Electron Spectroscopic Study of Indium Nitride Layers

Rudra Prasad Bhatta
ELECTRON SPECTROSCOPIC STUDY OF INDIUM NITRIDE LAYERS

by

RUDRA PRASAD BHATTA

Under the Direction of Brian D. Thoms

ABSTRACT

Surface structure, chemical composition, bonding configuration, film polarity, and electronic properties of InN layers grown by high pressure chemical vapor deposition (HPCVD) have been investigated. Sputtering at an angle of 50-70 degrees followed by atomic hydrogen cleaning (AHC) was successful in removing the carbon contaminants. AHC is found to be the most effective cleaning process to remove oxygen contaminants from InN layers in an ultrahigh vacuum (UHV) system and produced a well ordered surface. Auger electron spectroscopy (AES) confirmed the cleanliness of the surface, and low energy electron diffraction (LEED) yielded a 1×1 hexagonal pattern demonstrating a well-ordered surface.

High resolution electron energy loss spectra (HREELS) taken from the InN layers exhibited loss features at 550 cm⁻¹, 870 cm⁻¹ and 3260 cm⁻¹ which were assigned to Fuchs-Kliewer phonon, N-H bending, and N-H stretching vibrations, respectively. Assignments were
confirmed by observation of isotopic shifts following atomic deuterium dosing. No In-H species were observed indicating N-termination of the surface and N-polarity of the film. Broad conduction band plasmon excitations were observed centered at 3100 cm\(^{-1}\) to 4200 cm\(^{-1}\) in HREEL spectra acquired with 25 eV electrons, for a variety of samples grown with different conditions. Infrared reflectance data shows a consistent result with HREELS for the bulk plasma frequency. The plasmon excitations are shifted about 300 cm\(^{-1}\) higher in HREEL spectra acquired using 7 eV electrons due to the higher plasma frequency and carrier concentration at the surface than in the bulk, demonstrating a surface electron accumulation. Hydrogen completely desorbed from the InN surface upon annealing for 900 s at 425 °C or upon annealing for 30 s at 500 °C. Fitting the coverage versus temperature for anneals of either 30 or 900 s indicated that the desorption was best described by second order desorption kinetics with an activation energy and pre-exponential factor of 1.3±0.2 eV and 10\(^{-7.3±1.0}\) cm\(^2\)/s, respectively.

Vibrational spectra acquired from HREEL can be utilized to explain the surface composition, chemical bonding and surface termination, and film polarity of InN layers. The explanation of evidence of surface electron accumulation and extraction of hydrogen desorption kinetic parameters can be performed by utilizing HREEL spectra.

INDEX WORDS: Electron energy loss spectroscopy, Vibrational spectroscopy, Indium nitride, Nitride semiconductors, Surface structure composition, Surface electron accumulation, Hydrogen desorption
ELECTRON SPECTROSCOPIC STUDY OF INDIUM NITRIDE LAYERS

by

RUDRA PRASAD BHATTA

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Doctor of Philosophy

in the College of Arts and Sciences

Georgia State University

2008
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Rudra Prasad Bhatta
2008
ELECTRON SPECTROSCOPIC STUDY OF INDIUM NITRIDE LAYERS

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Office of Graduate Studies
College of Arts and Sciences
Georgia State University
May 2008
To my parents, lovely son Pradip

and

wife Sabitra
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7.4 Fitting of first and second order desorption kinetics to hydrogen coverage (determined from HREELS N-H stretch intensity) for InN sample B after preparation by atomic hydrogen cleaning and after heating for 30 s to 425, 450, 475, and 500 °C. Equation and parameters used in the fitting are described in the text.
Chapter 1
Introduction

Group III-V compound semiconductors play an important role in the field of optoelectronic and microelectronic device structures. The performance and efficiency of nitride-based devices depends upon various factors, among which are, the degree of surface cleanliness during the growth, film polarity and the phenomenon of electron accumulation. The main objectives of this project were to:

- determine the film polarity and surface structure of InN films grown by high pressure chemical vapor deposition,
- study and analyze the phenomenon of electron accumulation on the InN surface, and
- determine thermal desorption kinetics of hydrogen from the InN surface in order to elucidate the growth mechanism in the presence of hydrogen.

Chapter 2 includes the introduction to and motivation for this study. This chapter will explain the important properties and applications of group III-nitrides particularly InN and its application in optoelectronic and microelectronic device structures. Chapter 3 gives an overview of the experimental techniques which were implemented to perform this work. The surface structure, bonding and the film polarity are discussed in chapter 4. The phenomenon of surface electron accumulation is explained in chapter 5 while a comparative study of surface electron accumulation by high resolution electron energy loss spectroscopy and determination of carrier concentration with infrared absorption measurements is described in chapter 6. Recombinative
desorption of hydrogen from the N-polar InN surface along with the determination of the thermal kinetic parameters are investigated in chapter 7. The major conclusions are drawn and the directions of future work are discussed in chapter 8.

The experimental results presented in chapters 4 to 6 are already published in various scientific journals and the result presented in chapter 7 is submitted for publication to Surface Science. The titles of the articles, name list of the authors and the name of the journals they have been published are given below.

1. **Surface structure, composition, and polarity of indium nitride layers grown by high pressure chemical vapor deposition**
   
   R. P. Bhatta, B. D. Thoms, M. Alevli, V. Woods, and N. Dietz,
   

2. **Surface electron accumulation in indium nitride layers grown by high pressure chemical vapor deposition**
   
   R. P. Bhatta, B. D. Thoms, M. Alevli, and N. Dietz,
   

3. **Carrier concentration and surface electron accumulation in indium nitride layers grown by high pressure chemical vapor deposition**
   
   R. P. Bhatta, B. D. Thoms, A. Weerasekera, A. G. U. Perera, M. Alevli, and N. Dietz,
   

4. **Desorption of hydrogen from InN (000\(\bar{1}\)) surface observed by HREELS**
   
   R. P. Bhatta, B. D. Thoms, M. Alevli, and N. Dietz,
   
Chapter 2

III-Nitride semiconductors, properties and applications

2.1 Properties

When one of the group III elements, boron, aluminum, gallium or indium, is bonded to the group V element nitrogen, a III-nitride compound semiconductor is formed. AlN, GaN and InN are the most common III-nitrides presently being studied. The chemical bonds of these compounds are predominantly covalent. However, due to the large differences in electronegativity of the two constituents, there is also a significant ionic contribution to the bond, which determines the stabilities of the respective structural phases. The binary group III-nitrides AlN, GaN and InN are found to crystallize in the following three structural phases; wurtzite, zincblende and rock-salt. At ambient conditions, the thermodynamically stable phase is the wurtzite structure [1-3]. The zincblende structure is metastable and can be stabilized by heteroepitaxial thin film growth on the (001) crystal planes of cubic structures such as Si, MgO and GaAs [4]. A phase transition to the rock-salt structure takes place at high pressure [4].

The wurtzite and zincblende structures are similar in many aspects. In both the cases, the group III element is surrounded by four atoms of the group V element, which are arranged at the edges of a tetrahedron. Likewise the group V element is surrounded by four atoms of group III
elements. Also the twelve next-nearest neighbors are at the equal distance in both the structures. The main difference between wurtzite and zincblende structure is found only from third next-nearest neighbors, that is, they have different stacking sequences. The stacking sequence of the wurtzite structure along [0001] is ABAB, while that of zincblende structure along [001] direction is ABCABC, where A, B, and C refer to allowed sites of the III-N pairs of the closed-packed layers. A fault in stacking sequence may transform one structure into another or create a structural defect.

A phase transformation of the wurtzite towards the rock-salt (NaCl) structure can be found at higher pressures in ionic bonded crystals. This transformation results in changing the bond character mostly from covalent to more ionic and from four to six fold coordination of atoms. The structural phase transition was experimentally observed at pressures of 22.9 GPa, 52.2 GPa and 12.1 GPa for AlN, GaN and InN, respectively [5-7].

AlN, GaN & InN and ternary or quaternary alloys of it are direct band gap compound semiconductors. Their band gap energy cover the spectral range from deep ultraviolet (AlN = 6.2 eV) to near infrared (InN = 0.67 eV). However, controversy exists about the band gap energy of InN. The ternary and quaternary alloys of InN, GaN and AlN, if it is possible to stabilize such alloys may form a continuous alloy system (InGaN, InAlN, and AlGaInN), whose band gap energy may vary from 0.67 to 6.2 eV.

AlN exhibits many useful properties which make it useful for interesting applications. For example, its hardness, high thermal conductivity, and resistance to high temperature and caustic chemicals, make it an attractive material for electronic packaging applications. Due to its wide band gap and high resistivity, undoped AlN shows insulating material property. Because of the insulating behavior of AlN, a charging problem arises in the sample during Auger electron
spectroscopy (AES) and high resolution electron energy loss spectroscopy (HREELS) experiments on undoped AlN samples. Therefore AlN is not an easy material to study. Because of the reactivity of Al, high purity source material and an oxygen-free environment are required to grow AlN of good quality. With the availability of refined growth techniques, AlN is presently grown with much improved crystal quality, and shows both n- and p-type conduction.

Although GaN is more thoroughly studied than other group III-nitrides, it still is in need of extensive investigation of its properties in order to keep its name in the top list of the technologically important materials such as Si and GaAs. As grown undoped GaN always shows unintentional n-type conductivity. However, with improvements in the crystal growth and processing technologies, samples of high quality GaN with low background concentrations are routinely obtained. Successful growth of p-type GaN has led researchers to demonstrate excellent pn junction LEDs capable of working in various wavelength regimes.

Electronic properties, particularly carrier concentration and mobility, are the important factors affecting the performance and efficiency of electronic devices. A range of values of electron mobility and background concentration have been measured for all of the three nitrides, AlN, GaN, and InN, by using Hall effect measurements. Carrier mobility depends upon various factors, for example temperature, electric field, doping concentration and material quality of the semiconductors. If the lattice mismatch is large then the value of carrier mobility is low. Using a buffer layer during the nucleation reduces the strain which enhances the carrier mobility. Due to carrier concentrations less than $10^{16}$ cm$^{-3}$, native defects and impurities, the measured electrical properties of AlN are limited to the resistivity measurements. The background electron concentration for undoped GaN at room temperature has been reported to be nearly $10^{16}$ cm$^{-3}$ and the mobility around 1000 cm$^2$V$^{-1}$s$^{-1}$ while those of InN are reported as in the order of $10^{18}$
cm$^{-3}$ and 4000 cm$^{2}$V$^{-1}$s$^{-1}$ respectively [8]. The details of the structural and electronic properties of InN are discussed in the later sections.

Refractive index and dielectric constants of the materials are the factors affecting optical properties of the devices. The refractive index of AlN has been calculated in amorphous, polycrystalline and single epitaxial thin film. The value of refractive index is found to increase with increasing structural order, varying between 1.8 - 1.9 for amorphous films, 1.9 - 2.1 for polycrystalline films and 2.1 - 2.2 for single crystal epitaxial films [8]. The long wavelength range dielectric constant ($\varepsilon_0$), and high frequency dielectric ($\varepsilon_{\infty}$) of AlN vary in the range of 8.3 to 11.5 and 4.68 to 4.84, respectively. Ejder et al. [9], using transmission and absorption measurements, have reported the refractive index of GaN to be 2.33. Matsubara and Takagi [10], using optical reflectivity measurement, reported that the long wavelength range dielectric constant ($\varepsilon_0$) of GaN is 8.9 while, Barker and Ilegems [11], reported a slightly different value of 9.5 by using infrared reflectivity measurements of the phonon energy.

Tyagi et al. [12,13] performed reflection and transmission measurements, and were able to measure an index of refraction for InN of 3.05±.05 while Hovel and Cuomo [14] reported it to be 2.9, and Natarajaan et al. [15] measured it as 2.85. The static dielectric constant ($\varepsilon_0$) and high frequency dielectric ($\varepsilon_{\infty}$) of InN are estimated theoretically as 14.6 and 7.61, respectively [16,17].

