequency and carrier concentration at the surface than in the bulk which indicates surface electron accumulation. Infrared reflectance data acquired at various spots across the surface showed a similar variation in bulk plasma frequency. A three phase thin film reflection model fitted to the infrared data yielded carrier concentrations from 8.2×10^{19} to 1.5×10^{20} cm^{-3} and carrier mobilities from 105 to 210 $cm^2/V\,s$.
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I. INTRODUCTION

The properties of InN have attracted considerable research interest due to its potential in optoelectronic applications.[1,2] The group III-nitride alloy system (InN, GaN, and AlN) emits light over a wide spectral range from near infrared to ultraviolet wavelengths.[1,2] In addition, the high electron mobility and high saturation velocity of the electrons in InN and indium-rich InGaN alloys makes this material system of interest for applications in high frequency, high speed/high-electron-mobility transistors and related device structures.[1] In particular, it has a low effective electron mass resulting in a high mobility and high saturation velocity of the electrons.[1] Hence it has become a potential material for applications in high frequency, high speed, and high-electron-mobility transistors.[1] Recently, metal organic chemical vapor deposition and molecular beam epitaxy (MBE) have been considered as the most efficient growth techniques in order to grow III-V semiconductors.[1] However, the growth of InN and indium-rich group III-nitride alloys is challenging under low pressure process conditions due to higher equilibrium vapor pressure of nitrogen during growth and a low decomposition temperature compared to GaN and AlN.[3] High pressure chemical vapor deposition (HPCVD) was developed to address the thermodynamic problems associated with the vastly different partial pressures in the group III-nitride system, stabilizing indium-rich alloys at growth-temperatures comparable to GaN process conditions. The first InN growth results have shown that HPCVD is capable of growing stoichiometry-controlled high-quality InN layers at temperatures near 1100 K at reactor pressures around 15 bars.[3–5]

Surface electron accumulation on InN layers has been reported in several papers. Measurements of sheet carrier density versus InN film thickness led to a conclusion of excess surface charge in the work of Lu *et al.*[6] They also have reported Ohmic contacts for a number of metals without annealing and suggested that the Fermi level may be pinned above the conduction band minimum.[6] A series of papers by McConville and co-workers investigated surface electron accumulation on InN layers grown by MBE as measured by high-resolution electron energy loss spectroscopy (HREELS) and x-ray photoemission spectroscopy.[7–11] Mahboob *et al.* assign a broad loss feature centered near 2000 cm^{-1} in the HREEL spectra as due to the conduction band electron plasmon excitations.[11] They also report that the plasmon peak undergoes an ~240 cm^{-1} downward dispersion as the energy of the probing electron is increased from 10 to 30 eV indicating that the surface layer is of higher plasma frequency than the bulk. They simulated HREEL spectra using semiclassical dielectric theory applied to a four-layer model and determined a surface carrier concentration approximately ten times larger than the bulk value. They suggest that there exists an unusually low conduction band minimum at the Γ point in the band structure of InN which enables the existence of donor-type surface states in the conduction band. These surface states become ionized by losing electrons in the conduction band and hence these electrons accumulate on the surface. Hence electron accumulation is an inherent property of polar InN surface.[8]

In earlier HREELS studies, the authors have reported surface electron accumulation and surface NH termination of InN layers and therefore concluded that the layer was N polar.[12,13] The layers studied here also exhibit N polarity of the film. The HREEL spectra as a function of incident energy demonstrate surface electron accumulation for HPCVD-grown InN.[13] In this work, plasma frequency is determined

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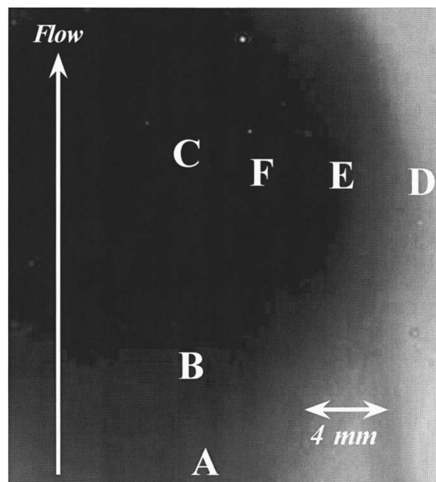

FIG. 1. Photograph of InN layer with locations marked for infrared reflectance measurements (A, B, and C) and HREELS (D, E, and F). Locations A and D are in the light region, B and E are in the transition zone from light to dark, and C and F are near the center of the dark region of the film. The gas flow direction during growth is indicated by the arrow.

using both HREELS and infrared (IR) reflectance measurements. Bulk plasma frequencies determined by model fitting of IR reflectance measurements agree with those determined using HREELS and allow determination of bulk carrier concentration and mobility. Although more recently grown films have shown considerable uniformity across the surface,[14] the layer studied here was grown under conditions to produce a variation in properties. Investigation of these properties is helpful in understanding the role of various growth parameters on stoichiometry and film quality.

