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OPTICAL AND STRUCTURAL PROPERTIES OF INDIUM NITRIDE EPILAYERS
GROWN BY HIGH-PRESSURE CHEMICAL VAPOR DEPOSITION AND VIBRATIONAL
STUDIES OF ZGP SINGLE CRYSTAL

by

RAMAZAN ATALAY

Under the Direction of Nikolaus Dietz

ABSTRACT

The objective of this dissertation is to shed light on the physical properties of InN epilayers grown by High-Pressure Chemical Vapor Deposition (HPCVD) for optical device applications. Physical properties of HPCVD grown InN layers were investigated by X-ray diffraction, Raman scattering, infrared reflection spectroscopies, and atomic force microscopy. The dependencies of physical properties as well as surface morphologies of InN layers grown either directly on sapphire substrates or on GaN/sapphire templates on varied growth conditions were studied. The effect of crucial growth parameters such as growth pressure, V/III molar ratio, precursor pulse separation, substrate material, and mass transport along the flow direction on the
optical and structural properties, as well as on the surface morphologies were investigated separately.

At present, growth of high-quality InN material by conventional growth techniques is limited due to low dissociation temperature of InN (~600 °C) and large difference in the partial pressures of TMI and NH₃ precursors. In this research, HPCVD technique, in which ambient nitrogen is injected into reaction zone at super-atmospheric growth pressures, was utilized to suppress surface dissociation of InN at high temperatures.

At high pressures, long-range and short-range orderings indicate that c-lattice constant is shorter and $E_2$(high) mode frequency is higher than those obtained from low-pressure growth techniques, revealing that InN structure compressed either due to a hydrostatic pressure during the growth or thermal contraction during the annealing. Although the influence of varied growth parameters usually exhibit consistent correlation between long-range and short-range crystalline orderings, inconsistent correlation of these indicate inclination of InN anisotropy.

InN layers, grown directly on $\alpha$-sapphire substrates, exhibit InN (1 0 1 1) Bragg reflex. This might be due to a high $c/a$ ratio of sapphire-grown InN epilayers compared to that of GaN/sapphire-grown InN epilayers. Optical analysis indicates that free carrier concentration, $n_e$, in the range of $1–50 \times 10^{18}$ cm$^{-3}$ exhibits consistent tendency with longitudinal-optic phonon. However, for high $n_e$ values, electrostatic forces dominate over inter-atomic forces, and consistent tendency between $n_e$ and LO phonon disappears.

Structural results reveal that growth temperature increases $\sim$6.6 °C/bar and V/III ratio affects indium migration and/or evaporation. The growth temperature and V/III ratio of InN thin films are optimized at $\sim$850 °C and 2400 molar ratio, respectively. Although high in-plane strain and $c/a$ ratio values are obtained for sapphire-grown epilayers, FWHM values of long-range and
short-range orderings and free carrier concentration value are still lower than those of GaN/sapphire-grown epilayers.

Finally, vibrational and optical properties of chalcopyrite ZGP crystal on the (001), (110), and (110) crystalline planes were investigated by Raman scattering and infrared (IR) reflection spectroscopies. Raman scattering exhibits a nonlinear polarizability on the \( c \)-plane, and a linear polarizability on the \( a \)- and \( b \)-planes of ZGP crystal. Also, birefringence of ZGP crystal was calculated from the hydrostatic pressure difference between (110) and (\( \bar{1} \)10) crystalline planes for mid-frequency \( B_2(\text{LO}) \) mode.

INDEX WORDS: Group III-nitrides, Indium nitride (InN), High-Pressure Chemical Vapor Deposition (HPCVD), Raman scattering spectroscopy, Infrared (IR) reflection spectroscopy, and X-ray diffraction
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This thesis is dedicated
to my loving family,
Ömer, Fatma, Nurşen, and Gülşen,
and my brothers-in-law,
Ahmet and Ömer,
for their endless love, encouragement, support,
and
sacrifices.
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CHAPTER 1

MOTIVATION AND OUTLINE OF RESEARCH

1.1. Motivation of Research

In the field of semiconductor devices, (binary or ternary) compound semiconductor materials can be uniquely chosen for the production of IR emission or sensing applications. Indium nitride (InN) has received a renewed attention due to the recent downward revision of its band gap from 1.8 eV to below 0.7 eV as well as for its superior electron transport properties [1, 2]. InN has the smallest effective mass of all the group-III nitride semiconductors, which leads to its predicted high-electron mobility [3] of ~4400 cm²V⁻¹s⁻¹, a high saturation velocity [2], and large drift velocity at room temperature. Possessing a direct bandgap of ~0.7 eV [2], InN is also a potential material for IR emission or sensing applications [4].

In addition to its potential use in high-frequency/high-power electronic devices [2-4] and infrared optoelectronics [5], ternary or quaternary alloy of In(AlGa)N material allows a tailoring of the bandgap from near-infrared to the ultraviolet (6.2 eV) spectral region. Therefore, the development and integration of InN and In-rich ternary alloys (e.g. In₁₋ₓGaₓN and In₁₋ₓAlₓN) opens new avenues for the fabrication of THz emitters or detectors [6], chemical sensor applications [7], and highly-efficient energy conversion devices, such as solid state lightning [8], multi-tandem photovoltaics [8], and monolithically integrated LED displays [9].
1.2. Outline of Research

The main objective of this thesis is to understand the physical properties of InN epilayers grown by High-Pressure Chemical Vapor Deposition (HPCVD) technique for optical device applications. The research approach taken in this thesis is to unite basic material research with a possible novel device application. The organization of this thesis is as the follows.

Chapter 2 briefly discusses physical properties of InN semiconductor material. Since growth parameters are vastly varied for the growth of InN epilayers, Chapter 2 discusses the differences between defects and dislocations.

Chapter 3 provides a detailed overview of the spectroscopic characterization techniques. This chapter is an introduction of the crystallographic, structural, optical, and optoelectronic properties of InN thin films by X-ray diffraction (XRD), Raman scattering spectroscopy, and infrared (IR) reflection spectroscopy.

Chapter 4 gives a detailed overview of an epitaxial growth techniques employed for the production of InN epilayers: Metalorganic Chemical Vapor Deposition (MOCVD), Molecular Beam Epitaxy (MBE), Hydride Vapor Phase Epitaxy (HVPE), and High-Pressure Chemical Vapor Deposition (HPCVD).

Chapter 5 presents a detailed investigation of the structural and optical properties obtained from InN epilayers grown by HPCVD. All epilayers are investigated by X-ray diffraction, Raman scattering and IR reflection spectrosopies and their results are cross-correlated as well. Since growth parameters are crucial factors in InN epitaxy, influence of reactor pressure, V/III molar ratio, precursor pulse separation, substrate material, and mass transport along the flow distance are discussed in detail.
Chapter 6 discusses the structural and optical properties of single crystal chalcopyrite (pnictide) zinc germanium phosphide (ZnGeP$_2$ also denoted as ZGP) along the (001), (110), and (110) crystalline faces were studied by Raman scattering and infrared (IR) reflection spectroscopies. The experimental results are compared with theoretical calculations of the vibrational modes in order to estimate the effect of point- and extended defects on the optical properties and birefringence of ZGP. The structural Raman tensor components were also used to calculate Raman intensity and to estimate the polarizability of the vibrational lattice dynamics.

Finally, Chapter 7 summaries results of this research and contemplates future directions for applications of these studies.
1.3. References


CHAPTER 2

PHYSICAL PROPERTIES OF INDIUM NITRIDE

2.1. Introduction

The estimated optoelectronics market was almost 22.5 billion dollars in 2011, and it is expected to grow 14% annually [1]. Demand for Light Emitting Diodes (LEDs) and Organic Light Emitting Diodes (OLEDs) is still growing [1]. Optoelectronics industry is mostly driven by Solid State Lightning (SSL) and laser technologies [1,2].

Indium nitride (InN) attracts a significant amount of attention among the group-III nitride semiconductors due to its smallest effective mass, high-predicted electron mobility, and smallest direct band gap [3,4]. InN material has a direct bandgap of ~0.64 eV [5] in the near infrared (IR) region, making it potential candidate for IR emission sensing applications [6]. In addition to potential applications in electronics and optoelectronics [7], ternary and quaternary alloying with gallium and aluminum allows us to tune the bandgap from the near infrared (~0.7 eV) to the ultraviolet (6 eV). As a result of this bandgap tunability, InN and In-rich alloys (In$_{1-x}$Ga$_x$N and In$_{1-x}$Al$_x$N) are very promising materials for the production of THz emitters and detectors [8], chemical sensor applications [9], and highly-efficient energy conversion devices such as, solid state lightning, multi-tandem photovoltaics [10], and monolithic displays (LEDs) [11].

However, the physical properties of the InN are not well-understood for potential device applications. A semiconductor device’s performance depends on not only its structural and electronic properties but also optimizations of these properties are crucial step for cost-effective
mass production [12]. Therefore, in this chapter, structural properties of InN including crystal structure, lattice dynamics, lattice parameters and electronic and optoelectronic properties are separately discussed in sections 2.2 and 2.3, respectively.

### 2.2. Structural Properties of InN

Indium nitride, like other group-III nitride members, crystalizes in the stable forms of wurtzite and zinc blende and exists in a pseudomorphic-stable rocksalt form [13–18]. Various growth techniques discussed in detail in Chapter 4 are utilized for the growth of different crystalline forms. The transitions of the wurtzite phase to the rocksalt were observed at high hydrostatic pressures [13–16]. For instance, group-III nitrides transform to the semiconducting rocksalt phase under the pressure of 21.6, 51.8, 16.6, and 850 GPa for InN, GaN, AlN, and BN, respectively [15].

Here, stable forms of zinc blende and wurtzite InN crystal structures are investigated and physical properties of InN material are listed in Table 2.1. The zinc blende, or rarely defined as a sphalerite form, InN crystal structure has cubic lattice symmetry, illustrated in Fig. 2.1a. The wurtzite InN crystal structure possesses hexagonal lattice symmetry, illustrated in Fig. 2.1b. A substance that can occur in more than one crystal form is said to be polymorphic (or phase separation) [19]. Conventional InN growth techniques often lead to single crystalline phase due to the great difference in the growth conditions [20].

The indium element has two valence electrons in an \( s \) orbital, one valance electron in a \( p \) orbital, for a total of three valence electrons. InN is a covalent network compound and indium to nitrogen bond is a co-ordinate covalent (or dative) bond [21]. In dative bond, the bond is formed by sharing of electron pair, but shared pair is contributed by one atom (nitrogen in this case);
therefore, co-ordinate covalent bond is semi polar bond. The interesting characteristic of covalent network compounds has four dative bonds available to form tetrahedral configuration regardless of hybridization [21]. Thus, each indium atom is surrounded by four nitrogen neighbors forming a tetrahedron or vice versa.

Figure 2.1 Ball and stick representation of a (a) zinc blende and (b) wurtzite unit cells [22].

In the case of wurtzite structure, a hexagonal primitive cell (basis) contains two indium atoms and two nitrogen atoms with two lattice parameters, \( a \) and \( c \). Ideal wurtzite structure belongs to the space group of \( C_{6v}^4 \) in the Schoenflies notation and \( P6_3mc \) in the Hermann-Mauguin notation [23]. The ideal hexagonal structure has a \( c/a = (8/3)^{1/2} = 1.633 \) lattice parameter ratios and a distortion parameter of \( u = 3/8 = 0.375 \) [23]. In generally, \( c/a \) lattice ratio is related to the spontaneous polarization and \( u \) parameter is related to the isotropicity of the structure. Since ideal wurtzite structure has two isotropic planes, isotropicity measurements are important in the wurtzite structure.
In the case of zinc blende, a cubic primitive cell contains one indium atom and one nitrogen atom with cubic lattice parameters of $a$. Ideal zinc blende structure belongs to the space group of $T_{d}^{2}$ in the Schoenflies notation and $F\bar{4}3m$ in the Hermann-Mauguin notation. The difference of the primitive cells of zinc blende and wurtzite structures are shown in the insets of Figs. 2.2a and 2.2b.

The wurtzite and zinc blende primitive cells differ in terms of both number of atoms and bond angle of the second nearest neighbors. In other words, stacking order of the basal planes are different [23]. The bond angle of second nearest neighbor is $0^\circ$ in a wurtzite structure; whereas, it is $60^\circ$ in a zinc blende structure shown in the insets of Figs. 2.2a and 2.2b, respectively. Due to tetrahedral bonding, in the wurtzite and zinc blende structures, there exist four nearest neighbors and 12 second nearest neighbors. However, stacking orders of wurtzite and zinc blende differ due to different second nearest neighboring angle [23]. The wurtzite structure consists of triangularly ordered alternating diatomic planes along the [001] direction; for instance, the stacking sequence of wurtzite InN material is $In_{1}$, $N_{1}$, $In_{2}$, and $N_{2}$, shown in Fig. 2.2b. The zinc blende structure, however, consists of triangularly ordered diatomic planes along the (111) plane [23]. Thus, the stacking sequence of zinc blende InN material is $In_{1}$, $N_{1}$, $In_{2}$, $N_{2}$, $In_{3}$, and $N_{3}$, shown in Fig. 2.2a. Therefore, the stacking of order of wurtzite and zinc blende structure can be summarized as $ABABAB...$ and $ABCABC...$, respectively.
InN, like other group-III nitrides, has lower $c/a$ ratio than the ideal value of 1.633; thus, wurtzite InN structure is slightly (1.31%) compressed along the $c$-axis (or 0001 direction) [24]. In other words, the intrinsic asymmetry of the tetrahedral bonding in the wurtzite group-III nitride materials leads to a negative spontaneous polarization. Spontaneous polarization increases from GaN over InN to AlN [25]. If polarization results from mechanical stress, it is called
piezoelectric polarization. Piezoelectric polarization is generally expressed negative for tensile and positive for compressive stress [26].

i. If the mechanical stress is tensile strain, the orientation of the spontaneous and piezoelectric polarization is parallel.

ii. If the mechanical stress is compressive strain, the orientation of the spontaneous and piezoelectric polarization is antiparallel.

Total polarization of the wurtzite structure is given by the following relation:

\[ P_{\text{Total}} = P_{\text{Piezoelectric}} + P_{\text{Spontaneous}}. \]  

(2.1)

However, mechanical strain associated with the dislocations may also be expected to have a pronounced influence on the piezoelectric effect, which is known to be strong in the nitride materials [27]. The force needed to enlarge of all the atoms along the c-axis in a wurtzite structure is very large; however, movements of the dislocations allow atoms in a crystal plane to slip by one another at a much lower force [28]. Because a low energy is required to move along the densest planes of atoms, dislocations enforce lowest energy direction of alignment within a grain of the material. This results in slip that occurs along parallel planes within the grain and that are known as slip bands, discussed in detail for the structural impurities. These parallel slip planes were observed in GaN epilayers grown on sapphire substrate [29]. Therefore, slip planes have a huge impact on the piezoelectric polarizations.

2.3. Electrical and Optoelectrical Properties of InN

Indium nitride has attracted renewed attention due to the recent downward revision of its band gap from 1.4 eV [34] to ~0.64 eV [5, 35] and its superior electron transport properties. Indium nitride’s electron transport properties include smallest effective mass, largest electron
mobility of \( \sim 4400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), and saturation drift velocity, listed in Table 2.1. Due to its direct bandgap of \( \sim 0.7 \text{ eV} \) in the near infrared (IR) region, it is a potential candidate of IR emission sensing applications [6]. In addition to potential applications for high-frequency electronic devices [36-38] and infrared optoelectronics [39-41], ternary and quaternary alloying of InN with gallium and aluminum allows us to tune the bandgap from the near infrared (\( \sim 0.7 \text{ eV} \)) to the ultraviolet (6 eV). As a result of this bandgap tunability, InN and In-rich alloys (e.g. In\(_{1-x}\)Ga\(_x\)N and In\(_{1-x}\)Al\(_x\)N) are very promising materials for the production of THz emitters and detectors [8], chemical sensor applications [9], and highly-efficient energy conversion devices such as solid state lightning, multi-tandem photovoltaics [10], and monolithic displays (LEDs) [11].

Since InN is the least studied material of the group-III nitrides and bulk form of InN is difficult to prepare, reliable experimental information regarding its electronic properties are scarce. Therefore, electronic properties of InN material must be well understood for potential device applications besides structural properties [42]. The temperature dependence of the direct bandgap is described by the following Varshni equation [43]:

\[
E_g(T) = E_g(0) - \frac{\alpha_e T^2}{\beta_e + T},
\]

(2.2)

where \( E_g(0) \) is the bandgap energy at absolute zero Kelvin, \( \alpha_E \) and \( \beta_E \) are physically associated with a Debye temperature of the crystal, \( T \) is a temperature, and \( \beta = 454 \text{ K} \) for InN. As briefly described in section 2.3, the rock salt phases of group-III nitrides cannot be synthesized and exist only under high pressures beyond the phase transition point. Also pressure dependency of the band of InN material can be expressed by following equation:

\[
E_g(P) = E_g(0) + gP + dP^2,
\]

(2.3)
where $g$ and $d$ are bandgap pressure coefficients with values of 41 meV/GPa and $-0.08$ meV GPa$^{-2}$, respectively [15]. The remaining electrical and optical properties of the InN material system, listed in Table 2.1, are discussed in the following chapters of this thesis.