Other structural, electronic, thermal and optical properties [4] of wurtzite AlN, GaN and InN are summarized in Table 2.1.
Table 2.1 Properties of wurtzite III-nitrides

<table>
<thead>
<tr>
<th>Parameters</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
<th>Reference:</th>
</tr>
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<tr>
<td>Band gap (eV)</td>
<td>6.2</td>
<td>3.39</td>
<td>0.7 to 1.89</td>
<td>4, 26, 31, 34</td>
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<td>Lattice constant (Å)</td>
<td>a = 3.112, c = 4.982</td>
<td>a = 3.189, c = 5.185</td>
<td>a = 3.548, c = 7.60</td>
<td>4</td>
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<td>Thermal conductivity (W/cm K)</td>
<td>2.85</td>
<td>2.0-2.1</td>
<td>0.45</td>
<td>8</td>
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<tr>
<td>Thermal expansion (x10^6 K^-1)</td>
<td>Δa/a = 4.2, Δc/c = 5.3</td>
<td>Δa/a = 5.59, Δc/c = 3.17</td>
<td>Δa/a ~ 3, Δc/c ~ 4</td>
<td>4</td>
</tr>
<tr>
<td>Index of refraction</td>
<td>2.15 ± 0.05</td>
<td>2.33</td>
<td>2.8 - 3.05</td>
<td>4, 9, 12, 13, 14, 15</td>
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<tr>
<td>Dielectric Constant</td>
<td>ε₀ = 8.5 ± 0.2, εₑ = 4.68-4.84</td>
<td>ε₀ = 10, εₑ = 5.5</td>
<td>ε₀ = 15.3, εₑ = 8.4</td>
<td>4, 8, 10, 11, 16, 17</td>
</tr>
<tr>
<td>Effective electron mass (mₑ)</td>
<td>0.48</td>
<td>0.2</td>
<td>0.06</td>
<td>4, 8</td>
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<tr>
<td>Electron mobility (cm²V⁻¹s⁻¹)</td>
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<td>1000 (Theo.), 900 (Expt.)</td>
<td>4400 (Theo.), 3980 (Expt.)</td>
<td>4, 8</td>
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<td>Peak drift velocity (x 10⁷ cms⁻¹)</td>
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<td>3.1</td>
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<td>Mass density (gcm⁻³)</td>
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<tr>
<td>Electron concentration (cm⁻³)</td>
<td>&lt; 10¹⁶</td>
<td>~10¹⁷</td>
<td>&gt;10¹⁹</td>
<td>4, 8</td>
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2.2 Applications

III-nitride semiconductors have been intensively investigated for last two decades for their potential applications in electronic, optoelectronic, and microelectronic device structures. The recent findings show that III-nitride semiconductors are also promising for nanostructured materials and nanodevices. The operation of optical devices, made up of GaN, AlN and their alloys can be extended to blue and beyond for electronics operative at high temperatures and caustic environment. Due to the low band gap of InN and wide band gap of AlN, GaN can be alloyed with Al and In to fabricate a wide range of energy band gaps. The operation of optical devices produced in this alloy system can be extended to wavelengths ranging from near infrared to the deep ultraviolet regime.

The fabrication of homo and heterojunction devices mainly based on GaN led to a rapid commercialization of light emitting diodes and laser diodes [18]. The practical and commercial applications of these materials can be used in traffic lights, back lighting of mobile phones, indoor lights, light indicators for electronic devices, optical storage and display and solid state lasers. Advanced GaN/AlGaN high power microwave transistors are also now commercially available. Although GaInN based LEDs, lasers diodes, and microwave transistors are well developed and commercialized, the potential application of GaN and its alloys as a high power, high temperature transistor and other optoelectronic applications are still actively being researched. AlN and InN are still less developed for applications in commercial device structures. Al_{x}Ga_{1-x}N is developed only for x = 0.5 in the application as photoconductor detectors [19] while In_{x}Ga_{1-x}N is still undeveloped except for small indium contents.
Due to the wide band gap of AlN and GaN, these are the potential materials for fabrication of UV emitters and detectors. UV-emitters can be used for curing, material identification, forensic location, disinfection and material processing applications. UV-detectors based on III-nitrides are useful in UV sensing applications such as high temperature flame sensing, automobile engine combustion sensing, burner monitoring in gas turbines, environmental monitoring, solar blind detectors, remote sensing of earth resources and missile plume detection for military use. Traditionally, this is accomplished using photomultiplier tubes, which have the complication of needing a vacuum tube. Vacuum tubes are physically large and fragile, require high voltage, are sensitive to magnetic fields and have higher cost than III-nitride based UV detectors.

The applications of III-nitride based materials are also investigated as non-linear optical switching elements based on photonic band gap structures for high speed optical communications. High frequency bands are required for communication systems, such as portable telephones, mobile telephone, and broadcasting satellites due to the availability of larger bandwidths. Conventionally, dielectric ceramic and surface acoustic wave (SAW) devices were used for these frequency applications. Lakin et al. [20] have carried out an extensive study of sputtered AlN for bulk acoustic wave resonators and filters operating at 1-2 GHz. AlN based SAW devices in particular have achieved operating frequencies, electromechanical coupling factors, transition losses and high temperature stabilities, which are useful for technical applications such as cheap electrical filters, sensors, or photorefractive grids.

Improved group III-nitride materials will provide the basis for novel devices that are of significant importance to space exploration missions due to their robustness against radiation damage. The wide band gap of GaN and AlN and their strong bond strength (2.88, 2.2 and 1.93 eV/bond for AlN, GaN and InN, respectively) [21] make III-nitride materials resistant to
radiation damage. Also, the properties of a high melting point and the high dissociation temperature of GaN and AlN make them promising materials for high temperature, high power transistors.

A continuous research effort is going on for fabrication of spintronic and terahertz device structures. Ferromagnetic materials like Mn incorporated into III-nitrides form another compound Ga$_x$Mn$_{1-x}$N, which is assumed to be a well suited material for spintronic device structures. Intense research focuses on material characterization and fabrication of device structures for possible application in quantum computing.

The possibility of application of III-nitride materials in terahertz device structures is being investigated. Meziani et al. [22] have investigated the optical characterization of InN layers in the THz range and concluded that InN is of great interest for realization of hyperfrequency/terahertz devices due to its high peak electron velocity, which is higher than those in GaAs and InAs.

Another important application of III-nitride semiconductors is in fabrication of quantum infrared (IR) detectors. Photoconductors are the most common type of quantum IR detectors which can be fabricated by using nitride semiconductors. The small bandgap of InN suggests that InN and its III-nitride alloys could be suitable materials for photovoltaic applications. A single chip of In$_x$Ga$_{1-x}$N could absorb the entire visible range of solar radiation and could result in high performing solar cells.

The potential of extending the band gap energies of group III-nitride alloys into the near infrared spectral region has generated considerable interest and extensive research efforts have been initiated world wide. The low band gap results of InN grown by various techniques have been reproduced by several groups using various material characterization techniques. The
potential applications and properties of InN in various sectors have been reported [23-29]. A brief synopsis of properties and applications of InN are given in the following section.
2.3 Indium nitride

2.3.1 Introduction and applications

In comparison to GaN and AlN, InN remains one of the least understood nitride semiconductors. The lack of attention to InN was mainly due to the following two reasons. First, high quality single crystalline InN is difficult to grow. Second, there exist alternative, well characterized semiconductors such as GaAs and AlGaAs, which have energy band gaps close to 1.89 eV, the band gap previously associated with InN.

Indium nitride, in the form of powder, was first grown by Juza and Hahn [30] in 1938, and many of its fundamental physical properties were first characterized by Tansley and Foley [31]. However, there were wide variations in the reported values of fundamental parameters, including the band gap, lattice constants, electron effective mass, etc. Additionally, after the realization of commercial importance of the In$_x$Ga$_{1-x}$N alloy system, growth of good quality InN was pursued by several groups but was not successful until the late 1980s. The major difficulty in the growth is associated with the low dissociation temperature of InN and high vapor pressure of nitrogen over InN.

Recently, due to advancement in growth techniques, high quality single crystalline InN has been obtained. A major breakthrough in InN research occurred few years ago, when the growth of good quality single crystalline films of InN by MBE on sapphire substrates was reported [32-34] and the band gap energy was claimed to be 0.67±0.05 eV [27,32,35]. Since then, the numbers of publications related to InN research have been increasing every year. Theoretical calculations and experimental data based on recently grown, high quality InN have shown that it has outstanding material properties such as small electron effective mass, large electron mobility, high peak and saturation velocities, and a small direct band gap [27].
Recent studies show that InN is a promising material in the fabrication of different types of device structures. LEDs, laser diodes and transistors normally involve In$_x$Ga$_{1-x}$N, with low indium fractions. However, there would be great advantages in being able to incorporate large fractions of indium in various device applications. For example, the use of wurtzite In$_x$Ga$_{1-x}$N with low x would permit photonic devices in the red wavelength regime and much faster electronic devices, because of the higher mobility and peak velocity than found in most of the other III-nitride materials [23]. The higher refractive index of InN compared to GaN and AlN is one of the important aspects of using it for photonic band edge design [36]. The use of InN-based optoelectronic devices offers the potential of an environmentally friendly red emitter with no toxic elements to replace GaAs-based devices. In addition, InN is a potential material for transparent conducting window material for heterojunction tandem solar cells [37].

InN thin films reveal a potential application as chemical and biological sensors. The electrical response of InN surface to chemical exposure was studied by Lu et al. [38] and demonstrated that InN surface shows a fast response to certain solvent exposures with a large increase in surface carrier density. This increase in surface charge is accompanied by an enhancement of an average Hall mobility and both decay gradually. Similarly, by performing Monte Carlo simulations it has been shown that InN is promising material for an emitter in the THz frequency range [39-42]. Other potential applications of InN are in fabrication of metal-semiconductor field effect transistor (MISFET) devices [43], anodes for Lithium - ion thin film batteries [44], and thermoelectric devices [45,46].
2.3.2 Growth techniques

The growth of InN is not as easy as that of GaN. Poor thermal stability, i.e. a dissociation temperature less than 600 °C, higher vapor pressure of nitrogen over InN, lack of lattice matched substrates, and a large disparity of the atomic radii of In and N are the major factors that increase the difficulty in obtaining good quality single crystalline InN. The first attempt at growth of InN, by using $\text{InF}_6(\text{NH}_4)_3$, was done by Juza and Hahn in 1938 [30] who reported that the crystal structure is wurtzite. The attempts at growth were continued for several years by Juza and Rebenua in 1956 [47], Renner in 1958 [48], Pastrnak and Souckova in 1963 [49], and Samsonov in 1969 [50]. In all of the above methods, InN, in the form of powder, was obtained either by interaction of an indium compound with ammonia or by thermal decomposition of complex compounds containing indium and nitrogen. Polycrystalline indium nitride with good electrical properties compared to previously grown samples, was grown by Hovel and Cuomo in 1972 by using the reactive radio frequency sputtering method on sapphire and silicon substrates at 600°C [14]. The films reported were polycrystalline. The growth of indium nitride films by sputtering was investigated extensively in 1980s and many of the fundamental properties of InN were studied by Tansley and Foley [31,51-53].

Despite the problems inherent to InN growth, some excellent work has been reported regarding InN growth by various techniques. Though InN can be grown by several techniques, such as sputtering, halide vapor phase epitaxy (HVPE), pulsed laser deposition (PLD) etc., at present the most commonly utilized successful growth techniques for the growth of single crystalline InN as well as for other nitrides and the nitride alloys are metallorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) [54,55]. However, the epitaxial growth of InN under low pressure conditions such as MOCVD and MBE is problematic because
the decomposition temperature of InN is low and the equilibrium pressure of nitrogen rises rapidly as the growth temperature is raised [25]. These problems of growth at low pressure create variations in the measured values of material properties due to point defect chemistry in InN which at present are not well understood [56]. On the other hand, low pressure growth is also problematic for the growth of III-nitride alloys due to the difficulty that InN can’t be grown at temperatures greater than 600 °C while good quality GaN, and AlN can’t be grown at temperatures lower than 1000 °C. Surface stabilization data, shown in the Fig. 2.1 [57], demonstrates that InN can be grown at much higher temperature if stabilized at high nitrogen pressures evoking the development of a novel high pressure chemical vapor deposition (HPCVD) system at Georgia State University in Dr. Dietz’s laboratory.

This approach allows the control of vastly different partial pressures of constituents involved in the growth of InN and indium-rich group III-nitride alloys [58-63]. The HPCVD reactor system utilizes the pulsed precursor injection technique, which is essential in order to achieve compression of the precursors to reactor pressure, minimization of gas phase reactions, optimization of nucleation kinetics and analysis of gas phase and surface decomposition dynamics in real-time.

A schematic diagram of the HPCVD reactor flow channel is shown in the Fig. 2.2 [63]. The flow channel is designed with a constant cross sectional area for the maintenance of laminar flow with the sapphire substrate at the center of the axis. Fig. 2.3 [63] shows the schematic cross section of the HPCVD reactor system containing the optical access ports and the center of the substrates. Two of the optical ports provide access to the flow channel and three ports in each of the two half sections of the reactor provide access to the growth surface. Various properties of HPCVD grown InN have been described in the literature [56,59,61,64].
Figure 2.1 Phase relations of InN shown by the decomposition curve separating InN and In+N2 phase fields. Open circles represent experimental conditions where metallic indium was observed. Shaded circles indicate that InN was stable. [57]
Figure 2.2 Schematic cross section of the reactor flow channel assembly showing flow direction.
Figure 2.3 Schematic cross section of the reactor containing the optical access ports.
2.3.3 Structural properties

It is essential to know and characterize the crystal structure of the InN in order to improve the quality and performance of the InN based device structures. X-ray diffraction (XRD) is a versatile nondestructive technique, which reveals detailed information about the chemical composition and crystallographic structure of any natural and manufactured materials. The microstructure of InN films, which may include dislocation, grain boundaries etc. are typically investigated by transmission electron microscopy (TEM). Rutherford back scattering spectrometry (RBS) measurements are used to assess film stoichiometry. These techniques are popular to investigate the crystal structure of the bulk. Low energy electron diffraction (LEED) is a technique used to analyze the crystal structure of the surface. The details of this technique are explained in chapter three.