II. EXPERIMENTAL METHODS

The InN layers used in this study were grown at a temperature of 1100–1120 K, a reactor pressure of 15 bars, and an ammonia to trimethylindium precursor ratio of 630 on a HPCVD-grown GaN buffer layer on a sapphire (0001) substrate. Details of the HPCVD reactor, the growth configuration, as well as real-time optical characterization techniques employed have been published elsewhere.[3,4]

Figure 1 shows a photograph of an InN layer investigated with the locations marked at which the HREELS analysis and IR reflectance measurement were performed. Both HREELS and IR reflection measurements average over an area of ~5 mm^2. The variation in color across the surface is indicative of differences in film properties caused by variations in stoichiometry. The section of the InN sample used in this study was chosen at the transition area, where the absorption edge is shifting downwards to lower energies along the flow direction due to InN stoichiometry variations. The sample was cut into smaller pieces to allow for IR reflectance (locations A, B, and C) and HREELS (locations D, E, and F) analyses. Locations A and D are both on the light colored outer region. Locations B and E are in the transition region from light to dark colored. Locations C and F are near the center of the dark region.

The ultrahigh vacuum (UHV) surface characterization system[15] had a base pressure of 1.8×10^{-10} torr. Before introduction into the UHV chamber, the InN sample was rinsed with isopropyl alcohol and then mounted on a tantalum sample holder and held in place by tantalum clips. Sample heating was achieved by electron bombardment of the back of the tantalum sample holder. A chromel-alumel thermocouple was attached to the mount next to the sample to measure sample temperature. HREELS experiments were performed in a specular geometry with an incident and scattered angle of 60° from the normal and incident electron energy ranges from 7 to 35 eV. The instrumental resolution obtained from the full width at half maximum of the elastic peak was typically 60 cm^{-1}.

The surfaces of the InN samples investigated were cleaned by bombardment with 1 keV Ar ions at an angle of 70° followed by atomic hydrogen cleaning (AHC). AHC was performed by backfilling the vacuum chamber with hydrogen to a pressure of 8.4×10^{-7} torr in the presence of a tungsten filament heated to 1850 K to produce atomic hydrogen. The samples were positioned 20 mm from the filament for 20 min (giving an exposure of 1000 l of H_2). Due to proximity to the heated filament, the sample temperature would raise to about 350 K. After this, the samples were heated to 600 K while remaining in front of the tungsten filament for an additional 20 min (an additional 1000 l of H_2). Auger electron spectroscopy and HREELS showed that surface carbon and oxygen contaminants had been removed from the surface. Low energy electron diffraction yielded a hexagonal 1×1 pattern over the entire surface of the film using electron energies from 40 to 170 eV.

Room temperature IR reflection measurements were performed over the frequency range of 200–8000 cm^{-1} (50–1.25 μm) using a fast Fourier transform infrared spectrometer.[16] All IR reflection spectra were taken under near normal (~8°) incident light arrangement to minimize the anisotropy effect in InN films.

III. RESULTS AND DISCUSSION

HREEL spectra of InN after AHC acquired at location F using a range of incident electron energies from 7 to 35 eV are shown in Fig. 2. The energy of the incident electrons was varied in order to obtain information from a range of probing depths. A strong loss feature, observed at 560 cm^{-1}, is assigned to Fuchs-Kliewer surface phonon excitations in agreement with earlier results.[7–12] In the HREEL spectra taken at lower incident energy, the probing electron brings the information only from few atomic layers of the surface. The HREEL spectrum taken using 7 eV electrons shows surface adsorbate loss features at 870 and 3260 cm^{-1} due to the bending and stretching vibrations of a surface N–H species as assigned previously.[12] The presence of N–H and lack of indium-related vibrations demonstrate N termination and therefore N polarity of the film since excess nitrogen would not be expected on the surface of an In-polar layer.[12]

A loss feature, due to the conduction band plasmon excitation with a peak in the range of 3100–3400 cm^{-1} for dif-

