Surface structure, composition, and polarity of indium nitride grown by high-pressure chemical vapor deposition

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Abstract

The structure and surface bonding configuration of InN layers grown by high- pressure chemical vapor deposition have been studied. Atomic hydrogen cleaning produced a contamination free surface. Low energy electron diffraction yielded a 1x1 hexagonal pattern demonstrating a well-ordered c-plane surface. High resolution electron energy loss spectra exhibited a Fuchs-Kliewer surface phonon and modes assigned to a surface N-H species. Assignments were confirmed by observation of isotopic shifts following atomic deuterium cleaning. No In-H species were observed, and since an N-H termination of the surface was observed, indicating N-termination of the surface and N-polarity of the indium nitride is indicated..

Research on the growth and characterization of indium nitride (InN) has increased tremendously in recent years largely due to the interest in exploring the AlN-GaN-InN alloy system for device applications in solid-state lighting, spintronics, and terahertz devices [1,2]. However, the range of device applications is strongly affected by the extent to which indium-rich heterostructures can be formed and by the bandgap of InN, both of which are currently not clear [2].

In comparison to the growth of $Ga_{1-x}Al_xN$ alloys and heterostructures – which can be accomplished by low-pressure metalorganic chemical vapor deposition (MOCVD) – the growth of InN and indium-rich group III-nitride alloys is more challenging due to the higher equilibrium vapor pressure of nitrogen during growth. This requires new different approaches in growing structures containing both indium-rich group III-nitride alloys along with wide bandgap group III-nitride layers [3]. InN films have been grown by a number of techniques including MOCVD and MBE [1] but many of the fundamental electrical and optical properties of InN are still in debate including the bandgap. High-pressure chemical vapor deposition (HPCVD) has been shown to overcome difficulties created by the difference in optimum growth conditions between InN and GaN [3-5]. Using HPCVD, stoichiometry controlled InN and GaN layers have been grown at temperatures near 1100 K.

Comparatively few studies have been done on the fundamental surface properties of InN. Studies of the surface structure and reactions are an important part of gaining an understanding of the growth mechanism. Surface structure and bonding affect kinetic processes during growth which determine the quality of the films and the performance of devices. In this work the surface structure, composition, and bonding of HPCVD-grown InN films after atomic hydrogen cleaning were investigated using several electron spectroscopic techniques. This characterization shows a well-ordered, hydrogenated, nitrogen-terminated InN surface.

The InN layers used in this study were grown by HPCVD at growth temperatures of 1100 K to 1120 K, a reactor pressure of 15 bar, and an ammonia to TMI precursor ratio of 200 [3]. The layers were deposited 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 [3-5].

The ultrahigh vacuum chamber (UHV) surface characterization system had a base pressure of 1.8×10^{-10} torr and details of the apparatus have been published previously [6]. Before introduction into the UHV chamber, the InN sample was rinsed with acetone and isopropyl alcohol, 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 in order to measure the sample temperature.

Auger electron spectroscopy (AES) of the as-inserted sample revealed oxygen and carbon contamination in addition to indium and nitrogen. The surface carbon was removed by sputtering with 1-keV nitrogen ions totaling 560 μC/cm^2 at an angle of 70° followed by 1000 μC/cm^2 at normal incidence. AES after the sputtering process showed that the surface carbon was effectively removed but that some oxygen remained. No low energy electron diffraction (LEED) pattern was observed prior to or after sputtering process.

McConville and coworkers have demonstrated that atomic hydrogen cleaning (AHC) is an effective way to remove surface contaminants, particularly oxygen, from InN and leave an ordered surface [7]. 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 sample was positioned 20 mm from the filament for 20 minutes (giving an exposure of 1000 L of H_2). During this time the sample heater was not used and the sample temperature rose to about 350 K due to proximity to the heated filament. After this, the sample was heated to 600 K while remaining in front of the tungsten filament for an additional 20 minutes (an additional 1000 L of H_2). Atomic deuterium cleaning (ADC) was performed in a similar way to aid in the assignment of vibrational modes.

After one cycle of AHC, a hexagonal 1x1 LEED pattern was observed. After several additional cleaning cycles the hexagonal diffraction pattern became sharper (Fig. 1) as observed at various electron energies from 39 to 120 eV. The LEED pattern indicates that the surface is c-plane oriented and well-ordered. AES showed no carbon and a small amount (<3%) of oxygen remaining. Piper *et al.* [7] have reported a similar hexagonal pattern from AHC-cleaned MBE-grown InN at an incident energy of 164 eV. They also report that AHC completely removes surface oxygen and carbon as measured by x-ray photoelectron spectroscopy.