By using all of the structural characterization techniques mentioned above, it has been shown in the literature that the crystal structure of indium nitride epitaxial layers is similar to that of GaN films prepared under the similar conditions. InN can crystallize in three different structures, wurtzite, zincblende and rock salt, similar to that of other nitrides. Thermodynamically, the stable crystal structure is the hexagonal wurtzite structure. However, InN can also be obtained in the cubic zincblende structures when grown on (001) crystal planes of cubic substrates like silicon and GaAs. The wurzite structure has a hexagonal unit cell and thus two lattice constants c and a. It contains six atoms of each type. The zincblende structure has a cubic unit cell, containing four indium atoms and four nitrogen atoms. The main difference between the cubic and the hexagonal structure is that they have a different stacking sequence of the closest packed diatomic planes (as explained in the introduction chapter). In both cubic and
hexagonal crystal structures, each indium atom is coordinated by four nitrogen atoms and each nitrogen atom is coordinated by four indium atoms as shown in the Fig. 2.4 [65].

The lattice constant values of InN may be influenced by the growth conditions, impurity concentrations, and the film stoichiometry. Juza & Hahn [30] first reported the crystal structure of InN to be wurtzite having lattice parameters $a = 3.53$ Å, and $c = 5.69$ Å. These values are quite close to $a = 3.5480$ Å, $c = 5.7600$ Å reported by Tansley & Foley [53], and $a = 3.544$ Å, $c = 5.718$ Å reported by Osamura et al. [66].
Figure 2.4 Crystal structures of InN.
2.3.4 Electronic properties

The values of carrier concentration and carrier mobility of the first polycrystalline InN films grown by radio frequency sputtering of metallic indium in a nitrogen atmosphere were reported to be in the high $10^{18}$ cm$^{-3}$ range and 250 cm$^2$V$^{-1}$s$^{-1}$ respectively [14]. Later, Lakin et al. reported carrier concentrations of samples prepared by similar methods in the order of high $10^{19}$ cm$^{-3}$ and carrier mobilities around 100 cm$^2$V$^{-1}$s$^{-1}$ [13,67]. But Tansley and Foley, who characterized most of the fundamental properties of InN, have reported carrier concentrations in the range of $10^{16}$ cm$^{-3}$ and carrier mobilities as high as 3980 cm$^2$V$^{-1}$s$^{-1}$ [51]. No one has reported a lower value for carrier concentration or a higher mobility. However, Butcher et al. [68] implemented the same technique and tried to reproduce the result but could not. Instead, they reported carrier concentrations around $3 \times 10^{19}$ cm$^{-3}$ and mobilities less than 100 cm$^2$V$^{-1}$s$^{-1}$, which are in close agreement with the values reported for polycrystalline samples.

Tansley and Foley have also reported that the band gap of InN is around 1.9 eV [53] which was universally accepted until around 2002. But from optical absorption, photoluminescence (PL) and photomodulated reflection (PR) measurements performed on MBE grown InN with low electron concentrations, it has been shown that the energy gap of InN is $0.67 \pm 0.05$ eV[27,32,35]. For these MBE grown samples, the lowest value of carrier concentration reported was $3 \times 10^{17}$ cm$^{-3}$ and the highest value of carrier mobility was 2200 cm$^2$V$^{-1}$s$^{-1}$ [69]. However, this interpretation of optical absorption and photoluminescence data for the band gap of InN has been questioned by Shubina et al. [70] who claimed that the band gap of InN is much wider than this newly accepted value. According to their report, the lower absorption edge is due to Mie scattering by metallic indium clusters, and the PL peak at 0.7 eV in
InN originates from optical transitions involving interface states between the indium clusters and the indium nitride matrix. Carrier concentrations in N-polar indium nitride layers grown by HPCVD have been studied by HREELS and room temperature infrared (IR) reflection measurements in the range of 200-8000 cm\(^{-1}\). The details are discussed later in the chapter 6.

### 2.3.5 Film Polarity

The wurtzite crystal structure of InN film is always polar along the c-direction, i.e. the +c direction has In-polarity and –c direction has N-polarity. In another way, when three of the bonds of a tetrahedrally coordinated indium atom point towards the substrate or opposite of the growth direction, the film has In- polarity. When three bonds point away from the substrate or along the growth direction, the film is N-polar. Fig. 2.5 shows the wurtzite crystal structure of N-polar InN and In-polar InN films [71].

Determination of polarity is an important issue in the characterization of nitride semiconductors since it affects the surface and bulk properties of epitaxially grown layers. Among the several methods used in the determination of polarity of InN, the easiest way is the wet etching of the crystal by KOH or NaOH solutions. However, this method is destructive and the sample can’t be used again once it is etched. The non-destructive techniques are convergent beam electron diffraction (CBED), coaxial impact collision ion scattering spectroscopy (CAICISS) and high resolution electron energy loss spectroscopy (HREELS). HREELS is a non-destructive technique, newly used in this dissertation to determine the InN film polarity.

Polarity affects doping, impurity incorporation, electronic and optical properties of the materials which affect performance of the device structures based on these materials. A variety of other processing such as etching, defect formation as well as the properties such as plasticity
and piezoelectricity depend on polarity. For GaN epitaxy, growth in Ga-polarity has been reported to be favorable getting high quality films both in MOCVD and MBE [72,73]. However, X. Wang and A. Yoshikawa [74] have reported that the surface morphology and the crystalline quality of N-polar InN are better than that of In-polar InN. They have reported the full width at half maximum (FWHM) of the x-ray rocking curve of 1 µm thick N-polar InN layers is about 200-250 arc seconds and that for In-polar InN layers is about 500 arc seconds. High crystalline quality is also shown by the lower value of the dislocation density in N-polar films than that in In-polar films. According to their report, the electrical properties of N-polar InN films are better than those of In-polar films. The room temperature mobilities of N-polar InN films were 500-1500 cm²V⁻¹s⁻¹ with electron concentrations of (1-10) × 10¹⁸ cm⁻³ while the mobilities of In-polar InN films were 300-900 cm²V⁻¹s⁻¹ with electron concentrations of (4-10) × 10¹⁸ cm⁻³.

Most of the InN films are grown on GaN or AlN buffer layers on sapphire substrates. X. Wang and A. Yoshikawa [74] have reported that the polarity of InN film depends on the polarity of the materials in the buffer layer. InN films grown on Ga-polar or Al-polar buffer layers were In-polar and InN films grown on N-polar GaN or AlN buffer layers were N-polar. In the case of InN grown on a sapphire substrate with an InN buffer layer, N-polar InN is generally obtained due to nitridation of the sapphire substrate before the deposition of InN.

The growth temperature of InN films is greatly influenced by the film polarity. InN could be grown on N-face GaN at 550 °C, whereas InN growth on Ga face GaN was realized at 450 °C [71]. Xu et al. have reported that the optimum growth temperature of N-polar InN films grown on N-face GaN by MBE was around 600 °C while the optimum growth temperature of In-polar films grown on Ga-face GaN was around 500 °C [75]. From these reports, it is well understood that the best growth temperature of N-polar InN is much higher than that of In-polar InN.
In contrast, Saito et al. [76] evaluated the polarity of single crystalline InN using CAICISS and reported a different result than that of Wang and Yoshikawa [74], Matsuda et al. [71] and Xu et al. [75] about the polarity dependent growth temperature and the assumptions made about dependence of polarity on the nitridation process. According to their report, prior to the growth of InN, a nitridation process was carried out at 550 °C for 1 hour. However, they obtained both In-polar and N-polar InN surfaces as well as a mixture of polarity. The polarity of InN grown at low temperature 300°C, has mainly N-polarity while InN grown at high temperature 550 °C, has In-polarity and that of two steps grown InN has a mixture of In-polarity and N- polarity. In two steps growth, InN was grown at high temperature (550 °C) on the low temperature (300 °C) InN buffer layer.

The HPCVD grown InN samples were grown at high temperature 825°C and the polarity was found to be N-polar and the details of the results about the polarity are discussed in chapter 4.
Figure 2.5 Wurtzite crystal structures of a) N-polar InN and b) In-polar InN. The arrows pointing upward represent the growth directions.


2.3.6 Surface electron accumulation

Surface electron accumulation is observed to be an intrinsic property of the InN epitaxial layer. Recently, this surface electron accumulation phenomenon on InN layers has attracted much attention because the high density of electrons on the surface has great technological importance such as formation of Ohmic contacts. However, the main cause of electron accumulation on the InN surface and how it is related to the surface atomic configuration are still not clear. We can find several explanations for surface electron accumulation on semiconductor surfaces reported in the literature. Electron accumulation layers at the semiconductor surfaces have been observed through techniques that include high resolution electron energy loss spectroscopy [77], angle-resolved photoemission spectroscopy [78] and electron tunneling spectroscopy [79]. Surface electron accumulation is not only observed in InN layers but also observed in both InAs and InSb [80]. The main reason for surface electron accumulation on InAs layer is the donor like intrinsic surface states whose energy spectrum is determined by the surface reconstructions [81]. Yamaguchi et al. have reported that electron accumulation on InAs/GaAs depends on the layer thickness and is induced by the quantum size effect [82]. They also have suggested that the dislocations due to lattice mismatch at the InAs/GaAs interface may also be responsible for surface electron accumulation.

The phenomenon of surface electron accumulation on InN layers was first observed by Mahboob et al. [83] by using (HREELS). According to their report, an intrinsic surface electron accumulation layer is found to exist and is explained in terms of a particularly low Γ-point conduction band minimum in wurtzite InN. The electron accumulation is a consequence of ionized donor type surface states pinning the surface Fermi level above the conduction band
minimum. Piper et al. [84] have calculated energy positions of Γ-point, conduction band minimum and valence band maximum of AlN, GaN and InN with respect to the branch point energy and concluded that the conduction band minimum lies far below the branch point energy and is the cause of electron accumulation in InN layers. This phenomenon is explained in Fig. 2.6.

D. Segev and C. G. Van De Walle have reported that the cause of electron accumulation on polar InN is In-In bonds leading to occupied surface states above the conduction band minimum [85]. In recent results from angle resolved photoelectron spectroscopy of InN, it has been reported that the electrons in the accumulation layers reside in discrete quantum well states, defined perpendicular to the film surface [86]. By using electron tunneling spectroscopy, Veal et al. [79] also have reported the native electron accumulation layer at the surface of n-type InN.

We also observed the phenomenon of surface electron accumulation on HPCVD grown InN [87]. The details and results of work on surface electron accumulation on the InN surface are discussed in chapter 5.
Figure 2.6 The calculated energy positions of $\Gamma$-point conduction band minimum (CBM) and valence band maximum of AlN, GaN and InN with respect to the branch point energy ($E_B$). The bulk Fermi levels for n-type GaN ($E_{F1}$) and InN ($E_{F2}$) are also shown, above and below the $E_B$, respectively. The inset schematically shows the variation of the formation energies with Fermi level of $V^+_N$ and $V^-_{III}$ for III-nitrides. [84]
2.3.7 Hydrogen desorption

Adsorption and desorption of hydrogen from nitride semiconductors are essential to understand in order to gain knowledge about the growth mechanism. Incorporation of hydrogen into the film or its adsorption on the surface is common during the growth, since hydrogen is present in the growth chamber in most growth techniques such as MOCVD and MBE. In HPCVD, the precursors used for the growth of the InN epitaxial layer are ammonia and trimethyl–indium, decomposition of which produces hydrogen in the growth chamber. Both positive and negative effects of hydrogen incorporation into the nitride film have been reported in the literature. Some of them have reported that presence of hydrogen on the surface during the growth prevents the incorporation of impurities, particularly carbon and oxygen, into the film and enhances the growth while others have reported that hydrogen etches the growth surface eventually reducing the growth rate.

The interaction of hydrogen with the semiconductor surfaces is of great fundamental and technological interest since the presence of hydrogen stabilizes the surface against surface reconstructions. The surface structure of the nitride semiconductors can be changed by the adsorption or desorption of any molecular species. Removal of surface adsorbates, such as hydrogen, leaves surface dangling bonds, which, depending on the proximity of neighbouring atoms and energy considerations, may cause surface reconstruction. Rzepewicz et al. [88] from his first principal calculations, reported that adsorption of three fourths of a monolayer of hydrogen stabilizes GaN surfaces of both polarities and results in 2×2 symmetry. However, a theoretical study done by Elsner et al. [89] suggested that three fourths monolayer hydrogen coverage results in a 1×1 periodicity for both polarities of GaN. Bermudez et al. [90] by using
electron energy loss spectroscopy and photoelectron spectroscopy have shown that adsorption of hydrogen affects the electronic properties of GaN (0001) surfaces. The effects of hydrogen adsorption or desorption from the InN surface on its structural and electronic properties have not investigated.

2.3.8 Thermal desorption kinetics

Thermal desorption kinetics of hydrogen from semiconductor surfaces are usually determined by using temperature programmed desorption (TPD) mass spectrometry or laser induced thermal desorption (LITD). The desorption rate depends upon the reaction order, $n$, and two desorption kinetic parameters, activation energy, $E$, and pre-exponential factor, $\nu$. The equation used to describe desorption rate is given by

$$\frac{d\theta}{dt} = \nu \theta^n \exp\left[-\frac{E}{kT}\right]$$

where $\theta$ is the surface coverage of hydrogen usually in units of monolayers (ML), $T$ is the sample temperature, $t$ the time and $k$ the Boltzman constant. The power and the subscript $n$ is called the desorption order which links the surface population with desorption rate. $E$ is the the activation energy, normally expressed in kcal/mol or J/mol or eV/particle and $\nu$ is the pre-exponential factor, units of which depends upon the value of $n$. For example if $n = 1$, then $\nu$ has units of s$^{-1}$ and if $n = 2$, then $\nu$ has units of ML$^{-1}$ s$^{-1}$ or cm$^2$ s$^{-1}$.