Table 2.1 Basic physical properties of wurtzite and zinc blende InN material at 300 K.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Syngony</th>
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<td>Zinc blende</td>
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</tr>
<tr>
<td>Electron thermal velocity, m s$^{-1}$</td>
<td></td>
<td>$3.4 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>Est. free carrier concentration, cm$^{-3}$</td>
<td></td>
<td>$3.5 \times 10^{19}$</td>
<td></td>
</tr>
<tr>
<td>IR refractive index</td>
<td></td>
<td>2.9–3.05 [48]</td>
<td></td>
</tr>
<tr>
<td>Optical phonon energy, meV</td>
<td></td>
<td>73 [51]</td>
<td></td>
</tr>
</tbody>
</table>
2.4. Defects and Impurities of InN

The structural (crystallographic) impurities play a major role for overall assessment of the physical properties and critically limit the efficiency of the potential device applications. Structural defects in any semiconductor material can be classified on the basis of their dimensionality as follows: (i) 0-dimensional (point), (ii) 1-dimensional (line), (iii) 2-dimensional (planar), and (iv) 3-dimensional (bulk) defects, summarized in Table 2.2 [30,31].

Point defects are observed where an atom is absent or is in an irregular place in the lattice structure. Point defects include interstitial and substitutional impurities, and vacancies, illustrated in detail in Fig. 2.3 [31]. Substitutional impurity occupying a position on the normal lattice site is formed either from dopant atom or from contaminant. Whereas, interstitial impurity occupying position between lattice sides results either from the alloying element or from a contaminant. Vacancy, an unoccupied lattice site, is generated either during the growth or under extreme mechanical stress [30]. Self-interstitial is a misplacement of an atom in the lattice site.

Figure 2.3 Schematic representations of various point defects in a crystal structure. (a) Interstitial impurity, (b) vacancy, (c) self-interstitial, and (d)–(e) substitutional impurities [31].
Dislocations are linear irregularities within the lattice line, i.e., a dislocation line. There are two types of dislocations, namely edge dislocations and screw dislocations. Dislocations are generated when an external or internal stress is present between two regions. The edge dislocation can be easily visualized as an extra half-plane of atoms in a lattice, and screw dislocations result when two lattice layers are ripped in reference to each other, which are depicted in Fig. 2.4.

![Schematic illustration of edge and screw dislocations in a crystal structure](image)

**Figure 2.4** Schematic illustration of edge and screw dislocations in a crystal structure [32].

A real crystal consists of number of small crystallites known as grains. Since the size of grains depend on several parameters, grain size can range from nanometers to millimeter across the lattice. Where two different grains meet with each other, they produce a grain boundary, which is different from both of them [32]. Microcracks are particularly insidious in single-crystal semiconductors because of the fragile nature and anisotropic mechanical properties of these materials [33]. A stacking fault is a one or two layer interruption in the stacking sequence of
atomic planes, and a change in the stacking sequence over a few atomic spacing produces a stacking fault whereas a change over atomic spacing produces a twin region [33].

Bulk defects are the biggest defects among the others and they are classified as voids, cracks, grooves, inclusions, and precipices. However, there are numerous reasons for the occurrence of the bulk defects and they are discussed in the analysis and results sections.

Table 2.2  Taxonomy of the crystallographic defects in reference to its dimension [30–32].

<table>
<thead>
<tr>
<th>Crystallographic defects</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0-dimensional (point) defects</strong></td>
</tr>
<tr>
<td>Substitutional</td>
</tr>
<tr>
<td>i. Dopant</td>
</tr>
<tr>
<td>ii. Contaminant</td>
</tr>
<tr>
<td><strong>1-dimensional (line) defects</strong></td>
</tr>
<tr>
<td>Screw dislocation</td>
</tr>
<tr>
<td><strong>2-dimensional (interfacial or planar) defects</strong></td>
</tr>
<tr>
<td>Twin plane</td>
</tr>
<tr>
<td><strong>3-dimensional (bulk or volume) defects</strong></td>
</tr>
<tr>
<td>Void (coalesced vacancy)</td>
</tr>
</tbody>
</table>

2.5. Summary

Besides difference in the stacking order of wurtzite and zinc blende structure, bond angle of the second nearest neighbors influences quantized lattice vibrations (spectroscopic selection rules), discussed in detail in section 3.2. Structural and optical properties of InN epilayers grown by High-Pressure Chemical Vapor Deposition are investigated in detail for varied growth parameters in Chapter 5.
2.6. References


CHAPTER 3

STRUCTURAL AND OPTICAL CHARACTERIZATION TECHNIQUES

3.1. Introduction

When electromagnetic (EM) light encounters matter, one of the following four things might happen. The EM light is partially or totally (i) reflected, (ii) scattered, (iii) transmitted, and (iv) absorbed. It is very well-known that all matter is composed of atoms; however, the nucleus is approximately 100000 times smaller than the atom itself. Therefore, when EM light (or waves) passes through matter, it is going through free space. On the other hand, it may have a chance to encounter the nucleus or an electron of an atom. The probability that the EM wave will pass through matter depends on numerous factors including the incoming EM wave’s energy, material composition, thickness, and density. This chapter briefly discusses spectroscopy and diffraction techniques to analyze optical, structural, and optoelectronic properties of semiconductor materials.

3.2. Optical Spectroscopy and Diffraction

As the low energy EM wave interacts with matter, it may transfer energy to the orbiting electrons of the material and perturb them periodically with some frequency, \( \nu \), [1,2]. The oscillation or perturbation of the electron cloud results in a periodic separation of positive and negative charges within the molecule, which is known as an induced dipole moment depicted in Fig. 3.1 [3]. The oscillation induced dipole moment is a source of EM radiation; thereby, resulting in scattered light. As high-energy EM wave such as X-rays and gamma rays interacts
with matter, it may transfer energy to orbiting electron or atomic nuclei of the material or it may be reflected from nucleus, which is known as diffraction. However, high–energy EM waves have enough energy to do more than just perturb the electrons. When high–energy EM waves encounter an atom, the result is an emission of an energetic electron from an atom or excitation of electrons.

Figure 3.1 Light scattering mechanism by an induced dipole moment [3].

In any multi-atom system such as crystalline solids, or macroscopic biological molecules in which the atoms are bonded to one another, each atom contributes at least one atomic orbital (one for Hydrogen) to the system of molecular orbitals in the system. To illustrate, for an N-atom system, there are at least N molecular orbitals and N energy levels, some of which may be degenerate (having the same energy level) produced by allowed combinations of the atomic orbitals [4]. Therefore, there are so many orbitals that the energy differences between them range from very small to enormous. Transition from one energy level to another energy level depends on numerous factors including conservation of momentum and energy and selection rules (i.e., allowed quantum number differences between two energy levels). In addition, in any multi-atom
system, the forces on both electrons and nuclei due to their electric charge are of the same order of magnitude. Thus, the change in their momenta as a result of these forces must also be equal.

Any multi-atom system is too complicated to evaluate perfectly its physical and chemical properties such as electronic, structural, and optical. Therefore, for simplicity consideration of an isolated molecule is a good place to start. An isolated molecule has various types of energy associated with different types of motion and intramolecular interaction. For example, a molecule possesses translational energy by the motion of the whole molecule in the space. It also possesses rotational energy due to rotation of the molecule around its center of gravity. Furthermore, it possesses vibrational energy due to periodic displacement of its atoms around their equilibrium (relaxed) positions. Since electrons are associated with atoms, an isolated molecule possesses electronic energy as well. Lastly, it possesses electronic spin and nuclear energies. Therefore, the incoming EM energy may have a large range of energies that can interact with various processes within molecules. This interaction results in translational, rotational, vibrational, electronic, nuclear, and spin energy changes within a molecule, all of which are quantized [5].

The nucleus is approximately 100000 times smaller than the atom itself, and there is a great difference in the mass of nucleus and orbiting electrons. Therefore, when nuclear motion (rotations and vibrations of atoms) is considered, the motion and perturbation of the electrons can be neglected. However, nuclear (atomic) motion is felt by electrons. This effect can be ignored because of two main reasons. First reason is that the electronic transitions (about $10^{-15}$ s) are quite fast compared to rotational transitions (about $10^{-10}$ s) and vibrational transitions ($10^{-13}$ s for diatomic complexes and $10^{-12}$ s for polyatomic complexes) [5]. Thus, the Born-Oppenheimer approximation [6] (i.e., adiabatic approximation) assumes for simplicity that the different types
of molecular energies associated with different internal motions are separable, and they can be treated independently by the following relation:

$$E_{\text{Total}} = E_{\text{Nuclear}} + E_{\text{Electron}}$$

$$= E_{\text{Vibration}} + E_{\text{Rotation}} + E_{\text{Translation}} + E_{\text{Electron}}.$$ (3.1)

The second reason is that an electronic transition usually requires the excitation of electrons by absorption of UV or visible EM radiation; whereas, rotational and vibrational transitions require UV-EM radiation, listed in detail in Table 3.1. Table 3.1 shows the various spectroscopic techniques that operate over different frequency regions within the EM spectrum. The high-energy requirement for electronic transitions leads to high transitional energy, which is approximately 50000 cm$^{-1}$ even for simplest case of a hydrogen molecule. The transitional energy of vibrations, however, requires excitations in the infrared region which range approximately from 100 to 4000 cm$^{-1}$ [7,8]. The transitional energy of rotations also require excitations in the far infrared region (from 10 to 100 cm$^{-1}$) and in the microwave region (from 0.1 to 10 cm$^{-1}$). Although these divisions of EM spectrum may not be justified universally, the neighboring regions are approximate and the molecular processes associated with each region are quite different. In general, neighboring spectroscopic processes are complementary techniques to each other. For instance, Electron Spin Resonance (ESR) spectroscopy can be employed in both the radio wave and microwave region. If Raman scattering and IR spectroscopies are employed together, they may explore all vibrational information in IR and far IR regions.
Table 3.1 Various spectroscopic processes and techniques for different excitation energies [5].

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Spectral region</th>
<th>Molecular effect</th>
<th>Spectroscopic process</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda &gt; 10$ cm</td>
<td>Radio waves</td>
<td>The energy changes arise from the reversal of spin of a nucleus or electron.</td>
<td>Nuclear Magnetic Resonance (NMR) Electron Spin Resonance (ESR)</td>
</tr>
<tr>
<td>$10$ cm $\geq \lambda &gt; 1$ cm</td>
<td>Microwaves</td>
<td>The energy changes arise from the reversal of spin of an electron.</td>
<td>Electron Spin Resonance (ESR)</td>
</tr>
<tr>
<td>$1$ cm $\geq \lambda &gt; 300$ µm</td>
<td>Microwaves</td>
<td>The energy changes arise from transitions to higher energy rotational levels of molecules.</td>
<td>Rotational spectroscopy</td>
</tr>
<tr>
<td>$300$ µm $\geq \lambda &gt; 30$ µm</td>
<td>Far infrared</td>
<td>The energy changes involve transitions between the rotational levels.</td>
<td>Far-infrared spectroscopy</td>
</tr>
<tr>
<td>$30$ µm $\geq \lambda &gt; 700$ nm</td>
<td>Infrared</td>
<td>The energy changes involve transitions between the vibrational and rotational levels of molecules.</td>
<td>Vibrational spectroscopy (specifically IR transmission and Raman spectroscopy)</td>
</tr>
<tr>
<td>$700$ nm $\geq \lambda &gt; 400$ nm</td>
<td>Visible</td>
<td>The energy changes involve valance electrons of molecules.</td>
<td>Electronic spectroscopy</td>
</tr>
<tr>
<td>$400$ nm $\geq \lambda &gt; 200$ nm</td>
<td>Ultra violet</td>
<td>The energy changes involve valance electrons of molecule.</td>
<td>UV-VIS spectroscopy</td>
</tr>
<tr>
<td>$200$ nm $\geq \lambda &gt; 10$ nm</td>
<td>Far UV</td>
<td>Dissociation of a molecule.</td>
<td>Far-UV spectroscopy</td>
</tr>
<tr>
<td>$10$ nm $\geq \lambda &gt; 10^{-2}$ nm</td>
<td>X-rays</td>
<td>The energy changes involve the inner electrons of an atom or a molecule.</td>
<td>X-ray: Diffraction, emission, and absorption</td>
</tr>
<tr>
<td>$10^{-2}$ nm $\geq \lambda$</td>
<td>γ-rays</td>
<td>Energy changes involve nuclear excitation.</td>
<td></td>
</tr>
</tbody>
</table>
Transitions between energy levels involve quantized energy, and they can be analyzed through spectroscopy [9]. Electronic spectroscopy involves the excitations of electrons by absorption of UV or visible EM radiation as depicted in Fig. 3.2. Since electronic energy levels are real and well-separated, the energy required to excite an electron to a higher level is quite high. Unless a semiconductor material possesses defect stages, the lowest energy transition between two electronic states usually generates the band gap (i.e., no electronic states exist in between) of the material. Since electronic spectroscopy requires a lot of energy, the radiation may either break bonds in organic compounds or transition between d orbitals split by the presence of ligand field in inorganic compounds. Electronic spectroscopy also obeys the Frank-Condon principle. It states that electrons respond much faster than nuclear motion; therefore, electronic excitations proceed without a change in the nuclear geometry. Each electronic energy level has numerous virtual vibrational energy levels associated with it.

Figure 3.2 Characteristic information acquired from electronic spectroscopy.
Similarly, each virtual vibrational energy level has numerous virtual rotational energy levels associated with it. However, translational energy levels are too close to each other for transitions to be observed spectroscopically. The separation of translational energy levels is many orders of magnitude smaller than $kT$ (0.0256 eV); therefore, possibility that translational transitions could be observed spectroscopically has been argued extensively. However, a new spectroscopic technique named Translational Energy Spectroscopy (TES) was described in the spectroscopic literature in 1995 [10]. It is clear that rotational and vibrational energy levels are separated far enough that they can be investigated by spectroscopic techniques. A spectrum is recorded by varying the energy of radiation incident on sample and monitoring how much radiation is absorbed or emitted for each energy state. From the vibrational and rotational transitions, dissociation energies, bond lengths, and force constants can be obtained.

In an $N$-atom system, besides $N$-molecular orbitals and $N$-energy levels, there are $3N$-molecular motions. Characteristic information regarding the molecular motions with respect to phase of molecule is listed in Table 3.2. In spectroscopic applications to condensed phases, vibrational transitions are detached from the rotational transitions. However, when analyzing liquid medium, a vibrational transition could be accompanied by rotational transition as well. Therefore, the resulting Raman feature could be a vibrational and rotational transition (also known as a roto-vibronic transition) [11]. In gas phase spectroscopy, rotational and vibrational molecular motions are observed and each investigation is in itself worthy of a Ph.D. dissertation.

On the other hand, recent studies have indicated that in analyzing semiconductor materials, it is quite possible to see roto-vibronic transitions due to gases in materials possessing $\text{H}_2$ as a trapped impurity [12].
Table 3.2 Molecular motions (i.e., translational, rotational, and vibrational) of a diatomic molecule.

<table>
<thead>
<tr>
<th>Motion</th>
<th>Symbolic</th>
<th>N-atomic DFs</th>
<th>Constant</th>
<th>Changing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Translation</td>
<td><img src="image" alt="Translation Diagram" /></td>
<td>3 DFs</td>
<td>Bond length and angle</td>
<td>Center of gravity</td>
</tr>
<tr>
<td>Rotation</td>
<td><img src="image" alt="Rotation Diagram" /></td>
<td>3 DFs</td>
<td>Center of gravity and bond angle</td>
<td>Angular momentum</td>
</tr>
<tr>
<td>Vibration</td>
<td><img src="image" alt="Vibration Diagram" /></td>
<td>3N-6</td>
<td>Center of gravity</td>
<td>Bond length and/or angle</td>
</tr>
</tbody>
</table>

In general, spectroscopy is a procedure of determining absorption, emission, or scattering of EM radiation with respect to varied energy. The two most important results are gathered from any spectrum are the position and intensity of a peak [13]:

i. The position of a peak in a spectrum is related to the difference in energy between two energy levels, $\Delta E$. 

ii. The intensity of the peak is related to the number of transitions that occur when radiation absorbed or emitted. This depends on:
   a. The population density of energy levels that obey a Boltzmann distribution.
   b. The selection rules for the particular form of the transition.

Molecular geometry, the relative positions of the atomic nuclei in the molecule, is one of the three constituents of molecular structure. The other two are electronic structure and intra molecular motion. Molecular geometry can be characterized by atomic coordinates if the molecule is fixed in a coordinate system or by so-called internal coordinates comprising of bond lengths, bond angles, and angles of internal rotation. Therefore, molecular geometry is the most important piece of structural information that can be sought in spectroscopic analyses.