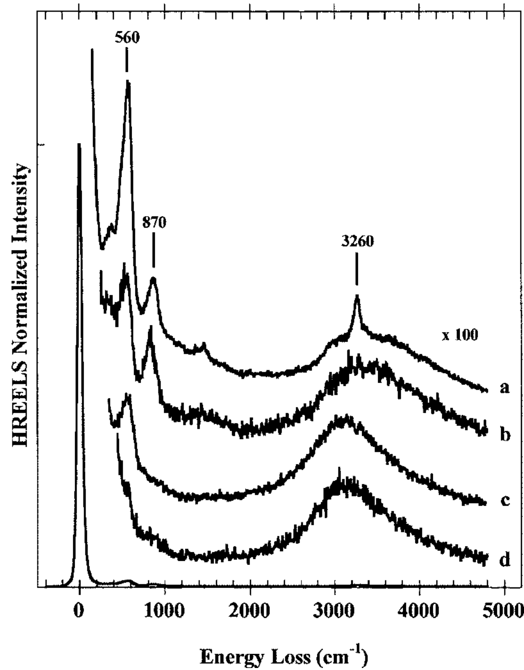

FIG. 2. HREELS of InN taken at location marked F in Fig. 1 after atomic hydrogen cleaning. Spectra were acquired in the specular direction with incident electron energies of (a) 7 eV, (b) 15 eV, (c) 25 eV, and (d) 35 eV.

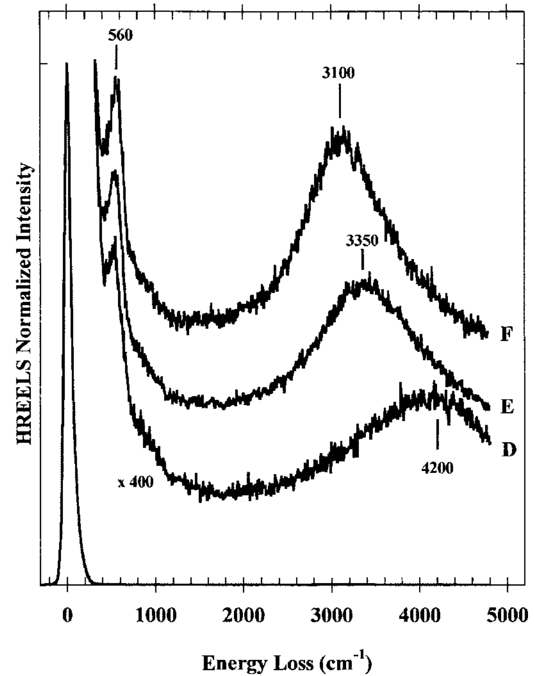

FIG. 3. HREELS of InN after atomic hydrogen cleaning. Spectra were acquired in the specular direction with an incident electron energy of 25 eV at locations marked D, E, and F as indicated in Fig. 1.

ferent incident electron energies, appears in each HREEL spectrum. The spectrum from 7 eV incident electrons shows a plasmon loss peaking near 3400 cm^{-1} while the spectra taken with incident electron energies of 25 and 35 eV show the plasmon peak shifted to a lower frequency of ~3100 cm^{-1}. Since the probing depth of the electrons increases with increasing incident energy, the shift of the plasmon loss feature indicates a lower plasma frequency in the bulk compared with the surface indicating an accumulation of electrons on the surface.[13] Since the probing depth of 25 and 35 eV electrons is considerably more than the thickness of the surface electron accumulation layer,[7–11] the position of the peak in the plasmon loss feature is assumed to be close to the bulk plasma frequency.

Figure 3 shows the HREEL spectra taken at various locations on the InN layer with incident electron energy of 25 eV. The spectra acquired at locations D, E, and F yield plasmon loss peaks at frequencies of 4200, 3350, and 3100 cm^{-1}, respectively. These data indicate that the bulk plasma frequency and therefore the bulk carrier concentration are lower in the darker regions of the film where the absorption edge occurs at lower energy.

Figure 4 depicts the IR reflectance data collected at locations centered on those marked A, B, and C in Fig. 1. In order to extract the bulk plasma frequency from the IR reflectance taken at each location, the data were fitted using a three phase thin film reflection model described in detail elsewhere.[14] Briefly, the dielectric functions are modeled assuming two contributions, a Lorentz oscillator for phonons and the classical Drude model for plasma permittivity. Initially, the IR reflection of (GaN/sapphire) structure was modeled and the best fit parameters of GaN layer were obtained from Levenberg-Marquardt's nonlinear fitting algorithm.[17] Thereafter, the best fit parameters for InN film were obtained by fitting InN/GaN/sapphire reflection while keeping parameters obtained for GaN/sapphire structure unchanged. The observed deviations between the experimental data and the fitting results in the wavelength region from 5000 to 8000 cm^{-1} are due to absorption centers below the band gap of InN, which are not included in the present fitting model. However, the energy positions of crests and valleys of experimental curves match with fitting curves giving correct film thickness.

From the model fitting the plasma frequency and Drude damping constant were determined for each spectrum as well as an average value of the high frequency dielectric constant of 8.6. The plasma frequencies and damping constants obtained from the fittings were then used to obtain the free carrier concentrations and carrier mobilities across the surface,[14] as listed in Table I. An electron effective mass of 0.09 times the free electron mass was used for the calculations[18] where variation of electron effective mass with carrier density is not taken into account.