There are 4 different possible values of coverage order, $n$, in any desorption process. A first order dependence of rate on coverage occurs when all the adsorbed particles have the same possibility of desorption. That implies a discrete or random distribution of the adsorbates on the surface and that all the adsorbates are independent of each other. The only binding is from the attachment with the surface and is the same for all.
The second order dependence occurs when the desorbed particles are the chemical combination of two identical adsorbed species and the combination of the species is made during the process of desorption. Each component has the distribution as first order, i.e. each one is randomly distributed and thus the possibility of combination is proportional to the square of the coverage.

The half order dependence is produced by an “island model” with adsorbed particles continuously attached to each one and occupying particular areas of the sample surface, that is, the surface particles are distributed in islands. The desorption energy of the particles on the border of the islands is smaller than that of those inside so they are easily activated. Roughly the border length depends on the square root of the coverage so we have a half order dependence.

There is also a zero order dependence case which implies coverage independence. In such cases, the surface has built up multiple layers of adsorbed species on the surface before annealing. As a result, the desorbed particle will not change the coverage at all and the desorption is only temperature dependent. The details of the thermal desorption process and different orders of desorption rates are explained in Y. Yang’s Ph. D. dissertation [91] study of hydrogen from GaN (0001).

Thermal kinetics includes the activation energy and pre-exponential factor. Activation energy is the minimum energy required to make possible of hydrogen desorption from the surface. The pre-exponential factor is a pre-exponential constant in the Arrhenius equation. The values of the kinetic parameters of hydrogen desorption from semiconductor surfaces may depend upon different sample preparation methods as desorption from steps and defect sites might occur at different rates. Investigation of the thermal kinetic parameters of hydrogen desorption from the InN surface gives us the feedback for understanding the growth mechanism.
and particularly the growth temperature, which ultimately helps to grow better quality film and hence better performing devices.

### 2.4 References

Chapter 3

Experimental techniques and methods

3.1 Introduction

The experimental techniques and the methods that are utilized to perform and complete this work are discussed in this chapter. A single technique is not sufficient to characterize any surface, so various techniques are implemented. The major techniques that have been implemented in this work are Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and high resolution electron energy loss spectroscopy (HREELS). The monitoring of surface cleanliness is done by AES while the structural characterization of the surface is done by qualitative analysis of recorded LEED pattern. HREELS, a surface sensitive vibrational spectroscopic technique, is employed to study the surface structure, composition and film polarity. With the help of HREEL spectra, the phenomenon of surface electron accumulation on the InN layers and thermal kinetic parameters of hydrogen desorption from the InN surface have been investigated. Though the description of these techniques and the experimental setups are explained in detail in Victor Bellito’s dissertation [1], a brief synopsis of each technique is presented in the following chapters.
3.2 Auger electron spectroscopy

Auger electrons were first identified in nuclear physics by Pierre Auger [2], a French physicist, in 1925 and the application of Auger electrons in surface chemical analysis was first suggested by Lander [3] in 1953. Auger electron spectroscopy (AES) is one of the most commonly used surface sensitive techniques for monitoring of surface cleanliness and determining surface composition [4-7]. The sensitivity of AES is ~ 1% of a monolayer except for hydrogen and helium. Since AES is a three electron process, it is not sensitive to hydrogen and helium.

In any Auger process, the atom is ionized by removal of an electron from the core level by an impinging high energy electron beam. The atom may decay to a lower energy state by emission of x-rays, or alternatively by ejecting an electron called an Auger electron, which leaves the atom in a doubly ionized state. The energy difference between these two states is given to the ejected Auger electron which will have a kinetic energy characteristic of the parent atom [8]. When the Auger transitions occur within the few Angstroms of the surface, the Auger electron may be ejected without loss of energy and give rise to peaks in the secondary electron energy distribution. The energy and shape of these Auger features can be used to identify the composition of the solid surfaces. AES is based upon the measurement of kinetic energies of the emitted electrons. The basic technique of AES has also been adopted for use in Auger depth profiling (ADP) and scanning Auger microscopy (SAM). ADP provides the quantitative compositional information as a function of depth below the surface, while SAM provides spatially resolved compositional information on heterogeneous samples.

Fig. 3.1 demonstrates the complete Auger process along with another possibility of the release of some energy in the form of x-rays. In the figure, a high energy beam of electrons
knocks out a core level electron from the atom with an energy state having energy $E_1$. The vacancy created by this is filled by the transfer of an electron from the higher energy level having energy $E_2$ with the release of an Auger electron from the energy level having energy $E_3$. The kinetic energy of the Auger electron is given by

$$E_{\text{kin}} = E_1 - E_2 - E_3$$

(1)

A correction for the work function has to be added to the kinetic energy formula if the emitted Auger electron is from the valence band of a solid. The kinetic energy of the Auger electron is independent of the mechanism of initial core hole formation and is characteristic of the material. Each element in a sample being studied will give rise to a characteristic spectrum of peaks at various kinetic energies.

In our lab, the analyzer used for acquisition of Auger data is a spherical grid type retarding field analyzer (RFA), and the experimental set up is similar to the LEED apparatus except for the electronics. The RFA type analyzer is one of the first types [9] of analyzer used in analyzing AES data although several other analyzers like the cylindrical mirror analyzer (CMA) are now commonly used. The 4 grid SPECTALEED optics system is used as the RFA by feeding a retarding voltage to the grids and detecting the passing electrons at the LEED screen. A schematic representation of the Auger system [1] is shown in Fig. 3.2. The two center grids (2 & 3) are connected so they can be used for energy discrimination, thus the energies of the electrons which succeed in reaching the fluorescent screen can be determined. The cathode is a lanthanum-hexaboride filament (LaB$_6$) which can emit electrons at low power inputs. The work function of this filament is 2.6 eV and the operating temperature is 1700 K. The filament is heated by passing a current of 1.2 Ampere in order to produce a consistent beam of electrons. The incident beam of electrons is accelerated to an energy of 3 keV and focused onto the surface of the
sample in order to initiate an Auger process. The correct sample position is essential for highest performance and ultimate energetic resolution. The surface of the sample should be placed in the center of the spherical curvature of screen and the grids. For this, the sample is positioned such that the sample motion parameters in UHV chamber are maintained at x = 23 mm, y = 9 mm, z = 23 mm and θ = 58°. The range of energy is from 100 – 500 eV to measure the composition at the surface of atoms like carbon, oxygen, nitrogen, and indium. Though there are many advantages of AES in surface analysis, it has some limitations too. Since the electron beam has high energy, it may damage the sample surface. The sample surface must be a conducting or semi-conducting solid surface. AES can’t be performed on insulating surfaces due to charging problems except with additional use of a flood gun. A flood gun is an electromechanical device that provides a steady flood of low-energy electrons to a desired target or "flood area." Typically, the target is an area on an insulator or semiconductor where another "writing gun" has just left a net positive charge.
Figure 3.1 Auger electron process

Energy

Vacuum level

Fermi level

Valence band

Core level

Initial state

Primary ionization

Relaxation by XRF

Or secondary ionization

Auger electron

$E_{\text{kin}} = E_1 - E_2 - E_3$

$E_1$

$E_2$

$E_3$

$E_{\text{kin}}$ = high energy e$^-$

$E_1$, $E_2$, $E_3$
Figure 3.2 Schematic representations of the AES apparatus
3.3 Low energy electron diffraction (LEED)

The fact that the electron behaves like a particle was well established in the early 20th century. But the hypothesis that the electron or a particle behaves like a wave was first proposed by de-Broglie in his doctoral dissertation work. He made an assumption that particles behave like a wave and the wavelength is associated with the momentum of the particle and the Planck’s constant. The first experimental evidence that particles really have an associated wavelength was given by Clinton J. Davidson and Lester H. Germer in 1927 in the famous Davidson-Germer experiment of electron diffraction. They were able to determine the electron wavelength. Davidson got the Nobel Prize in Physics for this finding of wave particle duality in an electron diffraction experiment. According to their result, electrons get diffracted from a crystal, the same way that the x-ray diffraction occurs in Bragg’s experiments. Later, electron diffraction experiments were commonly used to see the crystal structure on the surface of an epitaxial film.

Along with the chemical composition of the surface, the structure of the surface layers, i.e., the arrangement of atoms in these layers, must also be determined. Because of the advantages of using electrons in surface investigations, elastic electron diffraction naturally suggests itself as a possible tool. Two different geometries have been used to see the crystal structure which are glancing-incidence reflection high energy electron diffraction (RHEED) and the near normal incidence reflection of electrons called low energy electron diffraction (LEED). Between the two methods of electron diffraction, LEED is a true surface sensitive technique due to its low incident electron energy around 100 eV. The penetration depth of the 100 eV electron is on the order of 1 nm before being scattered while in x-ray diffraction, the energy of x-rays used is 30 keV and the penetration depth is on the order of $10^5$ nm [6]. The electron energy in RHEED experiments is 5-100 keV.
Determination of surface structure by LEED can be done quantitatively or qualitatively. In quantitative analysis, intensities of various diffracted beams are recorded and plotted as a function of the incident energy of the electron. The plot of I-V curve can be used to get the information about the atomic spacing by comparing it with theoretical curves [10]. In qualitative analysis, the diffraction pattern is recorded and the analysis of spot positions yield the information about size, symmetry and rotational alignment of the adsorbate or surface unit cell with respect to the substrate unit cell. The angular spacing between the beams gives the information about atomic spacing. The intensity of the background indicates the amount of surface disorder, i.e., bright spots and a dark background reveal that the surface is well ordered. In our experiment, we use the qualitative analysis method to see the crystal structure of InN.

The basic principle underlying the low energy electron diffraction is Bragg’s law. Electrons follow the wave-particle duality. From De-Broglie relation, the wavelength of the electron having momentum $P$ is given by $\lambda = \frac{h}{P}$ where momentum $P = mv = (2mE_k)^{1/2} = (2meV)^{1/2}$, $h = \text{Planck’s constant}$, $m = \text{mass of an electron}$, $e = \text{charge of an electron}$, $V = \text{accelerating voltage}$. If the incident energy of the electron is in the range of 20-200 eV, then the wavelength varies from 2.7 to 0.87 Å, matching with the lattice spacing which is one of the necessary conditions for diffraction effects associated with atomic structure to be observed.

A schematic diagram of the LEED apparatus [1] is given in the Fig. 3.3. The system consists of an electron gun (which produces the primary electron beam), the sample (mounted perpendicular to the electron gun), four hemispherical grids of high transparency, and a fluorescent screen which is maintained at a 6 keV positive potential. The beam of electrons produced from the cathode is focused electrostatically (approximate electron beam size, $\sim1 \text{ mm}^2$) and allowed to impinge on the surface of the sample. The focused beam of electrons scatters
from the surface at various directions. Grid 1, closest to the sample is grounded in order to provide a field free path for diffracted electrons from sample to the first grid. The second and third grids are biased with a few volts of positive potential relative to the gun filament, which allows the rejection of the inelastically scattered electrons. The fourth grid is also grounded and shields the retarding grids from the fluorescent screen potential. The high potential of the phosphor screen causes visible fluorescence when struck by the electrons. Thus elastically scattered electrons, after passage through the retarding field, are post-accelerated by a large positive potential and impinge on the spherical fluorescent screen where the diffraction pattern is displayed. The spots of the diffraction pattern are photographed by a digital camera through a window behind the fluorescent screen.
Figure 3.3 Schematic representations of the LEED apparatus
3.4 High resolution electron energy loss spectroscopy

Electron energy loss spectroscopy (EELS) is a technique which involves analyzing the energy distribution of inelastically scattered electrons from a solid, a liquid or gaseous specimen. This technique was developed by James Hillier and R. F. Baker in the mid 1940s but was not widely used over the next 40 years. The interaction of low energy electron (few electron volts) beam with the surface of a material was analyzed by the technique called high resolution electron energy loss spectroscopy (HREELS). A brief synopsis of HREELS is given in the following paragraph. However, a detailed account of the experimental methods and a theoretical explanation of the technique is given by H. Ibach and D. L. Mills in the book “Electron Energy Loss Spectroscopy and Surface Vibrations” [11].

HREELS is a non destructive and surface sensitive vibrational spectroscopic technique by which vibrations of adsorbates on the crystal surface and low energy electronic excitations can be studied. High-sensitivity (< 0.1% of a monolayer) and broad spectral range (0-1000 meV or 0-8000 cm⁻¹) make HREELS an ideal tool for exploring the properties of a wide variety of surfaces. These include (but are not limited to) single crystal metals, semiconductors and polycrystalline foils, and polymers. It is generally useful to combine the HREELS measurement with other surface analysis techniques, primarily those of LEED and AES which enable the HREELS data to be interpreted. A schematic representation of HREELS process is shown in the Fig. 3.4.