The interaction of vibrational spectroscopy with at least some other techniques is illustrated in Fig. 3.3 from the point of vibrational spectroscopy. Since Raman and infrared (IR) spectroscopies are the two most employed vibrational spectroscopic techniques, these two methods are complementary to each other due to the common nature of the vibrational phenomena that they are based on. They are also complementary because of the differing nature of the measuring techniques involved and their specific usefulness in different structural and methodological aspects [11]. The complementarity of Raman and IR spectroscopy results from the different selection rules, listed in Table 3.3. Selection rules determine the appearance in the Raman and IR spectrum of a band corresponding to a given vibration of the molecule [7,8].
In sections 3.2.1 and 3.2.2, we discuss in detail Raman scattering and infrared (IR) reflection spectroscopies, respectively. The remainder of the chapter is organized as follows. Following a detailed description of the Raman spectroscopy, we discuss in detail the vibrational properties of the hexagonal and cubic structures using group theory symmetry. We then discuss the infrared (IR) spectroscopies. After discussing X-ray diffraction in section 3.2.3, we will conclude this chapter with a summary of optical characterization techniques.
### Table 3.3  Infrared and Raman selection rules for diatomic rotations and vibrations.

<table>
<thead>
<tr>
<th>Type of transition</th>
<th>Symbolic</th>
<th>Infrared</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rotation†</strong></td>
<td>![Rotation Symbol]</td>
<td>1. The energy of photon matches the energy difference of rotational levels: $\hbar \nu = \Delta E_{rot}$</td>
<td>1. The energy difference of the incident and scattered photon matches the energy difference of rotational levels: $\hbar \nu_i - \hbar \nu_s = \Delta E_{rot}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. A permanent dipole moment is necessary</td>
<td>2. A permanent dipole moment is unnecessary</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Transitions occur between neighboring rotational levels: $\Delta J = 0, \pm 1$</td>
<td>3. $\Delta J = 0, \pm 1, \pm 2$</td>
</tr>
<tr>
<td><strong>Vibration</strong></td>
<td>![Vibration Symbol]</td>
<td>1. The energy of photon matches the energy difference of vibrational levels: $\hbar \nu = \Delta E_{vib}$</td>
<td>1. The energy difference of the incident and scattered phonon matches the energy difference of vibrational levels: $\hbar \nu_i - \hbar \nu_s = \Delta E_{vib}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. The dipole moment changes during vibration: $\left( \frac{\partial \mu}{\partial \theta} \right) \neq 0$</td>
<td>2. The polarizability changes during vibration: $\left( \frac{\partial \alpha}{\partial \theta} \right) \neq 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. $\Delta \nu = +1, +2, +3, \ldots$</td>
<td>3. $\Delta \nu = \pm 1, \pm 2, \pm 3, \ldots$</td>
</tr>
</tbody>
</table>

†It is usually observed in liquids; however, in solids they are almost damped.
3.2.1. Raman Spectroscopy

Scattering by a multi-atom system provides crucial information about the energies of electron states and electron-phonon interactions. Raman scattering provide unique information on the electromagnetic forces (i.e., force constants) responsible for chemical bonding. Therefore, Raman spectroscopy provides identification of the material (force constant), crucial information about phonon frequencies, energy of vibrational transitions, phonon-electron information, defects, mechanical strain, crystal orientation, and temperature [14]. In 1928, Chandrasekhara Venkata Raman experimentally showed and briefly described the diffraction of light from molecules [15], which ultimately led to his discovery. Therefore, he won the 1930 Nobel Prize in Physics for his work about molecular diffraction of light.

The interaction of incident EM radiation with electrons in a multi-atom system leads to exchange of energy in two ways; elastic or inelastic [16]. The elastic scattering process of radiation is called Rayleigh scattering, in which a photon interacts with an electron, polarizing the electron cloud and raising it to higher vibrational (vibronic) energy level. An electron, then, drops back to previous vibronic energy level, releasing a photon. The energy of incident photon equals to that of released (i.e., scattered) photon. If the interaction is inelastic, i.e., the energy of incident and scattered photons are different, the scattering process is called Raman scattering. There are two types of Raman scattering, Stokes scattering and anti-Stokes scattering [16].

i. In Stokes scattering, the electron decays from lower vibronic energy state to higher energy state than its original state, in which case the electron’s energy increases and the emitted photon has less energy and a longer wavelength than that of the absorbed photon.
ii. In anti-Stokes scattering, the electrons decay from higher vibronic energy state to lower vibronic energy state than its original state, in which case the electron’s energy decreases and the emitted photon possesses higher energy and a shorter wavelength than that of the absorbed photon.

Rayleigh, Stokes, and anti-Stokes scattering processes in Raman scattering are demonstrated in Fig. 3.4. Raman scattering is very weak and special optical elements are needed to eliminate strong Rayleigh scattering, because only about 1 in $10^7$ photons undergo Stokes scattering. The amount of anti-Stokes scattering is even less than Stokes scattering. This is mainly due to population of the vibronic energy levels, which obeys the Boltzmann distribution:

$$N \propto \exp \left( -\frac{E}{k_B T} \right). \quad (3.2)$$

Therefore, there are fewer electrons in the higher vibronic energy levels. The intensity ratio of anti-Stokes and Stokes scattering can be expressed in terms of difference between vibronic energy levels:

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = \exp \left( -\frac{\Delta E}{k_B T} \right). \quad (3.3)$$

Raman spectroscopy, however, is a challenging optical spectroscopy due to the difficulty of discrimination between inelastically scattered photons and elastic ones. Thus, an appropriate selection of instrumentation and optical parts is crucial. The essential components of a Raman spectrometer are a light source, an optical filter, a spectrometer, and a detector.
A monochromatic laser light source of very small beam diameter is required. The small size of the beam diameter not only increases spectral resolution but also narrows the investigated (probing) area. The excitation wavelength should be carefully selected by considering band gap, thickness, and resonance and fluorescence characteristics of the investigated material.

i. Ultraviolet laser is usually preferred for:
   a. Catalysts for resonance Raman scattering with an excitation of 244 nm.
   b. Wide bandgap semiconductors with an excitation of 325 nm.

ii. Visible laser is usually preferred for:
   a. Semiconductors with an excitation of either 488 or 532 nm.
   b. Minerals with an excitation in the range of 488 and 532 nm.
   c. Corrosion related compounds with an excitation of 632 nm.

iii. Near infrared laser is usually preferred for:
   a. Polymers and macromolecules with an excitation of 785 nm.
b. Medical and viral investigation purposes with an excitation of 830 nm.

An optical filter is necessary to eliminate elastically scattered photons from the inelastic ones. Improvements in optical technology have led to the development of a notch or edge filter with 99.99% cut off success. For instance,

i. A long-wave pass (LWP) edge filter is used for Stokes scattering.

ii. A short-wave pass (SWP) edge filter is used for anti-Stokes scattering.

iii. A notch filter enables both Stokes and anti-Stokes scattering.

A spectrometer is utilized to analyze the spectral behavior of the scattered radiation. A spectrometer can have a single, double, or even triple monochromator with a high density diffraction grating. The groove density of a grating has influence on resolution; for instance, one nm groove in the spectrometer is equivalent to:

i. 160 cm$^{-1}$ Raman shift at 250 nm laser excitation.

ii. 94 cm$^{-1}$ Raman shift at 325 nm laser excitation.

iii. 38 cm$^{-1}$ Raman shift at 514 nm laser excitation.

iv. 16 cm$^{-1}$ Raman shift at 785 nm laser excitation.

High-sensitivity radiation detection is essential. Charge-Coupled Device (CCD) detector arrays are generally used to optimize the optical integration time in the investigated spectral regime.

Raman spectroscopy is a valuable tool for characterization of various matters such as semiconductor materials, chemical complexes, and biological agents. It also provides information about the intramolecular forces (force constants) acting between the atoms in a molecule. Every material exhibits a characteristic Raman spectrum, which can be considered as
its fingerprint. Therefore, the information that can be acquired from Raman spectroscopy is crucial. The spectroscopic information can be extracted from a conventional Raman spectrum is depicted in Fig. 3.5 and summarized in Table 3.4. Raman spectroscopy, mainly, provides an identification of the material (i.e., force constant), crucial information about phonon frequencies, energy of vibrational transitions, phonon-electron information, defects, mechanical strain (plastic and elastic deformation), crystal orientation, and temperature [14].

![Figure 3.5](image)

Figure 3.5 Information content of a conventional Raman scattering spectrum.

<table>
<thead>
<tr>
<th><strong>Raman peak</strong></th>
<th><strong>Information</strong></th>
<th><strong>Corresponds</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Position</strong></td>
<td>Characteristic frequency</td>
<td>Identification of a material</td>
</tr>
<tr>
<td><strong>Shift</strong></td>
<td>Changes in frequency</td>
<td>Amount of deformation</td>
</tr>
<tr>
<td><strong>Height</strong></td>
<td>Number of transitions</td>
<td>Population of energy levels</td>
</tr>
<tr>
<td><strong>Profile/width</strong></td>
<td>Line-profile and linewidth</td>
<td>Domain size</td>
</tr>
<tr>
<td><strong>Polarization</strong></td>
<td>Selection rules</td>
<td>Crystal orientation</td>
</tr>
</tbody>
</table>
Raman spectroscopy yields information about the symmetry and frequencies of the vibrational modes in the crystals. Variations in phonon mode frequencies can be used to study the crystal quality and its structure. In an ordered crystal, the cation-anion bond distance is constant throughout the various lattice planes. The force constant is proportional to the strength of the bond linking cation and anion atoms. The chemical bonds in a crystal can be represented as a spring undergoing simple harmonic motion with a frequency given by:

\[ \nu = \frac{\hbar}{2\pi} \left( \frac{k}{\mu} \right)^{\frac{1}{2}} \]  (3.4)

where \( k \) is the force constant of the chemical bond and \( \mu \) is the reduced mass of the cation and anion atoms. Vibrational energies are quantized and given by

\[ E(\nu) = \left( \nu + \frac{1}{2} \right) \hbar \nu \]  (3.5)

where \( \nu \) is the vibrational quantum number (\( \nu = 0, 1, 2, \ldots, \infty \)). The Raman line frequency (seldomly expressed in terms of energy) is given by \( (E_f - E_i)/hc = \nu_{\text{vib}} \) in terms of \( \text{cm}^{-1} \), where \( E_f \) and \( E_i \) are the energy of the final and initial energy states, respectively. Therefore, the well-defined frequencies of the Raman lines can be utilized as a material identification. For instance, the composition percentage of ternary compounds can be evaluated from Raman spectroscopy of its binary compounds.

Due to perturbed cation-anion distances caused by impurities, mechanical strain, thermal contradiction, and hydrostatic pressure, shifting of the Raman peak position from the ideal position is observed. Since impurities, described in detail in section 2.3, can be present within the crystal structure in various forms, their influence on the Raman spectrum is also varied. In Raman spectroscopy defects can be observed by means of scattering of either internal electronic
excitations or localized vibrational modes. Several studies were reported on the effect of mechanical strain on the Raman peak profile for various semiconductor materials such as Si, GaN [14,18,19]. In general, compressive (pushing) biaxial ($\sigma_{xx} + \sigma_{yy}$) stress in the growth plane will result in an increase of Raman frequency, while tensile (pulling) stress results in a decrease of Raman frequency [20]. For instance GaN [21] shifts 4.4 cm$^{-1}$ and silicon [22] 2 cm$^{-1}$ per GPa strain. The thermal and hydrostatic pressure dependence of Raman spectroscopy gives crucial information about the elastic (reversible) deformation of semiconductor materials. Thermal contraction of bonding results in shifting of the Raman peak position towards the higher frequencies, while thermal expansion results in a decrease. In general, the influence of the hydrostatic pressure on the Raman peak positions is larger for epitaxial films than for bulk materials [19]. Increased hydrostatic pressure in the material leads to a shift towards higher Raman frequencies and an increase in the compressive strain.

Numerous factors have an impact on the Raman intensity, which is unique to each Raman instrument. Therefore, relative Raman intensity comparisons of different Raman bands measured with the same instrumentation are required. Since Raman spectroscopy involves a scattering mechanism, it also obeys light scattering theory in which scattering intensity is directly proportional to $(1/\lambda)^4$. Therefore, unless there is a resonance barrier, the Raman intensity of a green laser with an excitation of 532 nm results in scattering that is twice as intense as that for a red laser with an excitation of 632 nm. Raman intensity is also dependent on the number of atoms populating the initial state in the transition. By employing Eq. 3.2, the vibrational population density of lowest level is almost 100 times higher than that of second lowest level. In some cases, the peak height can be changed by a broadening mechanism, but area still unchanged as the total number of species is constant in the scattering. Finally, Raman
intensity/area gives clues about concentration of the solution in aqueous mediums and the thickness of the epilayers in semiconductor materials. Also, a comparison of two Raman band intensities yields the relative phonon absorption coefficients with respect to each other.

In the Raman spectroscopy, line shape profile and line width provide the most crucial information for quantitative analysis. When a molecule is vibrating, it dynamically interacts with its surrounding molecules. Therefore, each molecule can interact with its surrounding molecules in a slightly different way from others. The observed line shape is the sum of these individual molecular interactions. The relaxation time of a molecule from the excited level to ground level is called the amplitude correlation time ($\tau_a$). The coherent vibration time of molecules is called the coherence lifetime ($\tau_c$). There are two cases either $\tau_a \ll \tau_c$ or $\tau_a \gg \tau_c$.

i. In the first case, where $\tau_a \ll \tau_c$, the excited molecule relaxes before incoherence dominates. Then, the distribution of the Raman line shape has a Gaussian line-shape (i.e., heterogeneous) profile [23].

ii. In the second case, where $\tau_a \gg \tau_c$, the incoherence starts very quickly so dephasing is the dominant energy loss channel. Then, the distribution of the Raman line shape has a Lorentzian line-shape (i.e., homogeneous) profile [23].

Line widths are usually reported as full width at half maximum (FWHM). The line width is inversely proportional to the effective lifetime ($\tau$). Therefore, long loss of the excitation (long $\tau$) results in narrow peak indicating a well-ordered material. In addition, linewidth broadening of phonon modes is considered to be due to anharmonic coupling between different phonon modes. Although most Raman line shapes are symmetric, asymmetric broadening of the Raman spectra is due to either spatial inhomogeneity or phonon-electron contributions.
When a vibration changes the polarizability \((\alpha)\) of a molecule, it is active in the Raman scattering. This occurs when vibration changes symmetry of polarization density (i.e., \(\partial \alpha/\partial \vartheta = 0\)). Since Raman spectroscopy records changes in the molecular polarizability, the polarization of the incoming and scattered light has a paramount impact on the Raman spectroscopy. Polarized Raman spectroscopy probes information about molecular orientation and symmetry of the molecular vibrations, in addition to the general information provided from conventional Raman spectroscopy. If the parallel polarization of the scattered light is as intense as perpendicular polarization, the Raman line is depolarized. The depolarization factor, \(\rho\), is calculated for a particular peak given by:

\[
\rho = \frac{I_{\text{perpendicular}}}{I_{\text{parallel}}},
\]

\((3.6)\)

\(I_{\text{perpendicular}}\) and \(I_{\text{parallel}}\) are the Raman peak intensities of the perpendicular and parallel polarization geometry. If \(\rho < 0.75\), it is considered as polarized Raman spectroscopy. Polarized Raman measurements usually made from parallel to perpendicular polarization of either incident laser light or scattered light by rotating a polarizing optical element. Polarized Raman spectroscopy, which allows measurements of the molecular orientation and composition, is widely used in the study of crystal systems.

The polarization dependence of the phonon modes and Raman shift in the any crystal system has a great importance. For instance, the polarization dependence of the anisotropically strained GaN epilayers having ratio of strains as low as \(6 \times 10^{-3}\) can be studied by polarized Raman peaks [24]. Since polar phonons, discussed in detail in sections 3.2.1.1 and 3.2.1.2, split into longitudinal and transverse optical branches, the polarization dependency of the optical phonons is widely investigated by polarized Raman scattering [25].
Vibrational selection rules, listed in Table 3.3, are the first constraint for a possible vibrational transition from one vibronic level to another. Although both the polarizability and dipole moment depend on the vibrational motion of the molecule, either, in general, polarizability or dipole moment of the molecule changes during the same molecular vibration. The variation of the dipole moment or the polarizability responsible for the vibrational activity in the given spectrum relates to the molecule as a whole and not to its particular elements. For this reason, the symmetry of the molecule and the symmetry of vibration are the key point for the spectroscopic activity of a vibration. Therefore, the concept of any spectroscopic activity is directly related to overall symmetry of molecule. For instance, hexagonal and cubic structures of group-III nitrides exhibit quite different Raman and IR spectra, although both have the same bond length (force constant) and tetrahedral bonding geometry.

In order to determine crystal structure, numerous of techniques such as X-ray diffraction methods, vibrational, electronics and magnetic resonance spectroscopies are employed. The origin of the understanding of crystal structure is provided by quantum mechanics. The ultimate aim of any spectroscopic study is to understand the transitions involved and to interpret the results in terms of the crystal structure. The following two subsections of this chapter discuss the effects of the hexagonal and cubic structural forms on the Raman and IR (vibrational) spectroscopies, respectively.