The plasma frequencies of 4240, 3520, and 3120 cm^{-1} measured by IR reflection at locations A, B, and C are in good agreement with those measured from HREELS at locations D, E, and F, respectively. The variations of the plasma frequency and damping constant across the surface of the HPCVD-grown InN layer indicate variations in the bulk free carrier concentration and carrier mobility. As shown in Table I, a free carrier concentration of 8.0×10^{19} cm^{-3} and a carrier mobility of 210 $cm^2/V\ s$ were calculated for the dark central

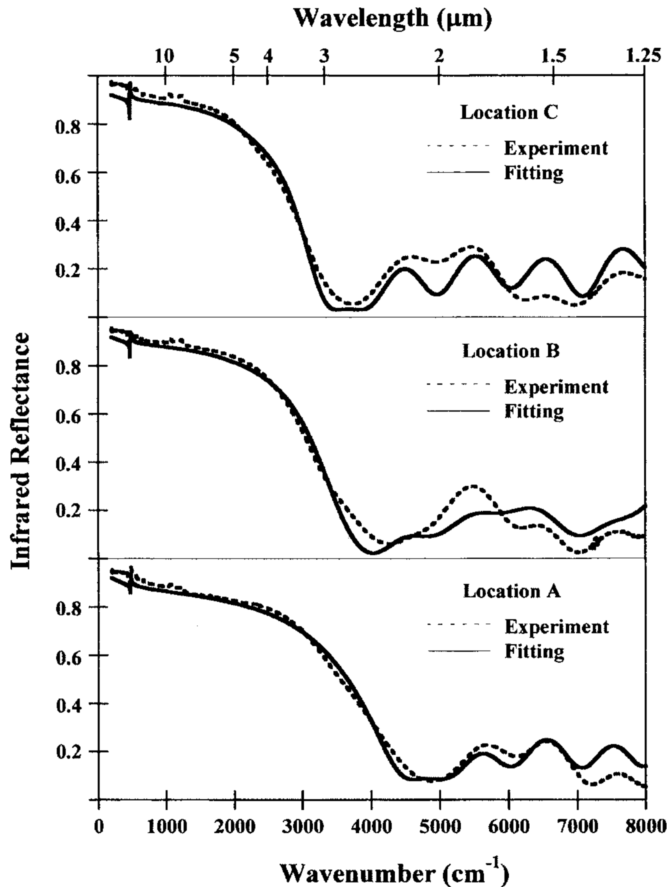

FIG. 4. Infrared reflectance measurements from three locations on InN layer (dashed lines). Results of fitting to a three-layer model (solid lines) to determine plasma frequency and damping constant.

region of the InN film while a free carrier concentration of 1.4×10^{20} cm^{-3} and a carrier mobility of 105 cm^2/V s were found for the lighter outer region. IR reflectance on more recently grown InN layers shows carrier concentrations near 7×10^{19} cm^{-3} and carrier mobilities near 430 cm^2/V s.[14]

It is unusual for one technique to yield information about both surface and bulk properties. In the work reported here, HREELS was used to determine the surface chemical species. This characterization of surface termination led to a conclusion regarding film polarity. The variation of incident electron energy allowed the adjustment of probing depth and measurements of plasma frequency for both bulk and surface layers. Overall, one technique was able to determine structural and chemical surface information as well as surface and bulk electronic properties. In addition, film polarity, a property of the entire layer, could also be inferred.

TABLE I. Plasma frequencies, free carrier concentrations, and carrier mobilities determined from a model fitting to the infrared reflectance data at several locations on the InN layer.

Location	Plasma frequency (cm^{-1})	Free carrier concentration (cm^{-3})	Carrier mobility (cm^2/V s)
A	4240	1.5×10^{20}	105
B	3520	1.1×10^{20}	170
C	3120	8.2×10^{19}	210

IV. CONCLUSION

In summary, high-pressure CVD-grown InN layers have been studied by HREELS and IR reflection measurements. HREELS taken at lower incident energy of the electron showed a shift to higher plasma frequency indicating a surface electron accumulation. HREELS also indicates that the layer is N polar and terminated by N–H species following atomic hydrogen cleaning. HREELS performed with 25 eV electrons at different spots across the surface yielded plasma frequencies between 3100 and 4200 cm^{-1}. The model fitting of IR reflectance data yielded bulk plasma frequencies between 3120 and 4240 cm^{-1}, in agreement with the HREELS data taken at corresponding spots across the surface. The parameters from the fitting of the IR data were used to determine free carrier concentrations from 8.2×10^{19} to 1.5×10^{20} cm^{-3} and carrier mobilities from 105 to 210 cm^2/V s.

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