In the HREELS technique, a highly monochromatic beam of electrons is incident on a surface at a particular angle and the electrons are scattered from the surface inelastically. The scattering of electrons may take place in two regimes, dipole scattering and impact scattering,
which explain the intensities and angular distribution of the observed energy loss peaks. Dipole scattering is small angle scattering with respect to the specular direction. The incident electrons interact with a long range (greater than atomic dimensions, 50 Å) field setup in the vacuum above the crystal surface by the oscillating dipoles. Dipolar scattering is produced not only by vibrational motions of adsorbed molecules and atoms in the crystal surface, but also by any elementary excitation of the sample accompanied by a fluctuation in charge density [11]. Impact scattering is the direct scattering of electrons from surface atoms. The impact scattering mechanism is due to a short range electrostatic interaction of the scattering electrons with the adsorbed atoms and substrate lattice. In this scattering regime, the scattering of electrons is large angle scattering with respect to specular direction where a fully microscopic description of the interaction of electrons with the vibrating substrate is required. The impact scattering mechanism becomes more important than the dipolar scattering mechanism when the incident energy of the incident electron is higher. Although the overall excitation probability in the impact scattering mechanism is higher, the contribution in specular direction may be relatively small due to scattering of electrons over a wide range of solid angle.

The scattered electrons lose energy by exciting the surface vibrational modes such as surface phonons and the adsorbate vibrational modes of the atoms and molecules on the surface. The energy of the scattered electrons can be given as

\[ E_{\text{scattered}} = E_{\text{incident}} - E_{\text{vibration}} \quad (2) \]

Inelastically scattered electrons then pass through a narrow slit (width of 1mm and length of 5 mm), an electrostatic lens system, a suitable energy analyzer to the channeltron and analyzed spectroscopically. Fig. 3.5 shows a block diagram of the spectrometer [12]. The incident beam must be highly monochromatic and the analyzer must be capable of high
resolution in order to get high resolution with the spectrometer. Resolution may be limited to the scattering properties and smoothness of the surface under study.

The frequency of vibrational modes is related to the bonding force and mass of the vibrating atoms. The electron energy losses due to adsorbate vibrational modes give molecular information which in turn identifies the adsorbed atoms or molecule on the surface.
Figure 3.4 Schematic representation of HREELS process

HREELS
Surface Vibrational Spectroscopy

$e^-$
E = 7-35 eV
60° from normal

$e^-$
$\Delta E < 500 \text{ meV (4000 cm}^{-1})$
specular collection

InN

Figure 3.5 Block diagram of an electron energy loss spectrometer.

Cathode — Monochromator — Lens — Sample — Lens — Analyzer — Detector
The HREELS apparatus used in our lab is the ELS3000 manufactured by LK technology. Based on the instrument developed by Prof. H. Ibach and his co-workers at the KFA, Julich, Germany, the performance of ELS3000 is exceptional. The spectrometer consists of a symmetrical system of input-output zoom lenses positioned between monochromator and analyzer that is used to focus and accelerate/decelerate the electron beam to and from the sample surface. A schematic representation of the ELS3000 spectrometer [1] is shown in the Fig. 3.6.

The cathode is a lanthanum-hexaboride (LaB$_6$) filament. A beam of low energy electrons from the cathode is monochromated and focused onto the sample surface using a 127˚ cylindrical deflector and a lens system. The energy of the electrons can be varied in the range of 1 to 200 eV. The electrons scatter off the sample and enter a second electrostatic system comprised of a double pass analyzer which measures the energies of the scattered electrons. A channeltron (electron multiplier) and pulse counting electronics are used to measure the count rate of the electrons reaching it. The analyzer is fixed in its orientation but both the monochromators as well as the sample can be rotated to investigate the angular distribution of the scattered electrons. Angle dependent studies are accomplished by rotation of the monochromator from a “straight through” position to 90˚. Dual magnetic shields are provided at the flange to interface with the chamber magnetic shields in order to minimize the ambient magnetic fields for satisfactory operation. In our experiment, the incident energy of the electrons is varied in the range of 7 to 35 eV and the loss energy up to 500 meV is detected. The energy loss of the electrons is typically expressed in meV or wave-number (cm$^{-1}$). The relation between wave-number and meV is 1 meV = 8.065 cm$^{-1}$. 
Figure 3.6 Schematic representation of HREELS spectrometer
3.5 Experimental methods applied

3.5.1. Atomic Hydrogen Cleaning

All of the samples used in this experiment are the InN samples grown by high pressure chemical vapor deposition (HPCVD). Before installing into the ultrahigh- vacuum (UHV) chamber, samples were exposed to the atmosphere, which causes their surface to get contaminated, so they need to be cleaned. In the cleaning process, samples were first rinsed with isopropyl alcohol and inserted into the UHV chamber. Samples are cleaned in UHV by sputtering with argon ions, atomic hydrogen exposure and annealing. Among the several cleaning processes atomic hydrogen cleaning (AHC) is one of the most efficient nondestructive techniques to remove oxygen contaminants from the surface. This technique was implemented by Prof. McConville and coworkers at University of Warwick, London [13] on different semiconductor surfaces and they concluded that this method is successful [14] in cleaning nitride semiconductors particularly InN. AHC is successful in cleaning semiconductor photocathodes [15]. The atomic hydrogen cleaning process has been proven successful in removing surface contaminants from other compound semiconductors like InSb [16] and InP [17]. The same technique was used here to clean HPCVD-grown InN surface and was successful at removing the oxygen contaminants completely and most of the carbon contaminants from the surface.

In the process of AHC, the upper chamber is back filled to a pressure of $8.4 \times 10^{-7}$ torr with molecular hydrogen through a leak valve. The leak valve joins upper chamber of UHV system and the gas handling system. The ion pump was closed with a poppet valve. The sample must be close to and facing the heated tungsten filament. The sample is placed at a distance of 20 mm facing towards the filament, which is heated to 1850 K. The tungsten filament was mounted between molybdenum posts by spark welding and heated resistively with a current of 3.9 amps.
The temperature of the heated filament was measured with a visible pyrometer. When molecular hydrogen interacts with the heated tungsten filament, it dissociates into atomic hydrogen. Atomic hydrogen is highly reactive on the InN surface and removes the contaminants like carbon or oxygen from the surface.

To obtain the correct position for the sample, the sample motion parameters in the UHV chamber are adjusted as $y = 40 \text{mm}$, $x = 5 \text{mm}$, $z = 31 \text{mm}$, and $\theta = 155^\circ$. The sample is kept in front of the heated filament for 20 minutes which is equivalent to the 1000 L exposure of $\text{H}_2$ (1 L $= 8.4 \times 10^{-7}$ torr $\times$ 1 sec.). Due to the proximity of the sample to the heated filament, its temperature raises to around 350 K. After the first 20 minutes the sample is heated to 600 K for another 20 minutes which is equivalent to an exposure of another 1000 L of $\text{H}_2$. After 40 minutes of atomic hydrogen exposure, the sample heater is turned off and the sample was pulled back slowly from the proximity of heated filament and allowed to cool down. When the temperature reaches to 475 K, the tungsten filament is turned off. The leak valve, joining gas handling system and upper chamber, was closed in order to stop the flow of molecular hydrogen into the chamber. The whole process is repeated for several cycles to remove the oxygen and carbon contaminants from the surface. The schematic of the hydrogen cleaning process is shown in the Fig. 3.7.
Figure 3.7 Atomic hydrogen cleaning process
3.5.2 Sputtering

The impact of ions on surfaces will cause removal of material from the surface. This phenomenon was recognized, named and used in commercial process long before it was understood at the atomic level. It is called sputtering. In sputtering, an energetic ion strikes the surface, penetrates and after a series of collisions with atoms in the solid, comes to rest or transfers its momentum to an atom or atoms at the surface, causing their ejection from the solid as neutrals or as positive or negative ions [6].

Sputtering done in our lab removes the contaminations at the topmost atomic layers of the InN sample surface by bombardment with argon ions. The argon ion beam has a cleaning effect on the sample surface by removing a surface layer. Sputtering is done with the help of ion gun. The Kimball Physics ILG-2C ion gun, with its matching IGPS-2C power supply, is used to produce argon ions. The gun uses a refractory oxide filament to generate ions by electron impact ionization of background gas or argon gas admitted through a leak valve. The gun can deliver 1 µA into an approximate 1mm spot, at a 20 mm distance at 1000 eV. Both beam energy and beam current are independently adjustable over a wide range.

In our experiment, for some of the samples, surface carbon impurities are removed by sputtering with 1 keV nitrogen ions with total flux of 560 µC/cm² at an angle of 70°, followed by 1000 µC/cm² at normal incidence. However, for some other improved samples, 500 eV argon ions at an angle of 70° for 5 minutes were sufficient to remove all the carbon impurities. AHC is effective to remove all of the oxygen contaminants but some of the remains of carbon contaminants remain on the InN sample. Sputtering, by argon or nitrogen ions, is successful in removing all of the carbon contaminants on the InN layers.
Though sputtering makes the surface more disordered, sputtering followed by AHC brings back the ordering of the surface. In order to avoid more surface destruction, the ion bombardment is not done directly; instead the argon ions are bombarded for 5 minutes at an angle of 70° from the normal. For perfecting the sputtering process, the sample is positioned such that the sample motion parameters in the UHV chamber are set at an angle $\theta = 330^\circ$, $y = 23$ mm, $x = 30$ mm, and $z = 23$ mm.

### 3.5.3 Annealing

In the annealing process, the sample temperature is ramped up linearly at the rate of 2° C per second, until it reaches a constant temperature. Annealing of the sample is done by bombardment of the sample mount from the back with an electron beam emitted by a heated filament behind the mount. The control of sample temperature during annealing is important for AHC as well as for desorption experiments. A slight change in the sample temperature may produce a considerable change in the material properties in case of InN, which has a low dissociation temperature.

The sample heating controlling is performed manually. The heating power, determined by the filament bias voltage and emission current, is adjusted by using a Gassman high voltage power supply to establish the desired sample temperature. The sample temperature is measured with the help of a K-type Chromel Alumel thermocouple attached on the hot-plate near to the sample.

When the sample is sputtered by argon ions, the surface becomes more rough and disordered. Some of the argon ions may diffuse into the film. Heat treatment may cause impurities from the bulk to diffuse to the surface. Also a well ordered and smooth surface can be
obtained by annealing the sample. In our experiment, the InN sample is annealed to 325 °C for 20 minutes during AHC. Similarly, after atomic hydrogen/deuterium dosing, the sample is annealed at a series of temperatures up to 500 °C for different time intervals to observe the desorption rate.

3.6 Gas handling and Dosing

Our gas handling system consists of four gas cylinders containing research purity gases of hydrogen, oxygen, deuterium, and argon, stored at high pressure. The system has the option to connect to gasses of nitrogen or ammonia. All the gas cylinders are connected to a common manifold via Nupro valves and finally are connected to the ultrahigh vacuum chamber by 0.25” stainless steel tubings as gas lines. A leak valve joins one of the gas lines from the manifold to the upper chamber of UHV system which is used to admit the gases for dosing purpose. Another leak valve joins second gas line from the manifold to the upper chamber via the ion gun which admits the gases for sputtering purposes. By adjusting the leak valves, the pressure in the UHV chamber can be controlled in the range of $10^{-9}$ to $10^{-4}$ torr. The gas lines are pumped independently by using a molecular drag pump and the pressure is measured with a convectron. The lowest pressure of the gas handling system observed is $\sim 1.5 \times 10^{-3}$ torr.

Dosing by atomic hydrogen or deuterium can be done at different levels of exposure at room temperature. The chamber is filled with molecular hydrogen to a pressure of $8.4 \times 10^{-7}$ torr. The sample is positioned at a distance of 20 mm for 10 minutes to face the tungsten filament (kept besides the opening of the leak valve in UHV) heated to 1800 K. This is an exposure of 500 L of hydrogen. In this process, molecular hydrogen interacts with the heated tungsten filament and cracks down into atomic hydrogen which reacts on the surface. By adjusting the pressure and time, different levels of exposures can be obtained.
3.7 References

Chapter 4

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

4.1 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. The 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, N-polarity indium nitride is indicated.
4.2 Introduction

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$_x$N 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 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.

4.3 Experimental Methods

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 trimethylindium (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 $1.8 \times 10^{-10}$ 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 with a flux totaling 560 µC/cm² at an angle of 70° followed by a 1000 µC/cm² flux 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 $8.4 \times 10^{-7}$ 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 $\text{H}_2$). 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 $\text{H}_2$). Atomic deuterium cleaning (ADC) was performed in a similar way to aid in the assignment of vibrational modes.

4.4 Results and Discussion

After one cycle of AHC, a hexagonal 1x1 LEED pattern was observed. After several additional cleaning cycles the hexagonal diffraction pattern became sharper (Fig. 4.1) 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.

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 60º 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. 4.2. 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 \textit{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 and was 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 \textit{InH} stretching vibration has been reported at 1650-1700 cm\(^{-1}\) in HREELS experiments [16-18] and at 1630-1680 cm\(^{-1}\) from \textit{ab initio} calculations [19] on InP surfaces. No loss features in this range were observed in the present work indicating that there is no presence of surface \textit{InH}.