3.2.1.1. **Hexagonal (Wurtzite) Structure**

Since wurtzite structure is discussed in more detail in section 2.2, here its effect on Raman spectroscopy will be discussed. Symmetric structures exhibit fewer peaks in the vibrational spectrum than the asymmetric structures. Therefore, the structural symmetry is a
consideration for a quantum mechanics [5]. The structural symmetry of crystals is defined in geometric terms. In group theory, five fundamental symmetry operations are used to specify crystal symmetry as following combinations:

i. The identity operation, \( E \), is a symmetric operation. It rotates a molecule about 0° (or 360°) along an axis passing through its center. Thus, it leaves the molecule unchanged.

ii. The rotation operation, \( C_n \), rotates a molecule along an axis passing through its center by an angle \( 2\pi/n \) and if the fixed is indistinguishable from the original, then an n-fold rotational symmetry exists, where \( n \) is an integer.

iii. The reflection operations, \( \sigma_{xz}, \sigma_{yz}, \sigma_{dh}, \) and \( \sigma_h \), are reflection processes. The reflection of a molecule around an infinite plane passing through a center produces a new molecule configuration, which is equivalent to previous configuration. The subscript letter(s) represent the reflection plane orientation.

iv. The inversion operation or center of symmetry is denoted by the symbol \( i \). A molecule having a center of inversion is called a centro-symmetric molecule. In such a molecule, for every atom there is another atom situated on the other side of center of inversion.

v. The rotation-reflection operation, \( S_n \), is a rotation around an axis by an angle \( 2\pi/n \) followed by a reflection in a plane perpendicular to the axis. This operator can be expressed in terms of other operators.

\[
S_n \times S_n = S_n^2 = (C_n \times \sigma_n)^2 = C_n^2 \times \sigma_n^2 = C_n^2 = C_n \times C_n
\]

(3.7)

Symmetry operations of an hexagonal structure are shown in Fig. 3.6. Besides the identity operation, \( E \), an hexagonal structure has a rotational symmetry for angles of \( \pm 1/3 \ pi \)
radian, where \( n = 1, 2, 3, 4, \) and 5. It also possesses six mirror planes in which three of them pass through opposite faces of the hexagon and the remaining three pass through opposite vertices of the hexagon. Although five rotations are the same type of operation, they belong to different subgroups \([26]\). Due to the diatomic arrangement of the hexagonal structure, each rotation repeats itself in every 120° rotation, but not in 60° increments. Therefore, five of the rotations belong to three subgroups. The two different mirror planes \( \sigma_v \) and \( \sigma_d \) belong to different classes. Hence, there are total of six different operational groups in the hexagonal structure.

Figure 3.6  Symmetry element representations of a wurtzite structure.

Character tables are very important in chemistry because crucial chemical information is related to particular symmetry properties, such as whether a transition between two states is allowed or not. The relations between symmetry operations and molecular spectroscopic techniques, such as NMR, IR and Raman spectroscopy, are usually discussed in terms of character tables. The character table for the \( C_{6v} \) point group symmetry is given in Table 3.5.
The Schoenflies symbol of the group is stored in the upper left corner and mode representations of molecular motions are listed in the first column of the character table. The next columns indicate the symmetry elements (conjugacy classes) for the group and remaining columns are assigned for the basis functions (spectroscopically active components). Each row indicates irreducible representations. Spectroscopy active components have the same symmetry properties as the atomic orbitals with the same names. \( R_x, R_y, \) and \( R_z \) behave as rotation about \( x, y, \) and \( z \), respectively [27]. They are correlated to the orbital angular momentum of the molecule. Their irreducible representations are derived from NMR spectroscopy. The \( p \) orbitals (\( p_x, p_y, \) and \( p_z \)) behave as \( x, y, \) and \( z \), and their dipole moment components are expressed as \( \mu_x = -ex, \mu_y = -ey, \) and \( \mu_z = -ez \). Since bond lengths behave as \( x, y, \) and \( z \), their irreducible representations relate to IR spectroscopy [27,28]. In addition, the dipole moment governs the strongest single phonon absorption and emission transitions, which enable us to understand electronic spectroscopy. Translations of the gas molecules also behave as \( x, y, \) and \( z \). The \( d \) orbitals (\( d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, \) and \( d_{z^2} \)) are related to \( xy, xz, yz, x^2 - y^2, \) and \( z^2 \). Weak electric quadrupole transitions become important in solid state NMR, discussed in the last paragraph of section 3.2. Their irreducible representations relate to Raman spectroscopy. Binary products may also indicate a possibility of two phonon transitions [29].

The \( f \) orbitals (\( d_{e^2}, d_{d^2}, d_{d^2}, d_{x^2}, d_{x^2}, d_{y^2}, d_{3(x^2-y^2)}, d_{(x^2-3y^2)} \) and \( d_{y(3x^2-y^2)} \)) depend upon \( z^3, xz^2, yz^2, \) \( xz, z(x^2 - y^2), x(x^2 - 3y^2), \) and \( y(3x^2 - y^2) \), and their irreducible representations have higher order contributions to numerous spectroscopic techniques. Finally, \( s \) orbitals represented as \( x^2 + y^2 + z^2 \) are intact in all circumstances, and thus they are neglected in spectroscopy.

The character table for the \( C_{6v} \) point group symmetry indicates six conjugacy classes, listed as \( E, C_6(z), C_3(z), C_2(z), \sigma_v, \) and \( \sigma_d \), and symmetry elements for each irreducible representation are given in the first column. The next columns indicate the symmetry elements (conjugacy classes) for the group and remaining columns are assigned for the basis functions (spectroscopically active components). Each row indicates irreducible representations. Spectroscopy active components have the same symmetry properties as the atomic orbitals with the same names. \( R_x, R_y, \) and \( R_z \) behave as rotation about \( x, y, \) and \( z \), respectively [27]. They are correlated to the orbital angular momentum of the molecule. Their irreducible representations are derived from NMR spectroscopy. The \( p \) orbitals (\( p_x, p_y, \) and \( p_z \)) behave as \( x, y, \) and \( z \), and their dipole moment components are expressed as \( \mu_x = -ex, \mu_y = -ey, \) and \( \mu_z = -ez \). Since bond lengths behave as \( x, y, \) and \( z \), their irreducible representations relate to IR spectroscopy [27,28]. In addition, the dipole moment governs the strongest single phonon absorption and emission transitions, which enable us to understand electronic spectroscopy. Translations of the gas molecules also behave as \( x, y, \) and \( z \). The \( d \) orbitals (\( d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, \) and \( d_{z^2} \)) are related to \( xy, xz, yz, x^2 - y^2, \) and \( z^2 \). Weak electric quadrupole transitions become important in solid state NMR, discussed in the last paragraph of section 3.2. Their irreducible representations relate to Raman spectroscopy. Binary products may also indicate a possibility of two phonon transitions [29].

The \( f \) orbitals (\( d_{e^2}, d_{d^2}, d_{d^2}, d_{x^2}, d_{x^2}, d_{y^2}, d_{3(x^2-y^2)}, d_{(x^2-3y^2)} \) and \( d_{y(3x^2-y^2)} \)) depend upon \( z^3, xz^2, yz^2, \) \( xz, z(x^2 - y^2), x(x^2 - 3y^2), \) and \( y(3x^2 - y^2) \), and their irreducible representations have higher order contributions to numerous spectroscopic techniques. Finally, \( s \) orbitals represented as \( x^2 + y^2 + z^2 \) are intact in all circumstances, and thus they are neglected in spectroscopy.

The character table for the \( C_{6v} \) point group symmetry indicates six conjugacy classes, listed as \( E, C_6(z), C_3(z), C_2(z), \sigma_v, \) and \( \sigma_d \), and symmetry elements for each irreducible representation are given in the first column. The next columns indicate the symmetry elements (conjugacy classes) for the group and remaining columns are assigned for the basis functions (spectroscopically active components). Each row indicates irreducible representations. Spectroscopy active components have the same symmetry properties as the atomic orbitals with the same names. \( R_x, R_y, \) and \( R_z \) behave as rotation about \( x, y, \) and \( z \), respectively [27]. They are correlated to the orbital angular momentum of the molecule. Their irreducible representations are derived from NMR spectroscopy. The \( p \) orbitals (\( p_x, p_y, \) and \( p_z \)) behave as \( x, y, \) and \( z \), and their dipole moment components are expressed as \( \mu_x = -ex, \mu_y = -ey, \) and \( \mu_z = -ez \). Since bond lengths behave as \( x, y, \) and \( z \), their irreducible representations relate to IR spectroscopy [27,28]. In addition, the dipole moment governs the strongest single phonon absorption and emission transitions, which enable us to understand electronic spectroscopy. Translations of the gas molecules also behave as \( x, y, \) and \( z \). The \( d \) orbitals (\( d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, \) and \( d_{z^2} \)) are related to \( xy, xz, yz, x^2 - y^2, \) and \( z^2 \). Weak electric quadrupole transitions become important in solid state NMR, discussed in the last paragraph of section 3.2. Their irreducible representations relate to Raman spectroscopy. Binary products may also indicate a possibility of two phonon transitions [29].

The \( f \) orbitals (\( d_{e^2}, d_{d^2}, d_{d^2}, d_{x^2}, d_{x^2}, d_{y^2}, d_{3(x^2-y^2)}, d_{(x^2-3y^2)} \) and \( d_{y(3x^2-y^2)} \)) depend upon \( z^3, xz^2, yz^2, \) \( xz, z(x^2 - y^2), x(x^2 - 3y^2), \) and \( y(3x^2 - y^2) \), and their irreducible representations have higher order contributions to numerous spectroscopic techniques. Finally, \( s \) orbitals represented as \( x^2 + y^2 + z^2 \) are intact in all circumstances, and thus they are neglected in spectroscopy.
representation, listed as $A_1$, $A_2$, $B_1$, $B_2$, $E_1$, and $E_2$. The subscripts one and two represent symmetric and antisymmetric vibrations to the perpendicular $C_2$ axis, respectively [27]. Since characters in the column of operation $E$ indicate the degeneracy of orbitals, symmetry elements of the group are classified as singly degenerate, $A_1, A_2, B_1, \text{ and } B_2$, and doubly degenerate, $E_1$ and $E_2$, modes. The character table, spectroscopically, indicates that $A_1, E_1$, and $E_2$ symmetries are polarizable, i.e., possess quadratic basis functions, so they are Raman active. Since $A_1$ and $E_1$ symmetries possess symmetry of translations, i.e., $p$ orbitals, they are IR active as well. $A_1$ and $E_1$ symmetries of translation transform as $d$ orbitals, they are polar modes and exhibit longitudinal (L) and transverse (T) splitting. Since $A_2, B_1, \text{ and } B_2$ symmetries lack translational symmetry and higher order terms, they are both silent in Raman and in IR.

However, due to the rotational activity of $E_1$ symmetry, the $E_1$ vibrational transition could be accompanied by a rotational transition (roto-vibronic transition) [8] in the hexagonal liquid mediums and materials [12] possessing H$_2$ trapped impurity.
### Table 3.5  Character table and symmetry operations of the $C_{6v}$ point group symmetry.

<table>
<thead>
<tr>
<th></th>
<th>$C_{6v}$</th>
<th>Symmetry elements for the group</th>
<th>Spectroscopy active component</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$\Gamma_1$</td>
<td>$\Delta_1$</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$\Gamma_2$</td>
<td>$\Delta_1'$</td>
<td>1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$\Gamma_3$</td>
<td>$\Delta_2$</td>
<td>1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$\Gamma_4$</td>
<td>$\Delta_2'$</td>
<td>1</td>
</tr>
<tr>
<td>$E_1$</td>
<td>$\Gamma_5$</td>
<td>$\Delta_3$</td>
<td>2</td>
</tr>
<tr>
<td>$E_2$</td>
<td>$\Gamma_6$</td>
<td>$\Delta_3'$</td>
<td>2</td>
</tr>
</tbody>
</table>

Note: Representation of the modes by Mulliken (M) notation have become almost standard in chemistry since 1980 but other forms of Bethe (B) and Bouckaert (BSW) notations are still used in the physics journals.
Since there are four atoms per wurtzite primitive cell, shown in Fig. 2.2b, a four-atom system belongs to \( C_{6v}^4 \) space group symmetry. The Symmetry Adapted Linear Combinations (SALC) of a molecule can help to determine binding symmetries. To construct SALC, identification of the point group of the molecule is essential to determine the nature of the modes [32].

The first step in determining stretching modes of a molecule is to add the characters contained in the \( x, y, \) and \( z \) rows (i.e., symmetry of translations or \( p \) orbitals) to obtain the total reducible representation, \( \Gamma_{xyz} \), of the \( xyz \) coordinates listed in the first row of Table 3.6. The next step is to investigate the number of atoms that remain unchanged when each symmetry element of group is applied, \( \Gamma_{uma} \). Last step is to multiply \( \Gamma_{xyz} \) and \( \Gamma_{uma} \) which gives the total reducible representation of the molecule (\( \Gamma_{\text{Total}} \)).

Table 3.6  Reducible representation of symmetry operations in a wurtzite structure.

<table>
<thead>
<tr>
<th>( C_{6v}^4 )</th>
<th>E</th>
<th>( 2C_4(z) )</th>
<th>( 2C_3(z) )</th>
<th>( C_2(z) )</th>
<th>( 3\sigma_v )</th>
<th>( 3\sigma_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_{xyz} )</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \Gamma_{uma} )</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>( \Gamma_{\text{Total}} )</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

For complex structure with a large reducible representation, identification of the irreducible component representation is quite difficult. However, the reduction of large dimension into a finite order enables us to understand the allowed motions by employing the following equation, i.e., reduction formula [33].
\[ n_i = \frac{1}{h} \sum_{r} \chi_i g_c \chi_r \] (3.8)

where \( n_i \) is the number of times the \( i^{th} \) irreducible representation occurs in the representation, \( h \) is the order of groups, i.e., the number of operations in the group, \( \chi_i \) is the character of the irreducible representation, \( g_c \) is the number of symmetry operations, and \( \chi_r \) is the character of the particular reducible representation for a particular symmetry element. Hence, using the Eq. 3.8 (i.e., reduction formula) and \( \Gamma_{\text{Total}} \) elements of Table 3.6, the irreducible representation of wurtzite structure for each mode is reconstructed. Accordingly, the irreducible representation of the quantized lattice motions in the wurtzite structure is summarized as:

\[ \Gamma_{\text{irreducible}} = 2A_1 + 2B_1 + 2E_1 + 2E_2. \] (3.9)

Since wurtzite structure has four atoms per primitive cell, there must be 12 energy states regarding lattice motions which are described with an irreducible representation. As stated in the character table discussion of the \( C_{6v} \) point group symmetry, \( B_1 \) is silent in any spectroscopy. Hence, the spectroscopically allowed lattice vibrations are expressed as:

\[ \Gamma_{\text{irreducible}} = 2A_1 + 2E_1 + 2E_2. \] (3.10)

A phonon is a quantized collective excitation in a periodic system and is usually referred to as a quasiparticle [34]. It also represents an excited state in the quantum mechanical quantization of the modes of vibrations of elastic structures of interacting particles. Phonons play a major role in many of the physical properties of solids, including a material’s thermal and electrical conductivities. Therefore, the study of phonons is an important subject in solid-state physics. In solid-state materials, there are four different normal vibrations of the lattice depicted in Fig. 3.7. In the acoustical branch, adjacent atoms move in phase with respect to each other and they move out of phase in the optical branch. These two branches further split into longitudinal
and transverse vibration normal to incoming light wave. Because of four quantized vibrations within the lattice, there exists four quantum mechanical quantizations one for each, namely, transverse acoustic (TA), longitudinal acoustic (LA), transverse optic (TO), and longitudinal optic (TO). Optical phonons have energy of ~33 meV at room temperature (300 K), however acoustic phonons have one or two orders less energy than optical vibrations. Therefore, the three acoustic and seven spectroscopically allowed optical phonon mode symmetries (i.e., lattice vibrations) of the wurtzite crystal are:

$$\Gamma_{\text{Acoustic}} + \Gamma_{\text{Optical}} = (A_1 + E_1) + (A_1 + E_1 + 2E_2).$$

(3.11)

Figure 3.7 Schematic illustrations of lattice vibrations. (a) Relaxed positions of the atoms, (b) transverse-acoustic, (c) longitudinal-acoustic, (d) transverse-optic, and (e) longitudinal-optic phonons.

It is important to know that atoms on the lattice vibrate along different directions within the crystal. Figure 3.8 depicts the scheme of vibrational modes in the wurtzite structure [35]. The $A_1$ and $B_1$ modes have atomic displacements parallel to $c$-axis, whereas the $E$ modes have atomic
displacements perpendicular to \( c \)-axis. Since \( A_1 \) and \( E_1 \) modes are polar, they exhibit longitudinal-optic (LO) and transverse-optic (TO) splitting. This is mainly due to the long-range Coulomb interaction with vibrations which leads to the energy differences between phonons polarized longitudinally and transverse in the propagation direction of incident light, depicted in Fig. 3.9 [36]. For instance, the \( A_1(LO) \) mode is polarized along the \( c \)-axis (\( z \)), while \( E_1(LO) \) mode is polarized perpendicular to \( c \)-axis (either in \( -x \) or \( y \)).

![Displacements for Raman (phonon) modes in a wurtzite structure](image1)

**Figure 3.8** Schematic displacements for Raman (phonon) modes in a wurtzite structure, where big and small spheres denote In and N atoms, respectively.