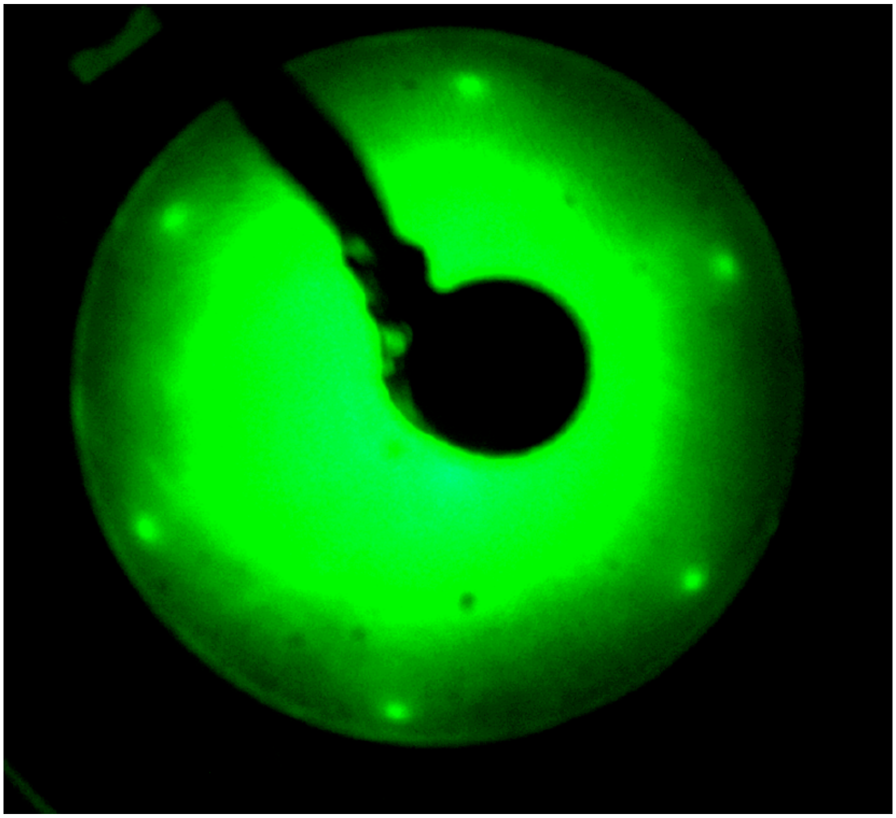

Figure1:

Low energy electron diffraction of AHC cleaned InN sample at incident electron energy of 39.5eV.

High resolution electron energy loss spectroscopy (HREELS), a surface sensitive vibrational spectroscopy, was performed in a specular geometry with an incident and scattered angle of 60° from the normal and an incident electron energy of 12.5 eV. The HREEL spectra obtained had a full width at half maximum for the elastic peak of 60 cm^{-1}.

HREEL spectra of InN after AHC and ADC are shown in Fig. 2. In both cases a strong loss feature is observed at 550 cm^{-1} which we assign to a Fuchs-Kliewer surface phonon [8]. This is in agreement with the previous assignment by McConville and coworkers [7] of a peak at ~530 cm^{-1} to a Fuchs-Kliewer phonon. McConville *et al.* also reported that no adsorbate peaks were observed after AHC, but a broad peak near 2000 cm^{-1} was assigned to a conduction band electron plasmon are interpreted as evidence for electron accumulation on n-type InN [9-12]. In the present study, no broad plasmon loss was found but adsorbate losses were observed.

A loss peak is seen at 3260 cm^{-1} (2410 cm^{-1}) for the AHC (ADC) surface. This peak is assigned to an NH (ND) stretching vibration in agreement with the well-known group frequency for NH stretching vibrations and by comparison to GaN [6,13-15]. The observation of a single NH stretch indicates a surface NH rather than NH_2 species.

The InH stretching vibration has been reported at 1650-1700 cm^{-1} in HREELS experiments [16-18] and at 1630-1680 cm^{-1} from *ab initio* calculations [19] on InP surfaces. No loss features in this range were observed in the present work indicating that there is no surface InH was present.