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 \textit{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. A 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.
4.5 Summary and Conclusions

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 InN(000$\bar{1}$), that is, N-polarity.
Figure 4.1 Low energy electron diffraction of AHC cleaned InN sample at incident electron energy of 39.5eV.
Figure 4.2 HREELS of InN after atomic hydrogen (deuterium) cleaning. Spectra were acquired in the specular direction with an incident electron energy of 12.5 eV.
4.6 References:


Chapter 5

Surface electron accumulation in indium nitride layers grown by high pressure chemical vapor deposition

5.1 Abstract

Surface termination and electronic properties of InN layers grown by high pressure chemical vapor deposition have been studied by high resolution electron energy loss spectroscopy (HREELS). HREEL spectra from InN after atomic hydrogen cleaning show N-H termination with no indium overlayer or droplets and indicate that the layer is N-polar. Broad conduction band plasmon excitations are observed centered at 3400 cm\(^{-1}\) in HREEL spectra with 7 eV incident electron energy which shift to 3100 cm\(^{-1}\) when the incident electron energies are 25 eV or greater. The shift of the plasmon excitations to lower energy when electrons with larger penetration depths are used is due to a higher charge density on the surface compared with the bulk, that is, a surface electron accumulation. These results indicate that the surface electron accumulation on InN does not require excess indium or In-In bonds.
5.2 Introduction

The physical properties of InN have attracted considerable research interest because of its transport properties such as high electron mobility and saturation velocity making it a promising candidate for use in high-speed devices [1,2]. In addition, InN-GaN-AlN alloys and heterostructures will enable unique optoelectronic devices, operating from near infrared to ultraviolet wavelength regime [1,3]. However, the range of device applications strongly depends on the material properties and quality and on the extent to which indium-rich alloys and heterostructures can be formed [3].

The growth of InN is challenging since InN and indium-rich group III-nitride alloys exhibit a high equilibrium vapor pressure of nitrogen during growth and a low decomposition temperature compared to GaN and AlN. These challenges also lead to difficulties in growing structures containing indium-rich III-nitrides embedded in layers of lower indium content [4]. InN films have been grown by a number of techniques including metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) but many of the fundamental electrical and optical properties are still in debate including the correct band gap energy [1,3]. High pressure chemical vapor deposition (HPCVD) has been developed to address these challenges and has been shown to be capable of growing high-quality InN [4-6]. Using HPCVD, stoichiometry controlled InN layers have been grown at temperatures around 1100 K [6].

There have been several reports regarding surface electron accumulation on InN layers. A number of investigations of carrier concentration as a function of film thickness have measured charge accumulation layers with electron densities over the range of \( 1.6 \times 10^{13} \) cm\(^{-2}\) [7-9]. Lu et al. [7] also reported ohmic contacts for a number of metals without annealing
and suggested that surface electron accumulation due to pinning of the Fermi level above the conduction band minimum was responsible. A series of papers by McConville and coworkers [10-15] report surface electron accumulation as measured by high resolution electron energy loss spectroscopy (HREELS) and x-ray photoemission spectroscopy on MBE-grown InN layers. Colakerol et al. [16] used angle-resolved photoemission spectroscopy to observe quantized energy levels in the surface electron accumulation layer on InN films grown by radio frequency plasma-assisted molecular beam epitaxy.

Surface electron accumulation has been reported to be due to a particularly low Γ-point conduction band minimum in both InAs [17] and InN [14]. In the case of InAs, the surface electron concentration is reported to depend on surface reconstruction [17,18]. The carrier concentration of an InN epifilm grown by MOCVD has been altered by exposure to a microwave hydrogen plasma [19]. The changes were suggested as due to the removal of surface contaminants such as oxygen and by the migration of indium clusters to the surface during etching. Indium clusters have been reported to be present in the bulk of InN layers [20,21] and both indium overlayers and droplets have been reported on InN surfaces [22,23]. The influence of In overlayers or droplets on electron accumulation at the InN surface is not yet understood. Segev and Van de Walle [24] have suggested that occupied surface states caused by In-In bonds are the cause of electron accumulation on InN surfaces.

In an earlier HREELS study of HPCVD-grown InN, the authors reported surface N-H termination and concluded that the film was N-polar [25]. The HREELS studies reported here were performed on different HPCVD InN layers grown under different process conditions, which also exhibit N-polarity. We report here surface electron accumulation on an InN layer as observed by HREELS on a surface of known termination with no indium overlayers or droplets.
5.3 Experimental Methods

The results presented here were acquired from an InN layer grown at a temperature of 1120 K, a reactor pressure of 15 bar, and an ammonia to trimethyl-indium 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 [4,5]. The spectra reported here were all acquired from the same sample, however similar results were observed from other InN films grown under similar conditions.

The ultrahigh vacuum (UHV) surface characterization system [26] had a base pressure of $1.8 \times 10^{-10}$ torr. The InN sample was rinsed with isopropyl alcohol and then attached to a tantalum sample holder using tantalum clips before introduction into the UHV chamber. Sample heating was accomplished by electron bombardment of the back of the tantalum sample holder. The sample temperature was measured with a chromel-alumel thermocouple attached to the mount next to the sample. HREELS experiments were performed in a specular scattering geometry with an incident and scattered angle of 60º from the normal and incident electron energy ranging from 7 eV to 35 eV. An instrumental resolution of 60 cm$^{-1}$ was obtained as determined from the elastic peak full width at half maximum.

The surface of the InN sample was first cleaned by bombardment of 1 keV Ar ions at an angle of 70º from the normal to remove surface carbon contamination from exposure to air during transport to the UHV chamber. When Auger electron spectroscopy showed removal of nearly all surface carbon, the sample was treated using atomic hydrogen cleaning (AHC) [10]. Atomic hydrogen exposures were performed by backfilling the vacuum chamber with hydrogen
to a pressure of $8.4 \times 10^{-7}$ Torr in the presence of a tungsten filament heated to 1850 K. The sample was positioned 20 mm from the filament for 20 minutes (giving an exposure of 1000 L of H$_2$) during which time 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$_2$). Auger electron spectroscopy (AES) and HREELS showed that surface carbon and oxygen contaminants had been removed. Low energy electron diffraction (LEED) yielded a hexagonal 1×1 pattern over the entire surface of the film using electron energies from 40 to 170 eV indicating good surface order and c-axis orientation of the InN layer.

5.4 Results and Discussions

HREEL spectra from the AHC-treated InN layer were acquired using a range of incident electron energies and are shown in Fig. 5.1. In all the spectra, a strong loss feature was observed at 560 cm$^{-1}$ which is assigned to Fuchs-Kliewer surface phonon excitations in agreement with previous reports [10-15,25]. The HREEL spectrum taken using 7 eV incident electron energy shows surface adsorbate loss features at 870 and 3260 cm$^{-1}$ due to the bending and stretching vibrations of a surface N-H species [25]. A small peak observed near 1430 cm$^{-1}$ is assigned to a combination loss of the Fuchs-Kliewer phonon and the N-H bending vibration. With the incident electron energy increased to 15 eV, the intensity of the N-H stretch decreased considerably while the N-H bend was almost unchanged. The difference in the dependence of the intensity of the two peaks on incident energy suggests that different scattering mechanisms are contributing. According to Ibach and Mills [27], the dipole scattering cross-section decreases with the increasing incident energy while the impact scattering cross-section is less predictable
and may even increase. Therefore, the excitation of the N-H stretch is attributed primarily to dipole scattering while the N-H bend has a considerable contribution due to impact scattering. As the incident energy is increased further, all modes due to surface vibrations decrease due to reduction in surface sensitivity with an increasing penetration depth of the electrons.

In-H stretching vibrations, typically found between 1650 and 1700 cm$^{-1}$ [28-31], are not observed in these spectra even with 7 eV incident electron energy. Since hydrogen desorption may occur from indium sites at the 600 K temperature used for AHC, additional room temperature hydrogen atom exposures were performed. HREEL spectra from the room temperature H-dosed surface were unchanged from those shown in Fig. 1 indicating that no reactive indium exists on this surface. The presence of N-H and lack of indium-related vibrations demonstrates N-termination of the surface and implies N-polarity of the film since N-termination would not be expected for In-polar films [32]. Along with the observed 1×1 surface order, this also shows that the surface is free of both indium overlayers and droplets.

The observation of an N-H terminated surface free of excess indium differs from the conclusion of several recent reports. An investigation by Draxler et al. [23] using coaxial impact collision ion scattering spectroscopy (CAICISS) determined that metallic In was present on N-polar InN surfaces after cleaning by atomic hydrogen. Piper et al. [22] also concluded that metallic In is sometimes present on the InN surface after AHC based on x-ray photoemission spectroscopy. They assign a component of the In4d peak to In-In bonds. However, the relative intensity of the In-In feature relative to the In-N component and the lack of surface sensitivity due to nearly 1500 eV photon and electron energies suggest that this component is more likely due to bulk indium clusters.
A broad loss feature, with a peak in the range of 3100 to 3400 cm\(^{-1}\) for different incident electron energies, also appears in each spectrum. Following the assignment of McConville and coworkers [10-15], we attribute these broad features as due to conduction band plasmon excitations. The plasmon peak energy decreases when the incident electron energy is increased.

In general, the shift of the plasmon loss feature in HREEL spectra with incident electron energy may be attributed to three causes: dispersion, the kinematic factor, and variation of the carrier concentration with depth. Froitzheim et al. [33] have reported that if the parallel momentum transfer vector is much smaller than the reciprocal lattice vector then the wave vector dependence on dielectric function \(\varepsilon(\omega,q)\) can be ignored. Under the conditions used in this study, the parallel momentum transfer vector is small (\(\leq 0.04\) Å\(^{-1}\)), so the role of dispersion in the shift of the plasmon peak position can be excluded.

According to Chen et al. [34], if the loss function contains a broad frequency response due to large damping constant, \(\Gamma\), which is typical for low mobility p-type semiconductors, then the kinematic effects play a role in determining the peak position for incident energies less than 5 eV. Since the present work was performed on an n-type semiconductor of higher carrier mobility (\(\sim 210\) cm\(^2\)/Vs) using incident electron energies of 7 to 35 eV, the kinematic factor is not important in determining the energy of the plasmon loss feature.

Excluding both the effects of the kinematic factor and dispersion, the shift of the plasmon peak position is attributed to a variation of carrier concentration with depth. As McConville and coworkers [10-15] demonstrated by performing semiclassical dielectric theory simulations, the position of the plasmon peak is related to the surface and bulk plasma frequencies. The shift of the plasmon feature to lower loss energy as the incident electron energy is increased means that the plasma frequency is larger for the surface than for the bulk and indicates an accumulation of
electrons on the surface. As seen in Fig. 5.1, the plasmon peak position shifts most dramatically when the incident electron energy is changed from 15 to 25 eV but there is almost no shift when incident energy changes from 7 to 15 eV or 25 to 35 eV. The shift of the plasmon feature with incident energy is determined by the depth profile of the carrier concentration along with the sampling depth of the electrons. HREEL spectra reported by Mahboob et al. [14] and Veal et al. [15] also show that most of the shift occurs as the incident energy is changed from 15 to 30 eV and this feature is reproduced in their simulations using a four or five layer slab model with an electron concentration that is large at the surface and decreasing deeper into the layer. The HREEL spectra reported here are therefore consistent with a surface electron accumulation layer.

In most of the reports of experimental observations of surface electron accumulation on InN layers neither film polarity nor surface termination is known. Piper et al. [10,13] have reported that the MBE-grown samples on which they observed surface charge accumulation were 75% In-polar and 25% N-polar as determined by CAICISS. Although HREEL spectra were used in a number of cases to study the surface electron accumulation, no surface adsorbate vibrational loss peaks were observed in those studies so surface termination could not be determined. In the present work, HREEL spectra at low incident electron energy yield N-H surface vibrations, which indicate both the surface termination and film polarity. The intensity of the N-H vibrations, the lack of In-H vibrations even after room temperature atomic hydrogen exposure, and the presence of a 1x1 LEED pattern are evidence that no indium was present on the surface. The electron accumulation observed here is therefore not caused by indium droplets, indium overlayers, or isolated In-In dimers on the InN surface. This finding is consistent with the pinning of the surface Fermi level in the conduction band but indicates that In-In bonds are not the only source of surface states in the conduction band.
5.5 Summary and Conclusions

In summary, InN layers grown by HPCVD and cleaned by atomic hydrogen have been studied by HREELS. Spectra taken with low incident electron energy demonstrated that the surface is N-H terminated and free of indium overlayers and droplets. Spectra acquired as a function of incident energy revealed the presence of a surface electron accumulation. These results strongly suggest that the electron accumulation on InN surfaces is not due to excess indium.
Figure 5.1 HREELS from an atomic hydrogen cleaned InN sample. 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.
5.6 References


Chapter 6

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

6.1 Abstract

The electronic and structural properties of an 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 cm$^{-1}$ to 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 $8.2 \times 10^{19}$ to $1.5 \times 10^{20}$ cm$^{-3}$ and carrier mobilities from 105 to 210 cm$^2$/Vs.
6.2 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]. Hence it has become a potential material for applications in high frequency, high speed, and high-electron-mobility transistors (HEMTs) [1]. Recently, metalorganic chemical vapor deposition (MOCVD) 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 1100K at reactor pressures around 15 bar [3,5].