![Polar phonon in a polar material](image2)

**Figure 3.9** Polar phonon in a polar material, where propagation of incident light is along the \( z \)-axis [36].
In Raman spectroscopy, scattering intensities and selection rules can be calculated from Raman intensity equation, expressed as:

$$I_{\text{Raman}} \approx \sum |e_i \cdot R_{\text{Raman}} \cdot e_s|^2$$

(3.12)

where $e_i$ and $e_s$ are polarization vectors of the incident and scattered radiation, respectively, and $R_{\text{Raman}}$ is the complex second ranking Raman tensor [37]. The tensor representations of the vibrational modes in a wurtzite structure are given in Appendix A.1 [37].

Since $E$ is a doubly degenerate mode, the Raman tensor of the $E_2$ is to be degenerate as well. Therefore, it can be split into two modes, namely $E_2$(low) and $E_2$(high). If orientation of the crystal axis and polarizations of incoming and scattered light are known, Raman scattering intensity for each vibrational mode is calculated from Eq. 3.12. The result might yield an angle dependent selection rules for symmetry allowed Raman modes, listed in Table 3.7. In general, Porto notation [38] is the most common notation to describe Raman scattering geometry, e.g., $y(x, z)\bar{y}$, where the symbols outside the parenthesis ($y$ and $\bar{y}$) denotes propagation of the incoming and scattered light, respectively. Similarly, the symbols inside the parenthesis ($x$ and $z$) denote polarization stage of the incoming and scattered light, respectively. In Raman scattering terminology, parallel (i.e., backscattering) and perpendicular geometries denote parallel and perpendicular polarization in reference to the polarization of the incident light. For instance, when polarized light from the laser source propagates parallel to the $\hat{z} \parallel c$ axis, and thus onto $c$-plane surface, and scattered light propagates parallel to $\hat{z} \parallel c$ axis, the resulting Raman intensity becomes if incoming and scattered light are co-polarized,
\[ I(A_i(z)) \approx \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}^2 = |a|^2, \]  
(3.13)

or when incident and scattered light are cross (perpendicularly) polarized,

\[ I(A_i(z)) \approx \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}^2 = 0. \]  
(3.14)

The above example shows how Raman intensity is related to polarization geometries of incident and scattered radiation. Since hexagonal structure has anisotropic \(a\)- and \(c\)-planes depicted in Fig. 3.10, the remaining optical phonon symmetries on \(a\)- and \(c\)-plane are calculated for oblique polarization angle dependency, as well.

Figure 3.10  Schematic illustration of a wurtzite structure and its coordinate system [39].

In the wurtzite structure, the \(c\) surface plane is orthogonal to two isotropic surface planes which are orthogonal to each other, as well. Therefore, optical phonon modes on the \(c\)-plane are
independent of incident light polarization. The selection rules for different sample orientations and scattering geometries are summarized in Table 3.7. Since $A_1$ Raman tensor has only diagonal elements, incident and scattered light must be co-polarized for $A_1$(LO) to be active on the $c$-plane. On the $c$-plane, $E_2$ phonon modes are allowed both in parallel and perpendicular polarization geometry; however, any components of the polar $E_1$ modes are not allowed. Table 3.7 indicates that LO branches of $E_1(y)$ and $E_1(–x)$ modes are forbidden both $c$- and $a$-plane in any polarization configuration settings along the backscattering geometry. Thus, its Raman activity requires perpendicular propagation geometry of incident and scattered light [39]. In addition to polarization geometry, optical modes on $a$-plane are dependent on the angle between polarization of the incident light and $x$-axes. Therefore, proper polarization geometry should be selected for coordinate axis for Raman activity of the optical phonons.

Table 3.7 Raman selection rules for $a$- and $c$-plane wurtzite structure for various polarization configurations along the backscattering geometry, where $\theta$ is the angle between $e_i$ and the $x$ axis (see Fig. 3.10) and $\chi$ is the phase difference.

<table>
<thead>
<tr>
<th>Raman mode</th>
<th>$a$-plane</th>
<th>$c$-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$e_i \parallel e_s$</td>
<td>$e_i \perp e_s$</td>
</tr>
<tr>
<td>$A_1(z)$</td>
<td>LO</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>TO</td>
<td>$</td>
</tr>
<tr>
<td>$E_1(–x)$</td>
<td>LO</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>TO</td>
<td>$</td>
</tr>
<tr>
<td>$E_1(y)$</td>
<td>LO</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>TO</td>
<td>0</td>
</tr>
<tr>
<td>$E_2$</td>
<td>$</td>
<td>d</td>
</tr>
</tbody>
</table>
A macroscopic (long-range) electric field, which is associated with the relative atomic displacement of the longitudinal phonons (LO), strengthens the bonding of a molecule [40]. Thus, strengthening the field shifts the LO frequency relative to the TO frequency. This process results in breaking degeneracies of electronic orbital states, due to excessive static field produced by the surrounding charges, known as Lydanne-Sachs-Teller and given by [41]:

$$\varepsilon_0 = \varepsilon_\infty \left(\frac{\omega_{\text{LO}}}{\omega_{\text{TO}}}\right)^2,$$

(3.15)

where $\varepsilon_0$ and $\varepsilon_\infty$ are the electric permittivity of free space (vacuum) and high frequency and $\omega_{\text{LO}}$ and $\omega_{\text{TO}}$ are the longitudinal and transverse optical phonon frequencies, respectively. The short-range inter-atomic forces are responsible for anisotropy in the uniaxial crystals [36,40,42]. If electrostatic forces dominate over inter-atomic forces, LO-TO splitting is greater than $A_1-E_1$ splitting depicted in Fig. 3.11a. If inter-atomic atomic forces dominate over electrostatic forces, $A_1-E_1$ splitting is greater than LO-TO splitting depicted in Fig. 3.11b.

Figure 3.11 Electrostatic and inter-atomic force influence on optical phonon splitting. (a) Electrostatic force dominates over inter-atomic force and (b) inter-atomic force dominates over electrostatic force [36].
In addition to the influence of electrostatic and inter-atomic forces, vibrational mode frequencies of InN are affected by substrate type, growth temperature, and growth technique.

The energy shifts of Raman phonon vibrations, given in reciprocal (cm\(^{-1}\)) units, for the hexagonal (wurtzite) structure are listed in Table 3.8.

Table 3.8  Frequencies of Raman phonon modes of the wurtzite InN material at 300 K [43].

<table>
<thead>
<tr>
<th>Reference</th>
<th>(E_2(\text{low}))</th>
<th>(A_1(\text{TO}))</th>
<th>(E_1(\text{TO}))</th>
<th>(E_2(\text{high}))</th>
<th>(A_1(\text{LO}))</th>
<th>(E_1(\text{LO}))</th>
<th>(B_1(\text{low}))</th>
<th>(B_1(\text{high}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref. 44</td>
<td></td>
<td></td>
<td></td>
<td>495</td>
<td>596</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref. 45</td>
<td></td>
<td></td>
<td></td>
<td>491</td>
<td>590</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref. 46</td>
<td>87</td>
<td>480</td>
<td>476</td>
<td>488</td>
<td>580</td>
<td>570</td>
<td>200</td>
<td>540</td>
</tr>
<tr>
<td>Refs. 47 and 48</td>
<td>87</td>
<td>447</td>
<td>475</td>
<td>488</td>
<td>586</td>
<td>593</td>
<td>220</td>
<td>565</td>
</tr>
<tr>
<td>Ref. 49</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>491</td>
<td>590</td>
</tr>
<tr>
<td>Ref. 50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>445</td>
<td>472</td>
</tr>
<tr>
<td>Ref. 51</td>
<td>88</td>
<td>440</td>
<td></td>
<td>490</td>
<td>590</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>104</td>
<td>440</td>
</tr>
<tr>
<td>Ref. 50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>93</td>
<td>443</td>
</tr>
<tr>
<td>Ref. 51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>83</td>
<td>443</td>
</tr>
<tr>
<td>Ref. 52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>85</td>
<td>449</td>
</tr>
</tbody>
</table>

3.2.1.2.  Cubic (Zinc blende) Structure

The other stable crystal form of InN semiconductor material is zinc blende structure. Since cubic structure is discussed in more detail in section 2.2, here its symmetry application on the Raman spectroscopy will be discussed. Since cubic structure has the highest symmetry order among 230 nonequivalent space groups in three-dimension, it spectroscopically exhibits the
fewest peaks in the vibrational spectrum when compared with other structures. Since a detailed
discussion of the general symmetry operations and group theory are stated in section 3.2.1.1,
only the main points will be discussed in here. Symmetry operations in a cubic structure are
shown in Fig. 3.12. Besides identity operation, \( E \), cubic structure consists of rotational symmetry
about its body diagonals by angles of \( \pm 2/3 \pi \) radian. It also possesses rotations about \( x \), \( y \), and \( z \)
directions. The rotation-reflection operator also corresponds to rotations of \( \pm 2/3 \pi \) about \( x \), \( y \),
and \( z \) directions. Furthermore, it possesses six diagonal reflection (mirror) planes which pass
through the opposite corners of cube. Hence, there are total of five different operational groups
in the cubic structure [54].

Figure 3.12 Symmetry element representations of a zinc blende structure.

The character table for \( T_d \) point group symmetry, given in Table 3.9, indicates that there
are five conjugacy classes listed as \( E \), \( C_3 \), \( C_2 \), \( S_4 \), and \( \sigma_d \) and symmetry elements for each
irreducible representation listed as \( A_1 \), \( A_2 \), \( E \), \( T_1 \), and \( T_2 \). The subscripts one and two represent
symmetric and antisymmetric vibrations perpendicular to either the \( C_2 \) or \( C_3 \) axis, respectively
[27]. Since characters in the column of operation \( E \) indicate the degeneracy of orbitals, symmetry
elements of the group are classified as singly degenerate $A_1$ and $A_2$, doubly degenerate $E$, and triply degenerate $T_1$ and $T_2$ modes. Spectroscopically, character table indicates that $A_1$, $E$, and $T_2$ symmetries are polarizable, i.e., possess quadratic basis functions, so they are Raman active. Since only $T_2$ symmetry possesses symmetry of translations, i.e., $p$ orbitals, it is IR active as well. Because the $T_2$ symmetry of translations transforms as $d$ orbitals, it is a polar mode and exhibits longitudinal and transverse splitting. Since $A_2$ and $T_1$ symmetries lack of translational symmetry and polarizability, they are silent both in Raman and in IR. However, only the $T_1$ mode has rotational symmetries, thus it is microwave active.

Table 3.9  Character table and symmetry operations of the $T_d$ point group symmetry.

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>Symmetry elements for the group</th>
<th>Spectroscopy active component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E $\ 8C_3\ 3C_2\ 6S_4\ 6\sigma_d$</td>
<td>Microwave</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1 1 1 1 1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1 1 1 $-1$ $-1$</td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>2 $-1$ 2 0 0</td>
<td></td>
</tr>
<tr>
<td>$T_1$</td>
<td>3 0 $-1$ 1 $-1$</td>
<td>$R_x, R_y, R_z$</td>
</tr>
<tr>
<td>$T_2$</td>
<td>3 0 $-1$ $-1$ 1</td>
<td>$x, y, z$</td>
</tr>
</tbody>
</table>

Since there are two atoms within the cubic primitive cell, shown in Fig. 2.2a, two-atom systems belongs to $T_d^2$ space group symmetry. The Symmetry Adapted Linear Combinations (SALC) [32], discussed in detail in the previous section, of a diatomic molecule are summarized in Table 3.10.
Table 3.10  Reducible representation of symmetry operations in the zinc blende structure.

<table>
<thead>
<tr>
<th>$\Gamma_d$</th>
<th>E</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6S_4$</th>
<th>$6\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{xyz}$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_{uma}$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\Gamma_{Total}$</td>
<td>6</td>
<td>0</td>
<td>-2</td>
<td>-2</td>
<td>2</td>
</tr>
</tbody>
</table>

Hence, using Eq. 3.8 (reduction formula) and the $\Gamma_{Total}$ elements of Table 3.10, the irreducible representation of zinc blende structure for each mode is reconstructed. Accordingly, the irreducible representation of the quantized lattice motions in the zinc blende structure is summarized as:

$$\Gamma_{\text{Irreducible}} = 2T_2.$$  \hfill (3.16)

Since cubic structure has two atoms per primitive cell, there must be six energy states regarding lattice motions which can be described by irreducible representations. Hence, spectroscopically allowed lattice vibrations are split in terms of acoustic and optical phonons given by the following relation:

$$\Gamma_{\text{acoustic}} + \Gamma_{\text{optical}} = T_2 + T_2.$$ \hfill (3.17)

As results of cubic symmetry considerations, the scattered Raman intensity could vanish for certain polarizations in a given scattering geometry. Since both acoustic and optical phonons in zinc blende zone center have $I'_{15}$ symmetry, which is triply degenerate, under symmetry operations, these three components transform into each other like $i$, $j$, and $k$ unit vectors [55]. Tensor representations of vibrational modes in a zinc blende structure are given in Appendix A.2 [55]. As an illustration of Raman selection rules in the zinc blende structure, we consider back
scattering geometry, i.e., incident and scattered propagation are parallel, from the (001) surface plane, depicted in Figure 3.13.

Figure 3.13  Miller indices and crystallographic planes of a zinc blende structure.

Since incident and scattered radiation are parallel, incident and scattered radiation should propagate along the $z$ and $-z$ directions, respectively. It is clear that none of the $T_2$ tensors have diagonal elements, and thus incident and scattered radiation should be cross (perpendicular) polarized. If incident light, propagating along the $z$–axis, is polarized along the $x$-axis, scattered light could be only polarized along the $z$-axis. Because $T_2$ is a triply degenerate mode, the suitable tensor, which has nonzero $yz$ element, is $T_2(x)$. Hence Raman scattering intensity by employing Eq. 3.18 is calculated as,

$$I_{R2(z)} \approx \begin{vmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & d & 1 & 0 & 0 \\ 0 & d & 0 & 0 & 0 & 0 \end{vmatrix}^2 = |d|^2.$$  \hspace{1cm} (3.18)

Since incident radiation propagates in $x$-axis and polarized along $y$-axis, scattered radiation propagates along the $-x$-axis, and polarized along the $z$-axis, and the phonon observed
in the back scattering geometry must vibrate along the z-axis. Therefore, the phonon assignment could be longitudinal-optic (LO), as shown in Fig. 3.9. Usually, Raman modes in the zinc blende structure are denoted as LO and TO instead of $T_2$(LO) and $T_2$(TO), respectively. Figure 3.14 depicts the scheme of optical vibrations and Table 3.11 summarizes the relative Raman intensities (selection rules) of the zinc blende structure along the (001) crystallographic orientation.

![Figure 3.14 Schematic displacements for Raman (phonon) modes in a zinc blende structure, where big and small spheres denote indium and nitrogen atoms, respectively.](image)

![Table 3.11 Raman selection rules for (001)-plane zinc blende structure for various polarization configurations along the backscattering geometry, where $e_i$ and $e_s$ are the polarization directions of incident and scattered light, respectively.](table)

<table>
<thead>
<tr>
<th>Scattering direction</th>
<th>Phonon mode from (001)-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_2$(LO)</td>
</tr>
<tr>
<td>$e_i$(100) and $e_s$(100)</td>
<td>0</td>
</tr>
<tr>
<td>$e_i$(100) and $e_s$(010)</td>
<td>$</td>
</tr>
<tr>
<td>$e_i$(110) and $e_s$(100)</td>
<td>$</td>
</tr>
<tr>
<td>$e_i$(100) and $e_s$(100)</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 3.11 indicates that only $T_2$(LO) is allowed in reference to (100), (010), and (001) cubic geometry, whereas various cubic lattice arrangements activate the $T_2$(TO) phonon mode, as well. Since $T_2$ is a triply degenerate mode and split into longitudinal and transverse branches, splitting of degeneracy is under investigation for various semiconductors. To illustrate, the doubly degenerate $T_2$(TO) and single $T_2$(LO) phonon with higher frequencies are observed in the Raman spectrum for ZnS material [56]. Since the LO mode has extra restoring force from the interaction of lattice vibration and the macroscopic electric field, this observation is consistent with the theoretical prediction.

Finally, in addition to electrostatic and inter-atomic forces influence, vibrational mode frequencies of the InN are affected by substrate type, growth temperature, and growth technique. The energy shifts of Raman phonon vibrations, given in reciprocal (cm$^{-1}$) units, for the cubic (zinc blende) structure are listed in Table 3.12.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$T_2$(LO)</th>
<th>$T_2$(TO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 57</td>
<td>588</td>
<td>457</td>
</tr>
<tr>
<td>Ref. 51</td>
<td>586</td>
<td>472</td>
</tr>
<tr>
<td>Ref. 58</td>
<td>586</td>
<td>470</td>
</tr>
</tbody>
</table>

### 3.2.2. Infrared (IR) Spectroscopy

Infrared spectroscopy or IR is an important vibrational tool and widely used to characterize both organic and inorganic materials [5]. IR spectroscopy, listed in Table 3.1, is employed to acquire information about the structure of a compound and assess the purity of a compound [1]. In other words, IR spectroscopy is utilized to identify chemical content to
quantitatively or semi-quantitatively. The IR region in the EM spectrum is divided into three regions: the near, mid, and far IR, summarized in Table 3.13. IR spectroscopy usually involves the interaction of interatomic bonds and EM radiation in the mid IR radiation frequencies between 4000 and 400 cm$^{-1}$ [7].