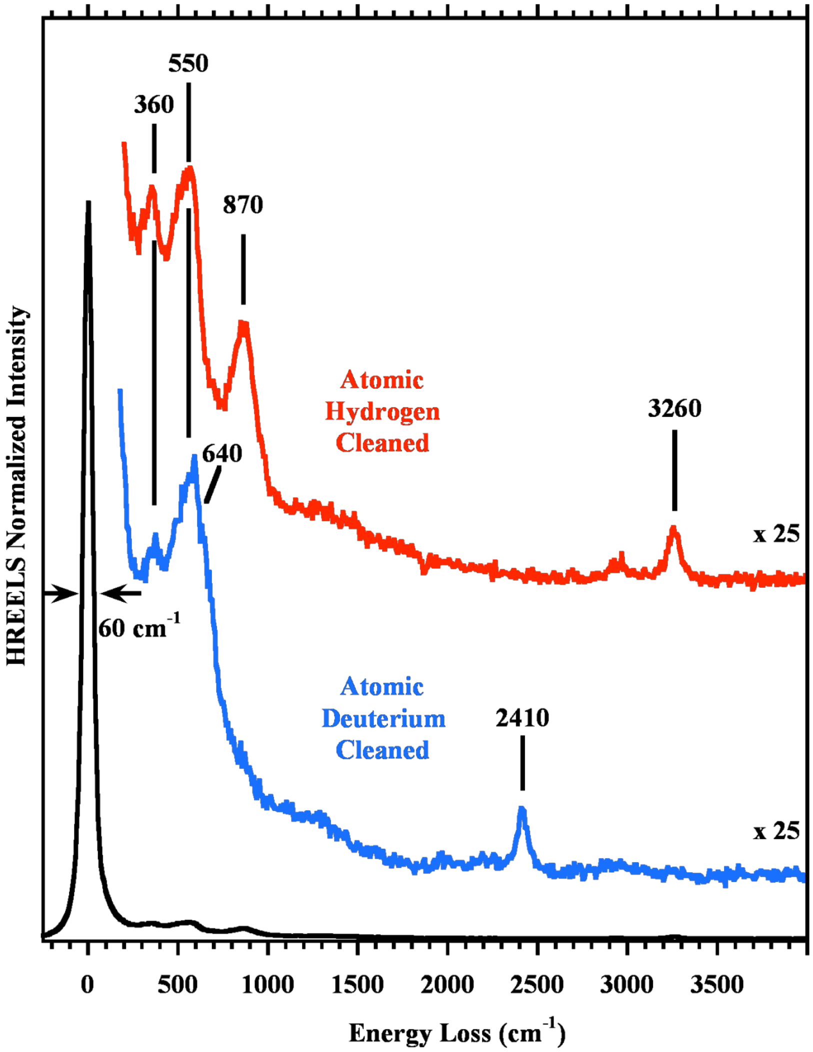

Figure 2:

HREELS of InN after atomic hydrogen (deuterium) cleaning. Spectra were acquired in the specular direction with an incident electron energy of 12.5 eV.

A loss peak is also observed at 870 cm^{-1} on the hydrogen-cleaned surface becoming a shoulder near 640 cm^{-1} on the deuterium-cleaned surface. The isotope shift of ~1.35 confirms that this is predominantly a vibration of surface hydrogen. Since the NH stretch is observed but InH stretch is not, we assign this feature to the bend of the surface NH. NH bending vibrations have not been reported from GaN surfaces. Gassman and coworkers report an NH bending mode on AlN at 1250 cm^{-1} [20]. Although NH$_2$ bending and rocking vibrations are often reported in the range of 1200-1500 cm^{-1}, recent work on ruthenium surfaces has shown that NH bending vibrations occur as low as 700 cm^{-1} [21,22].

Peaks are also observed near 360 cm^{-1} on both AHC and ADC surfaces, exhibiting little or no isotope shift. We suggest that these loss peaks are due to bouncing vibrations of the nitrogen surface atoms with the surface. A small CH stretching vibrational peak is seen at 2940 cm^{-1} due to residual surface carbon. Although no carbon is seen in AES after atomic hydrogen cleaning, HREELS is far more sensitive to a small amount of surface contamination than AES. It is worth noting that AES still shows a small amount of oxygen although no OH stretch is observed in HREELS after exposure to hydrogen atoms. This is due to the larger depth probed by AES compared with HREELS and indicates that AHC removes oxygen from only the first few layers of the film.

Studies of the polarity of InN films grown by various techniques have observed In-, N-, and mixed polarities [1]. The assignment of all adsorbate vibrations to surface NH implies nitrogen termination of the InN layer, which in turn implies nitrogen polarity. Ideal N-polar InN would have nitrogen surface atoms bonded to three second-layer In atoms. The surface nitrogen would then have one dangling bond normal to the surface. Saturation of three-fourths of the dangling bonds with hydrogen would satisfy electron counting rules for this polar surface. Three-fourths monolayer of hydrogen without rearrangement of the top-layer nitrogen atoms would still result in a 1x1 LEED pattern. Such an arrangement is consistent with both the HREELS and LEED observations reported in this work.

In summary, high-pressure CVD grown InN layers have been prepared by atomic hydrogen and deuterium cleaning. The LEED image shows a hexagonal 1x1. HREELS shows Fuchs-Kliewer phonons at 550 cm^{-1} and NH stretch and bend vibrational losses at 3260 and 870 cm^{-1}, respectively. No InH vibrations are observed. It is concluded that the orientation of the film is $\mathrm{InN}(000\bar{1})$, that is, N-polarity.

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