Surface electron accumulation on InN layers have 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 coworkers investigated surface electron accumulation on InN layers grown by MBE as measured by 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 a \(\sim 240\) cm\(^{-1}\) downward dispersion as the energy of the probing electron is increased from 10 to 30 eV indicating that the surface layer has a higher plasma frequency than does the bulk. They simulated HREEL spectra using semiclassical dielectric theory applied to a four-layer model and determined a surface carrier concentration \(\sim 10\) times larger than the bulk value. They suggest that there exists an unusually low conduction band minimum at the \(\Gamma\)-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, the plasma frequency is determined 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.

6.3 Experimental Methods

The InN layers used in this study were grown at a temperature of 1100 K to 1120 K, a reactor pressure of 15 bar, and an ammonia to trimethylindium (TMI) 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].

Fig. 6.1 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 are an average over an area of ~5 mm². 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) analysis. 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 $1.8 \times 10^{-10}$ 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 eV 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 minutes (giving an exposure of 1000 L of H₂). 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 minutes (an additional 1000 L of H₂). Auger electron spectroscopy (AES) 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.
6.4 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. 6.2. 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 demonstrates 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 to 3400 cm$^{-1}$ for different 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 energy 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 ~1 Å [7-11], the position of the peak in the plasmon loss feature is assumed to be close to the bulk plasma frequency.
Fig. 6.3 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.

Fig. 6.4 depicts the IR reflectance data collected at locations centered on those marked A, B, and C in Fig. 6.1. In order to extract the bulk plasma frequency from the IR reflectance taken at each location, the data were fit 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 a GaN/sapphire structure was modeled and the best fit parameters of the GaN layer were obtained from a Levenberg-Marquardt, 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 the 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 6.1. 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 6.1, a free carrier concentration of 8.0\(\times\)10\(^{19}\) cm\(^{-3}\) and carrier mobility of 210 cm\(^2\)/Vs were calculated for the dark central region of the InN film while a free carrier concentration of 1.5\(\times\)10\(^{20}\) cm\(^{-3}\) and carrier mobility of 105 cm\(^2\)/Vs were found for the lighter outer region. IR reflectance on more recently grown InN layers show carrier concentrations near 7\(\times\)10\(^{19}\) cm\(^{-3}\) and carrier mobilities near 430 cm\(^2\)/Vs [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.
6.5 Summary and 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 between \(8.2 \times 10^{19}\) to \(1.5 \times 10^{20}\) cm\(^{-3}\) and carrier mobilities from 105 to 210 cm\(^2\)/V.
Table 6.1 Plasma frequencies, free carrier concentrations and carrier mobilities determined from model fitting of the infrared reflectance data at several locations on the InN layer.

<table>
<thead>
<tr>
<th>Location</th>
<th>Plasma Frequency (cm(^{-1}))</th>
<th>Free Carrier Concentration (cm(^{-3}))</th>
<th>Carrier Mobility (cm(^2)/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4240</td>
<td>(1.5 \times 10^{20})</td>
<td>105</td>
</tr>
<tr>
<td>B</td>
<td>3520</td>
<td>(1.1 \times 10^{20})</td>
<td>170</td>
</tr>
<tr>
<td>C</td>
<td>3120</td>
<td>(8.2 \times 10^{19})</td>
<td>210</td>
</tr>
</tbody>
</table>
Figure 6.1 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.
Figure 6.2 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.
Figure 6.3 HREELS of InN after atomic hydrogen cleaning. Spectra were acquired in the specular direction with incident electron energy of 25 eV at locations marked D, E, and F as indicated in Fig. 6.1.
Figure 6.4 Infrared reflectance measurements from three locations on InN layer (dashed lines). Also shown are results of fitting to a three-layer model (solid lines) to determine plasma frequency and damping constant.
6.6 References


Chapter 7

Desorption of hydrogen from InN(000\bar{1}) surface observed by HREELS

7.1 Abstract

The kinetics of isothermal desorption of hydrogen from InN(000\bar{1}) have been investigated using surface vibrational spectroscopy. Reductions in intensity of the N-H stretching and bending vibrations in high resolution electron energy loss spectra upon annealing indicated loss of surface hydrogen and was attributed to recombinative desorption. Hydrogen completely desorbs from the InN surface upon annealing for 900 s at 425 °C or upon annealing for 30 s at 500 °C. The surface hydrogen coverage was determined using the intensity of the N-H stretching vibrational loss peak. Fitting the coverage versus temperature for anneals of either 30 or 900 s indicated that the desorption was best described by second order desorption kinetics with an activation energy and pre-exponential factor of 1.3±0.2 eV and 10^{-7.3±1.0} cm²/s, respectively. In addition to thermal desorption, an increase in the carrier concentration in the film was also observed upon annealing to 450 °C or higher as shown by a shift of the conduction band plasmon excitation to higher energy.
7.2 Introduction

Group III-nitride semiconductors GaN, AlN, InN and their alloys are promising materials for photonic, optoelectronic and microelectronic devices [1-3]. InN, one of the least studied nitride semiconductors, is a potential material for a wide range of applications including high electron mobility transistors [4], chemical and biological sensors [5], transparent conducting window material for heterojunction solar cells [6], thermoelectric devices [7] and terahertz radiation devices [8]. The development of the indium-rich InGaN alloy system will allow for tuning of the band gap over a wide spectral range from blue to infrared [9].

Surface reactions involving hydrogen are important steps in the growth mechanism of InN thin films. Surface hydrogen atoms produced by the decomposition of precursors during InN growth are most frequently eliminated by desorption after reacting with adsorbed methyl groups or other hydrogen atoms. Adsorbed hydrogen reduces the number of available reaction sites for indium and nitrogen precursors. Koukitu et al. [10] carried out a detailed thermodynamic study of the role of hydrogen during metal-organic chemical vapor deposition (MOCVD) growth of III-nitrides and showed that an increase in hydrogen partial pressure due to decomposition of growth precursors results in a decrease of the InN deposition rate and that the increase in H$_2$ can drive the system from the deposition mode into the etching mode. Hydrogen in the growth environment also affects the film composition. Losurdo et al. [11] reported that InN strongly reacts with atomic hydrogen causing depletion of nitrogen and the concurrent formation of indium droplets at the surface. Scholz et al. [12] reported that the indium incorporation rate in the growth of InGaN was nearly doubled when reducing the hydrogen content in the growth
chamber. Piner et al. [13] reported that the indium content drops significantly as the hydrogen flow increases for MOCVD-grown InN layers and atomic-layer-deposited InGaN.

Understanding the various effects of hydrogen on growth under a range of process conditions requires knowledge of the kinetic parameters for surface reactions. However, both qualitative and quantitative details of many of the important surface reactions occurring during InN growth are not yet known. In this work, high resolution electron energy loss spectroscopy (HREELS) has been used to determine the kinetic parameters for hydrogen desorption from the N-polar InN surface. In addition, the effects of heating on surface structure and electronic properties are also reported.

7.3 Experimental Methods

Two InN samples, referred to as samples A and B, grown by high pressure chemical vapor deposition (HPCVD) under similar conditions were investigated. The layers were grown at a temperature of ~810 °C, reactor pressure of 15 bar, and ammonia to trimethylindium ratios of 790 (sample A) and 630 (sample B). The layers were deposited on a GaN buffer layer grown on a sapphire (0001) substrate. Details of the HPCVD reactor, growth configuration, and real-time optical characterization techniques employed have been published elsewhere [14,15]. The samples were transported in air before being introduced into the ultrahigh vacuum chamber (UHV) surface characterization system. The UHV chamber had a base pressure of 1.8×10^{-10} torr and details of the surface science apparatus have been published previously [16]. Before introduction into the UHV chamber, the InN sample was rinsed with isopropyl alcohol, 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 record the sample temperature.

Auger electron spectroscopy (AES) of the as-inserted InN samples revealed oxygen and carbon contamination due to the exposure of sample to the atmosphere. Sample cleaning was achieved in two steps. In the first step, most of the carbon contaminants were removed by 0.5 keV argon ion sputtering at a glancing angle of 70° from the surface normal. In second step, atomic hydrogen cleaning (AHC) was performed by backfilling the vacuum chamber with hydrogen to a pressure of $8.4 \times 10^{-7}$ torr in the presence of a tungsten filament heated to 1575 °C to produce atomic hydrogen. The sample was positioned 20 mm from the filament for 20 minutes (giving an exposure of 1000 L of H$_2$). The sample temperature rose to approximately 75 °C, due to the proximity of the heated filament. After this, the sample was heated to 325 °C while remaining in front of the tungsten filament for an additional 20 minutes (an additional 1000 L of H$_2$).

The AES spectra after cleaning confirmed that the InN surface is free from contaminants. Low energy electron diffraction (LEED) showed a hexagonal 1x1 LEED pattern, demonstrating a well ordered surface. After cleaning, sample A was annealed to a series of temperatures from 375 to 425 °C for 900 s and the sample B was annealed at temperatures from 425 to 500 °C for 30 seconds. The surface was restored to its original condition through AHC between annealing treatments. HREELS experiments were performed in a specular geometry with incident and scattering angles of 60° from the normal and incident electron energy of 7.0 eV. The instrumental resolution determined from full width at half maximum of the elastic peak was 60 cm$^{-1}$. 
7.4 Results and discussion

HREEL spectra from sample A, taken after AHC and annealing to various temperatures for 900 s, are shown in Fig. 7.1. In the spectrum taken after AHC, a prominent peak appears at a loss energy of 560 cm\(^{-1}\) and is assigned to the Fuchs-Kliewer surface phonon [17]. The peaks at 3260 and 860 cm\(^{-1}\) are assigned to N-H stretching and bending vibrational modes, respectively [18]. At high hydrogen coverages, a small peak was observed at 1430 cm\(^{-1}\) and is assigned to a combination loss of the Fuchs-Kliewer phonon and the N-H bending vibration. The presence of N-H vibrations and the lack of In-H features indicates that the layer is nitrogen terminated consistent with N-polar InN(000\(\bar{1}\)) [19,20]. A broad feature centered at a loss energy of ~3800 cm\(^{-1}\) is due to the conduction band plasmon excitation [19,20].

The loss features in Fig. 7.1 due to Fuchs-Kliewer surface phonons and the conduction band plasmon excitation do not change upon annealing. After annealing to 375 °C, the intensity of both N-H stretch and bend decrease and disappear completely after heating the sample to 425 °C for 900 s. The reductions in intensity of N-H vibrations are attributed to recombinative desorption of hydrogen. In addition to the N-H vibrational peaks, a small feature appears at 2000 cm\(^{-1}\) as the N-H vibrations decrease. Although no firm assignment is made, the authors suggest that it may be due to a surface N-N vibrational mode. N-N stretching vibrational modes have been reported to occur over a wide range of frequencies. de Paola et al. [21] and Anton et al. [22] reported \(\nu(N-N)\) on Ru (001) at 2195 cm\(^{-1}\) and 2200-2250 cm\(^{-1}\), respectively. Grunz et al. [23] observed the N-N stretching mode on a Ni surface to be at 1490 cm\(^{-1}\) while Apen and Gland [24] identified the N-N stretching mode on the GaAs surface is at 1671 cm\(^{-1}\). The wide range of
frequencies observed for N-N stretches makes a firm assignment here difficult, but does demonstrate that its possible for the 2000 cm\(^{-1}\) peak to be due to a surface N-N bond.

Fig. 7.2 shows the results of a similar experiment on sample B, although with anneal times of 30 s. The spectrum acquired after AHC shows the same N-H vibrations at 860, 1430, and 860 cm\(^{-1}\) as well as the Fuchs-Kliewer phonon at 560 cm\(^{-1}\) as observed on sample A. However, a small C-H stretching vibrational peak is observed at 2950 cm\(^{-1}\) due to a small amount of residual carbon contamination on sample B. Also, the conduction band plasmon excitation is observed at a slightly lower frequency than on sample A indicating a slightly lower plasma frequency and therefore slightly lower carrier concentration. Samples A and B were grown using different ammonia to TMI ratios of 790 and 630, respectively, and are unintentionally n-type doped. The small difference in bulk carrier concentration would not be expected to significantly affect the process of hydrogen recombinative desorption.

As shown in Fig. 7.2, partial desorption of hydrogen is observed for anneals from 425 to 475 °C as seen by reductions in the N-H vibrations, while complete desorption of hydrogen is observed after heating to 500 °C for 30 s.