Table 3.13 The IR regions of the electromagnetic (EM) spectrum [59].

<table>
<thead>
<tr>
<th>IR</th>
<th>$\lambda$ (Wavelength)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near</td>
<td>0.75 to 3 $\mu$m</td>
</tr>
<tr>
<td></td>
<td>13333 to 4000 cm$^{-1}$</td>
</tr>
<tr>
<td>Mid</td>
<td>3 to 30 $\mu$m</td>
</tr>
<tr>
<td></td>
<td>4000 to 400 cm$^{-1}$</td>
</tr>
<tr>
<td>Far</td>
<td>30 to 300 $\mu$m</td>
</tr>
<tr>
<td></td>
<td>400 to 33 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Since chemical bonds in different materials absorb varying intensities and at varying frequencies, IR spectroscopy involves collecting absorption information and analyzing it in the form of a spectrum. Raman and IR spectroscopies are the two most commonly employed vibrational transition techniques for organic molecules and inorganic crystalline solids. Raman spectroscopy together with IR techniques will give almost complete information about the vibrational state of a molecule in the electronic ground state. These two methods are complementary to each other due to the common nature of the vibrational phenomena that they are based on. They are also complementary because of the differing nature of the measuring techniques involved and their specific usefulness in different structural and methodological aspects [11]. The complementarity of Raman and IR spectroscopy results from the different selection rules listed in Table 3.3 and restated below. Selection rules determine the appearance in
the Raman and IR spectrum of a band corresponding to a given vibration of the molecule. The selection rules may be summed up in two rules [7,8]:

i. If a vibration changes dipole moment, $\mu$, of a molecule, it is infrared (IR) active. This occurs when vibration changes the symmetry of the charge density distribution.

ii. If a vibration changes molecular polarizability, $\alpha$, it is active in the Raman scattering. This occurs when vibration changes symmetry of the polarization density.

For many solids, it is more convenient to record the spectrum in the reflection mode. When IR spectroscopy is configured to measure reflectance, the intensity of light reflected from a sample ($I$) is measured, and compared to the intensity of light reflected from a reference material ($I_0$). The ratio $I/I_0$ is called the reflectance, and is usually expressed as a percentage ($% R$). There are number of ways where IR spectroscopy could be modified to study atomic vibrations in crystalline solid materials, such as transmission, diffuse reflection, reflection-absorption, and multiple internal reflection IR spectroscopies [60]. Here, only reflection-absorption IR spectroscopy (RAIS) is investigated where the IR beam is reflected from the surface of a sample, illustrated in Fig. 3.15 [60]. It was shown that best sensitivity is obtained when using approximately 80° normal incidence geometry [61].

![Figure 3.15 Schematic representation of reflection-absorption infrared spectroscopy (RAIS) geometry [60].](image)
Since propagation of incident infrared beam is aligned at grazing incidence onto surface of a sample, perpendicular components of incident and reflected beams are aligned in opposite directions in reference each other, as shown in Fig. 3.15. Therefore, only the parallel component of the incident beam changes the dipole moment of the molecule, illustrated in Fig. 3.16 [60].

![Diagram](image)

**Figure 3.16** Schematic representation of dipole moment alignment when incident IR beam is aligned at grazing incidence onto surface [60].

This adds extra constraints to the IR selection rule. Thus, only certain vibrational modes whose dipole moment changes perpendicular (normal) to the surface of a sample are IR active. In a polar thin film, there exist two types of normal modes of vibration:

i. In TO modes, molecular vibrations are parallel to the plane of the film.

ii. In LO modes, molecular vibrations are perpendicular to the plane of the film.

When an electromagnetic wave is incident on the film with the electric field polarized perpendicular to the plane of incidence (i.e., an s wave, also known as transverse-electric wave), the radiation can only interact with the TO modes regardless of the angle of incidence $\theta_i$. In contrast, both the TO and LO modes can be excited by radiation that impinges on the film at an angle $\theta_i$ with the electric field polarized parallel to the plane of incidence, shown in Figure 3.17 [62].
Figure 3.17 Calculated IR transmission spectra at oblique incidence ($\theta_i = 45^\circ$) for TM waves impinging on a 400-nm-thick $w$-AlN thin films with the $c$-axis (a) perpendicular to both $B$ and film surface, (b) parallel to both $B$ and film surface, and (c) perpendicular to $B$ and parallel to film surface. The insets show the different geometries considered [62].
In the wurtzite (hexagonal) structure, two polar phonon modes of $A_1$ and $E_1$ possessing oscillating dipole moment perpendicular to the surface are IR active. In the zinc blende case, $T_2$ is IR active.

Table 3.14  Frequencies of IR phonon modes of the wurtzite InN material at 300 K.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$A_1$ (LO)</th>
<th>$A_1$ (TO)</th>
<th>$E_1$ (LO)</th>
<th>$E_1$ (TO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 63</td>
<td>590</td>
<td></td>
<td>485</td>
<td></td>
</tr>
<tr>
<td>Ref. 64</td>
<td>449</td>
<td></td>
<td>489</td>
<td></td>
</tr>
</tbody>
</table>

The optoelectronic properties, such as high-frequency dielectric function, free carrier concentration and mobility of the free carriers, and thickness of the each layer can be determined from the multilayer stack model [65,66]. Since the Born-Oppenheimer approximation [6], discussed in detail in section 3.2, assumes that the different types of molecular energies are separable, dielectric functions for the phonon and plasmon system are also separable. The dielectric function of the optoelectronic system can be described employing a well-known linear Drude-Lorentz model [67,68]:

$$
\varepsilon(\omega) = \varepsilon_\infty \left[ 1 + \frac{(\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2)}{(\omega_{\text{TO}}^2 - \omega^2 - i\omega\gamma)} - \frac{\omega_p^2}{(\omega^2 + i\omega\Gamma)} \right].
$$

(3.19)

where $\omega_p/\Gamma$, $\omega_{\text{LO}}/\gamma$, and $\omega_{\text{TO}}$ are the plasmon, LO phonon resonant-frequency/damping parameters, and TO phonon frequency, respectively. Although multilayer structure has numerous reflections and transmissions illustrated in Fig. 3.18, it can be regarded as an optical system with one input beam and one output beam [69]. Thus, a transfer matrix $T$ can be assigned to the multilayer stack system that relates the incident and reflected beams in a single parameter.
Figure 3.18  Schematic representation of a multiple reflections and transmissions from a multilayer stack.

Let \( M_1 \) and \( M_2 \) be characteristic matrices of top and bottom, and \( M_\text{s} \) are a characteristic matrix of the intermediate layer, respectively [70].

\[
M = M_1 M_\text{s} M_2, \quad (3.20)
\]

and each propagation with a thickness of \( a_i \) and wave number of \( k \).

\[
M_i = \begin{pmatrix}
\cos k a_i & \frac{1}{k} \sin k a_i \\
-k \sin k a_i & \cos k a_i
\end{pmatrix}, \quad (3.21)
\]

The resultant matrix is defined as the product of each characteristic matrix and the reflectivity is calculated as [70],

\[
R = \left| \frac{M_{\text{ef}}}{M_{\infty}} \right|^2, \quad (3.22)
\]
Finally, fitting parameters for the multilayer stack model are obtained from the Transfer Matrix model. For obtaining best fitting parameters, a damped least squares method known as Levenberg-Marquardt algorithm was utilized.

For quantitative optical and optoelectronic properties, best fitting parameters obtained from the multilayer stack model were utilized to extract free-carrier concentration, \( n_e \), and carrier mobility, of InN epilayers, given by the following relations, respectively [65,66]:

\[
n_e = \frac{\omega^2 m_e \varepsilon \varepsilon_0}{q^2},
\]

and

\[
\mu_e = \frac{q}{m_e \gamma_p},
\]

(3.23)

(3.24)

3.2.3. X-Ray Diffraction (XRD)

Vibrational spectroscopic techniques of Raman scattering and infrared (IR) reflection spectroscopies described in detail in sections 3.2.1 and 3.2.2, respectively, are descriptive for the dynamic structure (lattice vibrations) of atoms while X-ray diffraction technique can determine the static equilibrium arrangement of atoms. Therefore, X-ray diffraction is the most widely employed technique for molecular geometry and crystalline structure determination.

The physical structure of solid materials depends on the arrangements of atoms that make the solid. A crystal is a solid-phase material whose atoms are both uniformly packed and periodically extended in a three-dimensional space. The size and shape of a crystal can be described by three unit lattice vectors of \( \mathbf{a}, \mathbf{b}, \) and \( \mathbf{c} \). The axial lengths of \( a, b, \) and \( c, \) and the interaxial angles \( \alpha, \beta, \) and \( \gamma \) are the defining lattice values of the unit cell. Although there are
more than 230 crystal structures, a crystal, in terms of its unit cell, belongs to one of the seven crystal systems, listed in Table 3.15. As a result of this periodic extension, parallel planes of atoms are formed. Parallel planes are separated by a distance \( d \), which is known as \( d \)-spacing. Accordingly, axial unit length, i.e., lattice constant, can be calculated in reference to \( d \)-spacing.

Table 3.15  Symbolic, cell lengths, and cell angles of the various crystal systems.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Symbolic</th>
<th>Cell lengths</th>
<th>Cell angles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cubic</strong></td>
<td><img src="image" alt="Diagram" /></td>
<td>( a = b = c )</td>
<td>( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td><strong>Tetragonal</strong></td>
<td><img src="image" alt="Diagram" /></td>
<td>( a = b, c )</td>
<td>( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td><strong>Orthorhombic</strong></td>
<td><img src="image" alt="Diagram" /></td>
<td>( a, b, c )</td>
<td>( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td><strong>Hexagonal</strong></td>
<td><img src="image" alt="Diagram" /></td>
<td>( a = b, c )</td>
<td>( \alpha = \beta = 90^\circ, \gamma = 120^\circ )</td>
</tr>
<tr>
<td><strong>Rhombohedral</strong></td>
<td><img src="image" alt="Diagram" /></td>
<td>( a = b = c )</td>
<td>( \alpha = \beta = \gamma )</td>
</tr>
<tr>
<td><strong>Monoclinic</strong></td>
<td><img src="image" alt="Diagram" /></td>
<td>( a, b, c )</td>
<td>( \alpha, \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td><strong>Triclinic</strong></td>
<td><img src="image" alt="Diagram" /></td>
<td>( a, b, c )</td>
<td>( \alpha, \beta, \gamma )</td>
</tr>
</tbody>
</table>
As high-energy X-rays interact with a crystalline structure, they could be diffracted entirely by nucleus, known as the Bragg diffraction law. When X-rays hit a crystal at an arbitrary angle, the interference of the reflected X-rays can be either constructive or destructive [71]. Constructive diffraction of the X-rays from the lattice planes exhibits maximum interference fringes only at specific lattice plane of interest. According to Bragg’s law, the constructive diffraction of the waves from a lattice is given as following equation [71,72]:

\[ n(\lambda) = 2 \times d \times \sin \theta, \]

where \( n \) is the diffraction order, \( \lambda \) is the wavelength of X-ray, \( 2d \times \sin \theta \) is the path difference for a diffraction process. A schematic illustration depicting the spatial relationship between the Bragg diffraction and crystalline lattice is illustrated in Fig. 3.19.

![Diagram of X-ray diffraction from a single crystal.](image)

Figure 3.19. Schematic diagram of X-ray diffraction from a single crystal. Two monochromatic beams approach a crystalline solid and are scattered off at two different atoms by forming a constructive interference of reflected X-rays [73].
Different periodic distances, i.e., lattice planes, of an ordered crystal structure are shown in Fig. 3.20. To understand periodic distances within a lattice, a plane intersecting atoms of a unit cell across the three-dimensional lattice is constructed. Each plane intersects the lattice at \(a(h), b(k),\) and \(c(l)\) positions. The \(h, k,\) and \(l\) are known as Miller indices \((hkl)\) and are used to identify each lattice plane. Miller indices are the most common notation to define a crystalline plane and given in reference to reciprocal lattice vectors [74]. For hexagonal crystal systems, a four-index \((hkil)\) notation is often used [75]. The additional index, \(i,\) equal to \(-(h+k),\) helps show the equivalency of planes such as \((1 1 -2 0)\) and \((-2 1 1 0)\) [76]. A brief summary of notations for a hexagonal system is given in Table 3.16.

Figure 3.20 Various periodic distances are described within a lattice. (a) \((1 1 0)\), (b) \((\bar{1} 1 0)\), (c) \((0 1 0)\), and (d) \((2 3 0)\) [73].
Table 3.16 Summary of a bracketing notations used in X-ray diffraction.

<table>
<thead>
<tr>
<th>Three-index notation</th>
<th>Four-index notation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 5</td>
<td>1 0 –1 5</td>
<td>Reflection</td>
</tr>
<tr>
<td>(1 0 5)</td>
<td>(1 0 –1 5)</td>
<td>Plane</td>
</tr>
<tr>
<td>{1 0 5}</td>
<td>{1 0 –1 5}</td>
<td>Family of planes</td>
</tr>
<tr>
<td>[1 0 5]</td>
<td>[1 0 –1 5]</td>
<td>Direction</td>
</tr>
<tr>
<td>⟨1 0 5⟩</td>
<td>⟨1 0 –1 5⟩</td>
<td>Family of directions</td>
</tr>
</tbody>
</table>

Indium nitride (InN), like other group-III nitrides, crystalizes in either a hexagonal (wurtzite) or a simple cubic (zinc blende) form shown in Fig. 2.2. X-ray diffraction spectrum, like Raman and IR spectra, is strongly influenced from its crystal form. Since details of hexagonal and cubic forms are described in detail in section 2.2, only X-ray diffraction applications on both crystalline forms are investigated in this section.

A hexagonal structure has six base sides of the same length, all internal angles are 120°, and a height of hexagon correspond to c-lattice constant. Nearly all semiconductor materials regardless of their location in the periodic table have tetrahedral coordination geometry and are known as covalently bounded coordinate compounds [77]. The ratio of the height c of the hexagonal structure to its basal side a is called the c/a ratio. The c/a ratio is described in detail in section 2.2. The c/a ratio is essential for interpreting the spontaneous (polarization in unstrained lattice) polarization, listed in Table 3.17. The a- and c-lattice constants of the hexagonal crystalline structure can be calculated by employing the given equation,

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2},
\]  

(3.26)
where \( d_{hkl} \) is a \( d \)-spacing which is determined experimentally from Eq. 3.25 and \( h, k, \) and \( l \) are the corresponding Miller indices of a given lattice plane. The \( a \)- and \( c \)-lattice constants and \( c/a \) ratios of a hexagonal InN are listed in Table 3.17.

<table>
<thead>
<tr>
<th>Crystal form</th>
<th>( a ) (Å)</th>
<th>( c ) (Å)</th>
<th>( c/a )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal</td>
<td>3.5378 ± 0.0001</td>
<td>5.7033 ± 0.0001</td>
<td>1.6121 ± 0.0001</td>
<td>Ref. 79</td>
</tr>
<tr>
<td></td>
<td>3.5374 ± 0.0001</td>
<td>5.7024 ± 0.0005</td>
<td>1.6121 ± 0.0002</td>
<td>Ref. 80</td>
</tr>
<tr>
<td></td>
<td>3.5390 ± 0.0001</td>
<td>5.7083 ± 0.0001</td>
<td>1.6130 ± 0.0001</td>
<td>Ref. 81</td>
</tr>
<tr>
<td></td>
<td>3.5366 ± 0.0005</td>
<td>5.7009 ± 0.0005</td>
<td>1.6120 ± 0.0005</td>
<td>Ref. 82</td>
</tr>
<tr>
<td></td>
<td>3.57 ± 0.05</td>
<td>5.40 ± 0.05</td>
<td>1.52 ± 0.05</td>
<td>Ref. 83</td>
</tr>
</tbody>
</table>

An interactive powder diffraction data interpretation and indexing program was used to calculate \( d \)-spacing, Miller indices, and 2\( \theta \) Bragg reflection center for strain free hexagonal InN material, listed in Table 3.18 [78].
Table 3.18  Calculated d-spacing, Miller indices, and peak locations of hexagonal InN ($a = 3.5380$ Å, $c = 5.7030$ Å, and $\lambda = 1.540510$ Å).