There have been no published studies of hydrogen desorption from InN, but several groups have reported results for hydrogen desorption from N-polar GaN. Sung et al. [25] reported the desorption of hydrogen from the nitrogen sites on a GaN surface at 850 °C. In contrast, Chiang et al. [26] reported hydrogen desorption from Ga- sites of a GaN surface at 250 °C and from the N-sites at 500 °C. The desorption temperature from N-sites on InN reported in this paper is similar to the result for N-sites on GaN reported by Chiang et al. but much lower than that reported by Sung et al.
Understanding the mechanisms and kinetics of hydrogen desorption is important for developing both qualitative and quantitative models of the growth of indium-rich III-nitrides. The main source of hydrogen in MOCVD may come from carrier gas and the decomposition of ammonia precursors [27]. The methyl groups and hydrogen atoms formed during decomposition combine and may form methane (CH₄), ethane (C₂H₆) or molecular hydrogen (H₂), which desorb from the growth surface. The temperature region suitable for the deposition of high quality InN by MOCVD has been reported from 500 to 650 ºC, while it ranges from 450 to 550 ºC in molecular beam epitaxy [9] and from 455 to 510 ºC for halide vapor phase epitaxy [28]. This growth temperature regime suggests that the typical growth temperature of InN is in the same order at which hydrogen desorbs (425 to 500 ºC) from the InN surface. If the growth temperature would be lower than the hydrogen desorption temperature, sites on the InN growth surface could be occupied by hydrogen, which is produced during the precursor decomposition process. This would reduce the number of reaction sites available for adsorption of indium or nitrogen precursors and could affect the growth rate. At temperatures higher than required for hydrogen recombination, hydrogen desorption increases the number of reaction sites for precursors and may enhance the growth rate. At much higher surface temperatures, additional InN dissociation and the desorption of molecular nitrogen may occur [29,30].

The process of annealing at higher temperature also affects the electronic properties of the film. The broad loss feature due to the conduction band plasmon excitation peaked at \(~3700\) cm\(^{-1}\) for sample B after AHC and remained unchanged after annealing to 425 ºC. However, annealing to 450 ºC or above produced a shift of the plasmon excitation peak to higher energy, with the plasmon loss peaking at \(~4200\) cm\(^{-1}\) after heating to 500 ºC for 30 s. The increase in plasmon loss energy indicates a higher plasma frequency, correlating to an increase in the carrier
concentration. This is consistent with the report of Hung et al. [31] who pointed out that the carrier concentration rapidly increases while carrier mobility rapidly decreases from the values for InN grown by MBE, when annealed above 550-600 °C.

As shown in Fig. 7.2, the annealing of the sample at 475 °C or above result in a new HREELS peak at 400 cm$^{-1}$. The small vibrational frequency of this peak may indicate that it involves the bonding between surface nitrogen and the second layer indium atoms. This low frequency of vibration is due to high effective mass of indium, since the frequency of vibration is inversely proportional to the square root of the effective mass. After annealing for 30 s at 475 °C, several cycles of AHC are required to remove this new feature and to regain the initial surface ordering. Desorption kinetic parameters are often determined by performing temperature programmed desorption (TPD) experiments, however, in the case of hydrogen desorption from InN it would require temperatures in excess of 500 °C. Since heating to those temperatures may cause changes in the In-N bonds in the surface region as indicated by the development of the 400 cm$^{-1}$ loss peak, HREEL spectra were used to determine kinetic parameters instead of using TPD data.

To determine kinetic parameters from HREELS data, relative surface coverages were obtained by integrating the area under the N-H stretching vibrational peak in each normalized HREEL spectrum. A smooth background was assumed for the underlying conduction band plasmon loss. The normalized N-H stretch intensity is expected to be proportional to the surface coverage [32] since it has been shown in earlier work by the authors to be due to dipole scattering [19]. Plots of normalized N-H intensity versus annealing temperature are shown in Fig. 7.3 and Fig. 7.4 for 900 and 30 s annealing times, respectively. Although the sample was annealed to 325 °C during AHC, the exposure with atomic hydrogen continued until the sample
cooled down to \(-200 \, ^\circ C\). Therefore, N-H stretch intensities from each sample after AHC are plotted as equivalent to a \(200 \, ^\circ C\) anneal.

The data were fitted using both first order and second order desorption kinetics. For first order desorption the integrated intensities were fit using

\[
\frac{\theta}{\theta_0} = e^{-\nu_1 t \exp(-E/kT)}
\]

where \(\theta\) is the surface hydrogen coverage, \(\theta_0\) is the initial coverage, \(t\) is the anneal time, \(\nu_1\) is the first order preexponential factor, and \(E\) is the activation energy. From the fitting for first order desorption kinetics, no common set of values for activation energy and pre-exponential factor were found which produced good fits to both the 900 and 30 s anneal time data. The best individual first order fits were found to have an activation energy and pre-exponential factor, respectively, of 0.8 eV and 1100 s\(^{-1}\) for 900 s anneals and 0.7 eV and 2100 s\(^{-1}\) for 30 s anneals. The pre-exponential factors determined in these fits are far below the values expected. For the desorption of atoms that are mobile on the surface, a first-order or pseudo first order pre-exponential factor in the range of \(10^{13} \, s^{-1}\) is expected. For atoms that are immobile on the surface, the factor would be in the range of \(10^{16} \text{ to } 10^{17} \, s^{-1}\) [33].

For second order desorption, the integrated intensities were fit using

\[
\frac{\theta}{\theta_0} = \frac{1}{1 + \theta_0 \nu_2 t e^{-E/kT}}
\]

where \(\theta\) is the surface hydrogen coverage, \(\theta_0\) is the initial coverage, \(t\) is the anneal time, \(\nu_2\) is the second order pre-exponential factor, and \(E\) is the activation energy. Fitting to second order desorption kinetics yields a good fit to both sets of data using a common set of kinetic parameters with an activation energy of \(1.3 \pm 0.2 \, eV\) and a second order pre-exponential factor.
of $10^{-7.3\pm1.0}$ cm$^2$/s (equivalent to a pseudo-first order pre-exponential factor of $10^{7.5\pm1.0}$ s$^{-1}$). Therefore, we conclude that these data are more consistent with second order desorption kinetics, which is typical of hydrogen recombination on most III-V semiconductor surfaces.

The activation energy of $1.3 \pm 0.2$ eV determined here indicates considerable energy is reclaimed by surface relaxation or re-bonding of the surface nitrogen atoms. This re-bonding is consistent with the development of a HREELS loss peak at 2000 cm$^{-1}$ upon hydrogen desorption as seen in Figs. 7.1 and 7.2 and supports the suggestion that this peak is due to N-N bonding.

### 7.5 Summary and conclusions

The desorption of hydrogen from InN(000$\bar{1}$) was investigated by high resolution electron energy loss spectroscopy. Complete removal of surface hydrogen was observed after heating to 425 °C for 900 s or 500 °C for 30 s. The desorption is best described by second order kinetics with an activation energy of $1.3 \pm 0.2$ eV and a pre-exponential factor of $10^{-7.3\pm1.0}$ cm$^2$/s. Annealing to 450 °C or above produces a shift in conduction band plasmon excitation peak to higher loss energy demonstrating an increase in the free carrier concentration in the film.
Figure 7.1 HREEL spectra from sample A after preparation by atomic hydrogen cleaning (AHC) and after heating for 900 s to 375, 400, and 425 °C. The surface was restored to the same initial state with AHC prior to each heat treatment.
Figure 7.2 HREEL spectra from sample B after preparation by atomic hydrogen cleaning (AHC) and after heating for 30 s to 425, 450, 475, and 500 °C. The surface was restored to the same initial state with AHC prior to each heat treatment. The line marking the conduction band plasmon excitation is only provided as a guide to the eye.
Figure 7.3  Fitting of first and second order desorption kinetics to hydrogen coverage (determined from HREELS N-H stretch intensity) for InN sample A after preparation by atomic hydrogen cleaning and after heating for 900 s to 375, 400, and 425 °C. Equation and parameters used in the fitting are described in the text.
Figure 7.4  Fitting of first and second order desorption kinetics to hydrogen coverage (determined from HREELS N-H stretch intensity) for InN sample B after preparation by atomic hydrogen cleaning and after heating for 30 s to 425, 450, 475, and 500 °C. Equation and parameters used in the fitting are described in the text.
7.6 References


Chapter 8

Summary and Future work

8.1 Summary

We have investigated the surface structure, composition, bonding, and film polarity of InN layers grown by HPCVD. Two of the important aspects of InN surface properties are the phenomenon of surface electron accumulation and the process of hydrogen desorption. We have studied these by using various surface sensitive techniques. The surfaces of InN layers have been prepared by sputtering with argon ions followed by atomic hydrogen or deuterium cleaning in an UHV environment. The cleanliness of the sample was monitored by AES. The surface structure of the InN layers was characterized by LEED and other experimental characterizations were performed by using HREELS.

Sputtering of the surface by 0.5 keV argon ions at a glancing angle of 70° with the normal to the surface was successful in removing all the surface carbon contaminants accumulated on the surface due to its exposure to the atmosphere. Oxygen contaminants were removed from the surface by AHC. The confirmation of removal of the contaminants from the surface was carried out using AES data taken from the various spots on the sample. AHC not only cleans the surface
but also helps to improve the surface order of the samples. LEED image taken from clean InN layers showed a clear hexagonal 1x1 pattern demonstrating the surface was well ordered and c-plane oriented.

HREELS taken at incident energy of 7 eV showed Fuchs-Kliewer phonons at 550 cm\(^{-1}\) and N-H stretch and bend vibrational losses at 3260 and 870 cm\(^{-1}\), respectively. In-H stretching vibrations are expected to be in between 1600-1700 cm\(^{-1}\), but were not observed in the HREEL spectra. Spectra taken at low incident electron energy demonstrated that the surface is N-H terminated and the film is InN(000\(\bar{1}\)), which is, N-polarity and free of indium over layers and droplets.

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\(^{-1}\), which is in good agreement with the HREEL spectra taken at corresponding spots across the surface. The parameters from the fitting of the IR data were used to determine free carrier concentrations between 8.2 \(\times\) 10\(^{19}\) to 1.5 \(\times\) 10\(^{20}\) cm\(^{-3}\) and carrier mobilities from 105 to 210 cm\(^2\)/Vs.

HREEL spectra taken from the same sample at lower incident electron energy showed a shift to higher plasma frequency in comparison to the spectra taken at higher incident energy indicating a surface electron accumulation. The observation of only N-H vibrations not In-H vibrations in HREEL spectra strongly suggest that the electron accumulation on InN surfaces is not due to excess indium.

The desorption of hydrogen from InN(000\(\bar{1}\)) surface was examined in two phases, one by annealing the hydrogenated surface for 30 seconds and another for 900 seconds. Complete removal of surface hydrogen was observed after heating to 425 °C for 900 s or 500 °C for 30 s.
Annealing to 450 °C or above in UHV produces a shift in conduction band plasmon excitation peak to higher loss energy demonstrating an increase in the free carrier concentration in the film. This demonstrates that the electronic properties of InN change after annealing to 450 °C or above in UHV.

The thermal kinetic parameters of hydrogen desorption from a hydrogenated InN(000\(\overline{1}\)) surface were studied by acquiring HREEL spectra. Thermal parameters, particularly activation energy and pre-exponential factor, were extracted by fitting the intensities of N-H vibrational loss features in HREEL spectra. The normalized intensity of N-H vibrational loss in HREEL spectra is expected to be proportional to the surface coverage. A consistent best fit could not be obtained for a common set of values of kinetic parameters for both the data acquired from a 30 s anneal and 900 s anneal in first order desorption kinetics to surface coverage. Desorption is best described by second order kinetics with an activation energy of 1.3 ± 0.2 eV and a pre-exponential factor of \(10^{-7.3±1.0}\) cm\(^2\)/s.
8.2 Future Work

**Reaction of trimethylindium and ammonia on the indium nitride surface**

Trimethylindium and ammonia are the common precursors used during the growth of InN by most CVD processes. During the growth these precursors will decompose into their constituents and various gas phase or surface reactions may occur. It is essential to understand what may be the possible constituents formed during the decomposition process of the precursors and what may be the possible gas phase and surface reactions that are most likely. Understanding about the phenomenon of precursor decomposition, constituent’s adsorption on the surface, diffusion into the film and desorption from the surface would yield insight into the growth process. Investigation of surface reactions of trimethylindium or ammonia on the bare or hydrogenated indium nitride surface, by using HREELS would be able to address the above questions.

A theoretical model of gas phase and surface reactions during the growth of InN by HPCVD is presented by B. H. Cardelino [1]. Including all possible adduct formations between group III and group V species and subsequent release of methyl group or hydrogen atoms, a total of 47 species can be formed and 79 possible reactions may occur in the gas phase. Keeping track of all of the possible species, and determining the probability of their formation and their expected life times are extremely difficult. However, the dissociation of TMI was modeled using 4 different reactions which includes six species \( \text{In} (\text{CH}_3)_3 \), \( \text{In} (\text{CH}_3)_2 \), \( \text{In} (\text{CH}_3) \), In, CH₃, and C₂H₆. The dissociation of ammonia was modeled using 5 different equations which also include six different species; \( \text{NH}_3 \), \( \text{NH}_2 \), \( \text{NH} \), N, H, and H₂. Investigation of surface reactions of these
species with the bare and hydrogenated InN surface would give microscopic insight of the
growth mechanism.

We have already studied the reactions of atomic hydrogen on bare InN surface by using
HREELS and reported the results. Now, by decomposing TMI and ammonia in UHV, the
reactions of species on bare and hydrogenated InN surface can be studied by using the same
 technique. This will not only help to study the reaction types but also would be a great feedback
in order to understand the growth mechanism microscopically.

8.3 References