<table>
<thead>
<tr>
<th>Line</th>
<th>d-spacing (Å)</th>
<th>Miller indices</th>
<th>$2\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0640</td>
<td>1 0 0</td>
<td>29.12</td>
</tr>
<tr>
<td>2</td>
<td>2.8515</td>
<td>0 0 2</td>
<td>31.34</td>
</tr>
<tr>
<td>3</td>
<td>2.6991</td>
<td>1 0 1</td>
<td>33.16</td>
</tr>
<tr>
<td>4</td>
<td>2.0874</td>
<td>1 0 2</td>
<td>43.31</td>
</tr>
<tr>
<td>5</td>
<td>1.7690</td>
<td>1 1 0</td>
<td>51.62</td>
</tr>
<tr>
<td>6</td>
<td>1.6154</td>
<td>1 0 3</td>
<td>56.96</td>
</tr>
<tr>
<td>7</td>
<td>1.5320</td>
<td>2 0 0</td>
<td>60.37</td>
</tr>
<tr>
<td>8</td>
<td>1.5032</td>
<td>1 1 2</td>
<td>61.65</td>
</tr>
<tr>
<td>9</td>
<td>1.4795</td>
<td>2 0 1</td>
<td>62.75</td>
</tr>
<tr>
<td>10</td>
<td>1.4258</td>
<td>0 0 4</td>
<td>65.40</td>
</tr>
<tr>
<td>11</td>
<td>1.3496</td>
<td>2 0 2</td>
<td>69.60</td>
</tr>
<tr>
<td>12</td>
<td>1.2927</td>
<td>1 0 4</td>
<td>73.15</td>
</tr>
<tr>
<td>13</td>
<td>1.1929</td>
<td>2 0 3</td>
<td>80.44</td>
</tr>
<tr>
<td>14</td>
<td>1.1581</td>
<td>2 1 0</td>
<td>83.38</td>
</tr>
<tr>
<td>15</td>
<td>1.1349</td>
<td>2 1 1</td>
<td>85.48</td>
</tr>
<tr>
<td>16</td>
<td>1.1101</td>
<td>1 1 4</td>
<td>87.87</td>
</tr>
<tr>
<td>17</td>
<td>1.0730</td>
<td>2 1 2</td>
<td>91.76</td>
</tr>
<tr>
<td>18</td>
<td>1.0689</td>
<td>1 0 5</td>
<td>92.20</td>
</tr>
<tr>
<td>19</td>
<td>1.0437</td>
<td>2 0 4</td>
<td>95.12</td>
</tr>
<tr>
<td>20</td>
<td>1.0213</td>
<td>3 0 0</td>
<td>97.91</td>
</tr>
<tr>
<td>21</td>
<td>1.0053</td>
<td>3 0 1</td>
<td>100.02</td>
</tr>
<tr>
<td>22</td>
<td>0.9615</td>
<td>3 0 2</td>
<td>106.47</td>
</tr>
<tr>
<td>23</td>
<td>0.9505</td>
<td>0 0 6</td>
<td>108.26</td>
</tr>
<tr>
<td>24</td>
<td>0.9149</td>
<td>2 0 5</td>
<td>114.69</td>
</tr>
<tr>
<td>25</td>
<td>0.8997</td>
<td>3 0 3</td>
<td>117.77</td>
</tr>
<tr>
<td>26</td>
<td>0.8845</td>
<td>2 2 0</td>
<td>121.11</td>
</tr>
</tbody>
</table>
Since the other stable InN structure is a zinc blende form, the $a$-lattice constant of the cubic structure can be calculated by employing the given equation,

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2},$$

(3.27)

where $d_{hkl}$ is a $d$-spacing which is determined experimentally from Eq. 3.25 and $h, k,$ and $l$ are the corresponding Miller indices of a given lattice plane. Since the cubic form of InN is metastable in reference to hexagonal form, the minimum and maximum $a$-lattice constant values are relatively high. The $a$-lattice constant of a cubic InN are listed in Table 3.19.

Table 3.19  Cubic $a$-lattice constant of nominally strain free InN.

<table>
<thead>
<tr>
<th>Crystal form</th>
<th>$a$ (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>5.01 ± 0.01</td>
<td>Ref. 84</td>
</tr>
<tr>
<td></td>
<td>5.01 ± 0.01</td>
<td>Ref. 85</td>
</tr>
<tr>
<td></td>
<td>4.986 ± 0.02</td>
<td>Ref. 86</td>
</tr>
<tr>
<td></td>
<td>5.017 ± 0.02</td>
<td>Ref. 87</td>
</tr>
<tr>
<td></td>
<td>4.986 ± 0.02</td>
<td>Ref. 88</td>
</tr>
</tbody>
</table>

An interactive powder diffraction data interpretation and indexing program was also used to calculate $d$-spacing, Miller indices, and $2\theta$ Bragg reflection center for strain free cubic InN material, listed in Table 3.20.
Table 3.20  Calculated $d$-spacing, Miller indices, and peak positions of cubic InN ($a = 5.01$ and $\lambda = 1.540510 \text{Å}$).

<table>
<thead>
<tr>
<th>Line</th>
<th>$d$-spacing (Å)</th>
<th>Indices</th>
<th>$2\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5000</td>
<td>2 0 0</td>
<td>35.89</td>
</tr>
<tr>
<td>2</td>
<td>1.7678</td>
<td>2 2 0</td>
<td>51.66</td>
</tr>
<tr>
<td>3</td>
<td>1.5076</td>
<td>3 1 1</td>
<td>61.45</td>
</tr>
<tr>
<td>4</td>
<td>1.4434</td>
<td>2 2 2</td>
<td>64.50</td>
</tr>
<tr>
<td>5</td>
<td>1.2500</td>
<td>4 0 0</td>
<td>76.08</td>
</tr>
<tr>
<td>6</td>
<td>1.1180</td>
<td>4 2 0</td>
<td>87.09</td>
</tr>
<tr>
<td>7</td>
<td>1.0206</td>
<td>4 2 2</td>
<td>98.00</td>
</tr>
<tr>
<td>8</td>
<td>0.9623</td>
<td>5 1 1</td>
<td>106.35</td>
</tr>
<tr>
<td>9</td>
<td>0.8839</td>
<td>4 4 0</td>
<td>121.25</td>
</tr>
<tr>
<td>10</td>
<td>0.8452</td>
<td>5 3 1</td>
<td>131.39</td>
</tr>
<tr>
<td>11</td>
<td>0.8333</td>
<td>6 0 0</td>
<td>135.13</td>
</tr>
<tr>
<td>12</td>
<td>0.7906</td>
<td>6 2 0</td>
<td>153.97</td>
</tr>
</tbody>
</table>

Besides lattice space calculation, the X-ray diffraction technique yields information about crystalline structure, and thus X-ray diffraction analysis should be further utilized. The diffraction information withdrawn from X-ray diffraction is depicted in Fig. 3.21 and it is summarized in Table 3.21.

The position of a diffraction peak provides information about the location of lattice plane in the crystal structure. Each peak measures the $d$-spacing representing a family of lattice planes. Since different materials have different bond lengths, unit cell parameters should vary linearly with the ternary alloying of two binaries known as Vegard’s law [89]. The Vegard’s law states that, at a constant temperature, the volume of an alloy can be determined from a linear
interpolation of its constituent's volumes, and the lattice constant of ternary alloy is given by [90]:

\[ a_{A_{x}B_{1-x}C} = (1-x)a_{BC} - xa_{AC}, \] (3.28)

where \( x \) is the alloy composition or mole fraction of \( AC \), and \( a_{AC} \) and \( a_{BC} \) are the lattice constant of \( AC \) and \( BC \), respectively.

Each Bragg diffraction peak also has an associated intensity, which might differ from other peaks in the spectrum and is related to the relative strength of diffraction. Variations in measured intensity are related to the variations in the diffraction intensity of the crystal structure and their arrangements [91]. Two factors influence the scattering intensity, namely the electron and atom. The detailed explanations of these two processes are given in Ref. 92.

Figure 3.21  Information content of a conventional X-ray diffraction spectrum.
Table 3.21 Characteristic information acquired from X-ray diffraction spectrum.

<table>
<thead>
<tr>
<th>X-ray diffraction peak</th>
<th>Information</th>
<th>Corresponds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>Lattice parameter</td>
<td>$d$-spacing</td>
</tr>
<tr>
<td>Height</td>
<td>Maximum intensity</td>
<td>Number of crystallites</td>
</tr>
<tr>
<td>Area</td>
<td>Number of transitions</td>
<td>Phase amount (in mixture) Crystal structure (contents of unit cell)</td>
</tr>
<tr>
<td>Width</td>
<td>Crystallite size</td>
<td>Defects (strain, disorder) depend on peak shape, as well.</td>
</tr>
<tr>
<td>Shape</td>
<td>Crystallite size</td>
<td>Defects (strain, disorder) depend on peak width, as well.</td>
</tr>
</tbody>
</table>

In the X-ray diffraction technique, peak width and profile provide the most crucial information for quantitative analysis. When X-rays are diffracted from a nucleus, it statically interacts with its surrounding nucleus to some extent. Therefore, each nucleus can interact with its surrounding nuclei in reference to (long range) ordering. The observed peak shape is the sum of these individual nuclei, and thus the peak width and shape of the X-ray diffraction spectrum can be interpreted as a degree of crystalline ordering. The broadening of crystallite size was first observed by Scherrer [93] and he formulated the well-known crystallite size broadening relation, given by the following equation:

$$D_{2\theta} = \frac{K \cdot \lambda}{\beta_{2\theta} \cdot \sin \theta},$$

(3.29)

where $K$ is a shape factor constant usually taken to be 0.94, $\lambda$ is the X-ray wavelength in Å, $\beta_{2\theta}$ is a line shape broadening at full-width at half maximum of reflection peak in radians, and $\theta$ is a
Bragg angle. $D$ is an average size of crystalline domains, which may be smaller or equal to grain size.

The Scherrer equation is limited to nanoscale dimensions; therefore, the Scherrer formula is not applicable to grains larger than 0.1 μm. It is important to realize that the Scherrer formula provides a lower bound on the crystallite size because many factors contribute to the linewidth of diffraction peak. Besides crystallite size, inhomogeneous strain and instrumental broadening are the most well-known contributions. In addition to crystalline domain size calculations, X-ray diffraction analysis can be used to estimate extended defect sizes. Systematic shifts of atoms from their ideal position leads to an in-plane strain causing broadening in the diffraction line [93]. The strain of the films is determined by using the following equation:

$$
\varepsilon_{2\theta} = \frac{\beta_{2\theta}}{4 \cdot \tan \theta}.
$$

(3.30)

3.3. Summary

In summary, optical characterizations are important tools in semiconductor material development due to their nondestructive ability to analyze structural and optical properties of materials. When Raman scattering is utilized together with infrared (IR) reflection and X-ray diffraction spectroscopies exclusive characteristic information such as bonding force constant, vibrational frequency, thickness, free carrier concentration, free carrier mobility, lattice spacing, and quality of crystallinity can be obtained. Subsequent chapters will elaborate the characteristic features and significance of such combined spectroscopic work.
3.4. References


[78] E. Wu, POWD, an interactive powder diffraction data interpretation and indexing program, Ver 2.1, School of Physical Science, Finder’s University of South Australia, Bedford Park.


CHAPTER 4

GROWTH OF INDIUM NITRIDE LAYERS

4.1. Epitaxial Growth Process

In the 19th century, mineralogists noticed that two different naturally occurring crystal forms could grow together with definite and unique orientation relationship [1]. First artificial reproduction of a crystal growth from solution was reported by Frankenheim in 1836 [2–3]. In 1928, Royer established the necessary conditions for the oriented overgrowth, which is known as epitaxy, i.e., arrangement on [4]. Epitaxial growth process is one of the most important stages to fabricate various electronic and optical devices. Modern electronic and optical devices require very sophisticated structure, which are composed of thin layers with various compositions. The occurrence of the epitaxy depends on various parameters of which the most crucial are [5–7]:

i. Thermodynamic driving force, involving phase transitions and interface formation.

ii. Lattice misfit between substrate and epilayer, given by the following relation:

\[
\text{Lattice misfit} (\%) = \left( \frac{a_s - a_f}{a_s} \right) \cdot 100, \tag{4.1}
\]

where \(a_s\) and \(a_f\) are corresponding lattice constants of the substrate and epilayer, respectively.

At the macroscopic scale, phase is a physically distinguishable and distinct form of a material; however, phase transitions and interface formation at the microscopic scale is a daunting task. The growth phenomena at the atomic scale extend themselves with characteristic time scales of femto \((10^{-15})\) or pico \((10^{-12})\) seconds, while industrial growth applications for the
micron or millimeter dimensions typically take milliseconds or more to grow and to evolve morphologically. Therefore, integration of the atomistic processes, illustrated in Fig. 4.1, into thin film growth is the crucial and daunting task for the production of industrial and research quality thin films [8,9]. Some of the atomistic processes in epitaxial growth technique, depicted in Fig. 4.1, include (i) deposition followed by the (ii) diffusion of the atom, i.e., adatom, on the terrace, or its (iii) nucleation, or (iv) the attachment of an adatom to an existing island, or (v) the reverse process of an adatom detachment from existing island, i.e., desorption [9]. The adatom might diffuse along a trace (called surface diffusion), or down a step, or on top of an island to nucleate. Although order of the atomistic processes taking place during the epitaxy slightly varies, these processes, here, are discussed in the order stated above.

Figure 4.1 Schematic illustrations of atomistic processes take place during the epitaxial growth mechanism [10].

Application of thermodynamics to an epitaxy is an equilibrium condition at constant temperature and pressure [11]. Thermodynamic equilibrium is a state where the Gibbs free
energy per mole, $G$, is a minimum [12], and the Gibbs free energy is expressed in terms of enthalpy, $H$, and entropy, $S$:

$$G = H - TS,$$

and

$$H = U + pV,$$

where $U$ is an internal energy, $V$ is a volume, and $p$ is a pressure of a system. Since epitaxy is an off equilibrium thermodynamic relation, it requires a mass transport, which is a complex process [11]. At the mass transport process, two processes are involved, namely, flow dynamics and diffusion. Although mass transport process consists of nonlinear and coupled partial differential equations that represent conversations of mass, momentum, energy, and species are discussed in detail in elsewhere [3,13], basic equation for mass transport process can be summarized as follows:

$$\frac{\partial \rho}{\partial t} + \nabla (\rho \nu) = 0,$$

where $\rho$ is a density and $\nu$ is a velocity of species. It is obvious that either sum or each term must be zero; therefore, there are two types of mass transport process in the epitaxial growth.

i. If first term is a positive, i.e., the concentration of species increases with time, epitaxial process is defined a deposition.

ii. If first term is a negative, i.e., the concentration of species decreases with time, epitaxial process is defined a annealing or desorption.

iii. If each term is zero, i.e., both concentration of species and flux of species remain constant, epitaxial process defined a steady state.
Although, deposition process is the most complicated process in epitaxy due to thermodynamic, kinetic, chemical, and physical constraints, deposition process in epitaxy is driven by three well-known processes [14]:

i. If deposition process is imposed by a concentration gradient of free (active) radicals, it is defined a diffusion.

ii. If deposition process is imposed by a heat gradient of free radicals, it is defined a convection.

iii. If deposition process is imposed by an electric gradient of free radicals, it is defined a migration.

In the gas phase, an active radical is free and it can make reactions with other atoms, known as gas phase reaction. If an atom freely moves in the gas phase, it may impinge on the substrate and make bond with a nearest neighbor on the substrate. On a completely flat crystal surface, the adsorbed atom cannot make as much as VSPER allowed bonds. A flat portion of the crystal surface is called a terrace. When heights of two consecutive terraces differ, there is a step between them. When atom impinges on a flat terrace, the atom makes only a few bonds with underlying atoms or layer. The bond connection is so weak that the atom can migrate on the surface. During the migration, the adsorbed atom (adatom) may reach step edge. Step also may provide some additional bonds parallel to the terrace, but the number of bonds are still less than its VSPER allowed. Finally, the adatom can slide along the step edge by diffusion, and may reach the empty or kink position where adatom is totally incorporated.

The kinetics of adsorption and thermal desorption processes play a crucial role in epitaxial growth. In the growth mechanism, where these processes are performed, dynamic equilibrium occurs between the substrate surface and vapor atoms. Adsorption isotherms are
graphical representations of the surface coverage dependency of pressure at constant temperature. The rate of adsorption proportional to pressure, $p$, and the number $N (1 - \delta)$ of vacant adsorption sites on the surface is given by the following equation [15]:

$$\frac{d\delta}{dt} = k_a p N (1 - \delta).$$

(4.5)

Here, $\delta$ is the fractional coverage, $k_a$ is the rate constant for the adsorption, and $N$ is the total number of the available adsorption sites on the surface. It is good to know that adsorption probability does not depend on the occupancy of the neighboring adsorption site on the substrate surface [16]. There are two basic mechanisms of surface adsorption of radicals. The basis of distinction is the chemistry (nature) of the bonding between surface and adsorbent.

i. Physical adsorption, also called physisorption, is a weak bonding between surface and adsorbent. The only possible bonding type is Van der Waals and there is no significant reconstruction of electron density in the bonding.

ii. Chemical adsorption, also called chemisorption, is a real chemical bond which maybe in the form of either covalent or ionic character. There is a substantial surface reconstruction of electron density between substrate and adsorbate.

The growth process of epitaxial films is as the same as that of bulk crystal, except the influence of the substrate material at the initial stages [17]. This influence essentially comes from the lattice misfit and thermal stress from the crystal-film interface. Five possible modes of crystal growth may be distinguished in epitaxy, namely: (i) the Volmer-Weber, (ii) the Frank-van der Merwe mode, (iii) the Stranski-Krastanov, (iv) columnar, and (v) step flow mode. However, the columnar and step flow mode are fundamentally different growth chemistry than others. The three most frequently observed modes are illustrated schematically in Fig. 4.2. In the VW-mode,
small clusters are nucleated directly on a substrate, and then they grow into islands. This is due to deposited atoms are more strongly bounded to each other than substrate. This type of growth is seen metals on alkali halides, graphite, and mica. In the FK-mode, atoms are more strongly bounded to substrate more than other atoms, and the SK-mode is an intermediate case. After forming the first monolayer, growth is unfavorable and islands are formed on top of this intermediated layer. This is due to monotonic decrease in the binding energy of energy after layer-by-layer growth.

Figure 4.2 Cross sectional illustration of primary thin-film growth modes. (a) Volmer-Weber, (b) Frank-van der Merwe, and (c) Stranski-Krastanov. Each mode is shown for several different amounts of surface coverage, $\Theta$ [18].

The rest of the chapter is organized as follows: First, a brief description of epitaxial growth techniques for InN and then a detailed discussion of the most extensively employed growth techniques for InN epitaxy, namely: (i) Hydride Vapor Phase Epitaxy (HVPE), (ii) Molecular Beam Epitaxy (MBE), (iii) Metal-Organic Chemical Vapor Chemical Deposition (MOCVD), and (iv) High-Pressure Chemical Vapor Deposition (HPCVD). Finally, substrates used for InN epitaxy is discussed in detail.
4.2. Epitaxial Growth Techniques for InN

The growth of InN material is the most difficult among the group-III nitrides because the equilibrium vapor pressure of nitrogen over the InN is several orders higher than AlN and GaN as shown in Fig. 4.3 [19]. Due to the low dissociation temperature of InN (~600 °C) and large differences in the partial pressures of the group III-V constituents, the growth of InN requires a low growth temperature. Therefore, presently employed low-temperature growth techniques for InN and indium-rich group III-nitrides are: Hydride Vapor Phase Epitaxy (HVPE) [20–22], Molecular Beam Epitaxy (MBE) [23–25], Metalorganic Chemical Vapor Deposition (MOCVD) [26–28], and High Pressure Chemical Vapor Deposition (HPCVD) [29–31].

![Figure 4.3 Thermal decomposition of group III-nitrides as a function of temperature [19].](image)

Other growth methods including sputtering [32–34], reactive evaporation [35,36], electron beam plasma technique [37], liquid phase epitaxy [38], pulsed-laser deposition [39], and metalorganic-MBE [40] are employed for growth of InN. Because these growth techniques
encompass different chemistries, here, only HVPE, MBE, MOCVD, HPCVD techniques are discussed in detail in the following sections.

4.2.1. **Hydride Vapor Phase Epitaxy (HVPE)**

The first epitaxial growth of InN was demonstrated by Hydride Vapor Phase Epitaxy (HVPE) in 1977 [20]. Recently, HVPE has received much attention due to its high growth rate compared with that of MOCVD and MBE. HVPE also very similar to MOCVD is a chemical vapor deposition method, which is carried out in a hot wall reactor (horizontal or vertical) at atmospheric pressure. The source materials generally used for the HVPE growth of InN are indium monochloride (InCl) or indium trichloride (InCl$_3$) as In source, and ammonia or monomethylhydrazine (MMH) with the chemical formula CH$_3$(NH)NH$_2$ as N source [41,42,43]. Since the optimum temperature range for InCl$_3$ evaporation is found between 450 and 520 °C [20], in general, the growth of InN epilayers by HVPE is obtained in the range of growth temperature from 455 to 510 °C and of the V/III ratio from 500 to 2000 [22,36]. Takashi et al. also obtained hexagonal InN epitaxial layer reproducibly at a growth temperature as high as 750 °C, and found that a high input partial pressure of InCl$_3$ was necessary for the growth of InN at high temperature [44].

4.2.2. **Molecular Beam Epitaxy (MBE)**

Molecular Beam Epitaxy (MBE) is a growth technique, which is used to deposit ‘molecular beam’ of a source material. An MBE reactor is a modified version of Ultra High Vacuum (UHV) (~10$^{-10}$ Torr) evaporator system [45]. In the MBE growth of III-nitrides, the solid sources of the group III elements such as Al, Ga, and In are used in general but nitrogen is supplied by the gas source of N$_2$ and NH$_3$. In general, this type of MBE system is called gas
source MBE [23]. The metalorganic sources are also sometimes used as the group III element sources and then it is called metalorganic MBE (or MOMBE) [46]. Since, in both types of MBE growth process, crucial parameter is the nitrogen source. The dissociation energy of the $N_2$ molecules is as high as 9.5 eV; therefore, in order to obtain atomic reactive nitrogen, the $N_2$ molecules are dissociated by the radio frequency (rf)-plasma or the electron cyclotron resonance (ECR) method [41]. In $N_2$ case, governing chemical reaction is given by equation:

$$In_g + N_g \rightarrow InN_s.$$  \hspace{1cm} (4.6)

For the MBE system using an NH$_3$ source, the governing chemical reaction is:

$$In_g + NH_{3(g)} \rightarrow InN_s + (3/2)H_{2(g)}.$$  \hspace{1cm} (4.7)

The equilibrium partial pressure and growth rate are calculated for input V/III ratio, input partial pressure of indium and growth temperature. The growth of single phase high quality InN epilayers by MBE were reported with the band-gap of 0.7eV [47] and the growth of InN is processed in the growth temperature regime of 450 to 600 °C.

**4.2.3. Metalorganic Chemical Vapor Deposition (MOCVD)**

Metal-Organic Chemical Vapor Deposition (MOCVD)–also denoted as ‘metalorganic vapor phase epitaxy’ (MOVPE), ‘organometallic chemical vapor deposition’ (OMCVD), or ‘organometallic vapor phase epitaxy’ (OMVPE)–is a nonequilibrium epitaxial growth process where reactants are transported over a heated substrate [13]. Sequential chemical reactions in CVD process are expressed as (i) gas phase diffusion, (ii) gas phase reaction, (iii) mass transport and adsorption, (iv) diffusion, (v) incorporation, (vi) desorption, (vii) nucleation, and (viii) gas exhaust [48]. Growth parameters employed in the MOCVD process tend to vary as widely as the
specific reactor system used; however, the choice of growth parameters can be summarized in terms of the precursor materials, growth parameters, and precursor ratios.

4.2.3.1 Growth Temperature

Dependence of the growth rate on the growth temperature in the MOCVD process is illustrated schematically in Fig. 4.4 [49]. At low temperatures, growth rate is controlled by kinetic surface reactions. In the intermediate temperature range, from about 550 to 750 °C, growth rate is limited by the mass transport of constituents through a boundary layer to a substrate surface. Since diffusion through the boundary layer is weakly dependent on temperature, growth rate almost remains constant in this regime. Total laminar flow velocity is the crucial parameter in determining the boundary layer thickness; therefore, thinner boundary layer leads to more rapid diffusion [50]. Finally, at high temperature regime, growth rate decreases with increasing temperature. This is believed to be the direct results of thermodynamic effect, or of reactant depletion due to upstream reactions [13].

Figure 4.4 Thermal regimes of the growth rate in MOCVD [49].
4.2.3.2 Precursor Materials

In the growth of InN material, reactant gaseous delivered via organometallic precursors of trimethylindium (TMI) and ammonia (NH₃) are utilized as a source of group-III and -V atoms, respectively. TMI consists of one indium atom bonded to three methyl groups with a chemical formula of In(CH₃)₃. Indium, with an atomic number 49, has filled 5s² and unfilled 5p¹ electronic states. Based on the valence-shell electron pair repulsion (VSEPR) theory, these bonds hybridize (overlap to each other) to form a planar, trigonal sp² configuration. One methyl group is attached to each sp² orbital, with a bond angle of 120°, leading to the configuration shown in Fig. 4.5.

![Molecular structure of trimethylindium (TMI).](image)

Figure 4.5 Molecular structure of trimethylindium (TMI).

The kinetics of TMI pyrolysis, i.e., decomposition, is still unclear; however, decomposition studies of TMI in a toluene [51], helium [52], hydrogen [53], and nitrogen [54] carrier gases at various temperatures is given by the following relations:

\[
\text{In(CH}_3\text{)}_3 \rightarrow \text{In(CH}_3\text{)}_2 + \text{CH}_3, \tag{4.8}
\]

\[
\text{In(CH}_3\text{)}_2 \rightarrow \text{InCH}_3 + \text{CH}_3, \tag{4.9}
\]

\[
n - \text{InCH}_3 \rightarrow [\text{InCH}_3]_n(s), \tag{4.10}
\]
\[ \text{InCH}_3 \rightarrow \text{In}^+ + \text{CH}_3^- . \] (4.11)

TMI pyrolysis in hydrogen and nitrogen proceeds via a sequential loss of methyl radicals (Eqs. 4.8 and 4.9) and at temperatures below 480 °C, an involatile bonding is formed due to the diffusion of a monomethylindium (Eq. 4.10) molecule to the substrate [51,53].

Ammonia or azane consists of one nitrogen atom bonded to three hydrogen atoms with a chemical formula of \( \text{NH}_3 \). Nitrogen, with an atomic number 7, has filled \( 2s^2 \) and unfilled \( 3p_x, 3p_y, \) and \( 3p_z \) electronic states. These bonds hybridize to form a tetrahedral \( sp^3 \) configuration with a bond angle of 107.8° and with one unbounded lone pair, shown in Fig. 4.6.

![Molecular structure of ammonia (NH\textsubscript{3}).](image)

Figure 4.6 Molecular structure of ammonia (NH\textsubscript{3}).

Ammonia is directly or indirectly the precursor to most nitrogen-containing semiconductor materials. Ammonia dissociates into its constituents hydrogen and nitrogen according to the given reaction:

\[ 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 . \] (4.12)

The dissociation rate of ammonia depends on temperature, pressure, and catalysts being used. Figure 4.7 shows a nearly complete conversion from ammonia to hydrogen and nitrogen at high temperatures and atmospheric pressure. Complete decomposition temperature of ammonia is approximately at 600, 700, and 800 °C for 1 (or atmospheric), 5, and 15 bar, respectively [55].
Figure 4.7 Thermal decomposition of ammonia (NH₃) [52].

Ammonia has relatively large bond strength, and its homogeneous decomposition proceeds only at high temperatures (see Figure 4.7). However, as the introduction of N₂, H₂, and organometallic precursors to the gas stream will catalyze NH₃ decomposition at much lower temperatures.

4.2.3.3 Precursor Ratio

Besides growth temperature, precursors’ ratio is the most important growth parameter in the MOCVD growth mechanism; however, influence of V/III ratio (molar ratio of NH₃ to TMI) on the InN materials is complicated. Since high ammonia pressure is required to prevent N-desorption from the growth surface, high V/III ratio (> 20000) is required to suppress vacancies on the nitrogen sublattice [56–58]. However, low V/III ratio is necessary (12000< V/III ratio <18000) to increase growth rate, where surface diffusion of indium adatoms increases to find
energetically favored sites to form stable InN bonds [59–61]. On the other hand, several V/III ratios are reported to avoid In and N vacancies this could be due to the differences in MOCVD system such as reactor height and flow dynamics [60,62]. In addition to nucleation parameters, in the presence of high V/III ratio, group III-V semiconductor will tend to be group-V terminated, which is believed that group-V dimer surface reconstruction maybe be 2 × 1 depending on the other condition as well [63].

4.2.4. High-Pressure Chemical Vapor Deposition (HPCVD)

The growth of high-quality InN material at low pressure is limited due to low dissociation temperature of InN (~600 °C) and enormous gap between partial pressures of trimethylindium and ammonia precursor. Since ammonia is a very stable molecule and its cracking efficiency is quite low at low temperatures [53], very high ammonia pressure is required to achieve epitaxial growth of InN which results in treading dislocations at the grain boundaries [64]. Although plasma-assisted MBE demonstrated that high-quality InN epilayers could be achieved with low-pressure deposition techniques, integration of InN epilayers into wide band gap group III-nitride heterostructure is a challenging task. Thermodynamic estimates suggest that the surface for highly volatile compounds of InN and related alloys can be stabilized at much higher temperatures if stabilized at high pressures of the volatile gas species [29–31].

HPCVD growth technique utilizes pressure dependency of the surface reaction chemistry to stabilize surface radicals at higher growth pressure in reference to conventional low-pressure growth techniques such as MBE and MOCVD. High growth temperature provides two advantages for the InN epitaxial growth, that is:
i. High mobility of surface radicals on the growth surface may lead to better structural quality (discussed in section 5.1).

ii. High-pressure approach may enable to reduce processing window between InN and GaN to overcome stabilization challenge of ternary InGaN alloys.

Although there are significant experimental studies of the InN growth, theoretical and thermodynamic studies of the InN material system is still inadequate. Therefore, thermodynamic \( p-T-x \) relations are derived from the InN decomposition process which is given by the following relation:

\[
\text{InN}_{(s)} \rightarrow \text{In}_{(s)} + \frac{1}{2} \text{N}_{2(s)}.
\] (4.13)

McChesney et al. [19] showed linear decomposition relation of group-III nitride materials given by the following equation:

\[
p(N_i) \rightarrow p_o \left[ \Delta H \left( \frac{1}{T} - \frac{1}{T_o} \right) \right],
\] (4.14)

where \( \Delta H \) is a decomposition heat, \( R \) is a universal gas constant, and \( T \) is an equilibrium temperature. Results of pressure-temperature relations for group III-nitrides are demonstrated in Fig. 4.3. The relation indicates that nitrogen pressure \( \leq 10^2 \) bar and substrate temperature \( \leq 900 \) K, surface decomposition of InN could be effectively suppressed.

HPCVD growth system consists of a horizontal flow channel reactor [65]. In order to prevent uncontrolled deposition on the opposite site, a symmetrical sample design was chosen. The schematic view and the image of the inner shell of HPCVD reactor are shown in Fig. 4.8. In
order to optimize the precursor and carrier gas consumption, a narrow flow channel with a height of 1mm was implemented.

Figure 4.8  (a) Schematic representation of the HPCVD inner reactor showing flow direction. (b) Cross sectional image of the HPCVD reactor parts [65].

The schematic representation of the inner reactor embedded to outer shell is illustrated in Fig. 4.9. Since *in-situ* characterization is valuable tool in order to understand surface chemistry and thin film properties during the growth process, noninvasive optical ports are located perpendicular to gas flow direction. In HPCVD system, three *in-situ* optical characterization techniques embedded to monitor precursor delivery kinetics by ultraviolet absorption spectroscopy, surface topography by laser light scattering, and growth chemistry by principal angle reflection spectroscopy [29].
4.3. Substrates Used for InN Epitaxy

Relatively low melting temperatures and dissociation pressures of InN make it difficult to obtain large-single InN crystals. Therefore, single crystal InN films have been grown on number of substrates listed in Table 4.1. Sapphire (0001) is the most extensively used substrate material for the epitaxial growth of InN due to its wide availability, low cost, hexagonal symmetry, transparent nature, and stability at high temperatures (~1100 °C) required for chemical vapor deposition techniques. However, it has a poor structural quality and high thermal mismatch with InN compared with the other substrates. The large lattice mismatch and thermal expansion coefficient difference can results in extremely threading dislocations, high density of structural defects, and in-plane strain [66]. Sapphire is also an insulating material; therefore, it is not preferred as a substrate for electrical applications. On the other hand, high quality epitaxial InN films have been grown easily on sapphire substrates by the conventional growth methods, HVPE, MBE, MOCVD, and HPCVD.
Table 4.1  Lattice constants of wurtzite InN and its substrates.

<table>
<thead>
<tr>
<th>Properties</th>
<th>InN</th>
<th>GaN</th>
<th>Sapphire ($\alpha$-Al$_2$O$_3$)</th>
<th>6H-SiC</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>Wurtzite</td>
<td>Wurtzite</td>
<td>Hexagonal</td>
<td>Wurtzite</td>
<td>Diamond</td>
</tr>
<tr>
<td>Native substrate</td>
<td>No</td>
<td>No</td>
<td>-</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>3.5378</td>
<td>3.189</td>
<td>4.758</td>
<td>3.08</td>
<td></td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.7033</td>
<td>5.185</td>
<td>12.991</td>
<td>15.12</td>
<td>5.43</td>
</tr>
<tr>
<td>Lattice mismatch with InN (%)</td>
<td>0</td>
<td>9.8</td>
<td>–25</td>
<td>12.9</td>
<td>–8</td>
</tr>
<tr>
<td>$\alpha_a$ ($10^{-6}$ K$^{-1}$)</td>
<td>4</td>
<td>5.59</td>
<td>7.5</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>$\alpha_c$ ($10^{-6}$ K$^{-1}$)</td>
<td>3.17</td>
<td>3.17</td>
<td>8.5</td>
<td>4.7</td>
<td>3.59</td>
</tr>
</tbody>
</table>

Being the most extensively used substrate material, it is profound to understand sapphire’s physical properties. Sapphire belongs to a trigonal crystal system and space group of R$3c$ [67–69]. The trigonal crystal system is the only crystal system whose point groups have more than one lattice system associated with their space groups of hexagonal and rhombohedral lattices [67,69]. The representations of the $\alpha$-sapphire i.e., corundum structure are illustrated in Fig. 4.10. The lattice structure of hexagonal unit cell consists of closed packed aluminum planes alternated with oxygen planes stacked by Al-O ionic bonds. Since one third of the aluminum positions are vacant, vacant sites produce two third stoichiometric ratio of aluminum to oxygen in sapphire. Due to the aluminum site vacancies and ionic bonding, all sapphire surfaces utilized for InN epitaxy including (0001) are nonpolar.
Figure 4.10 Lattice structure of sapphire crystal along: (a) [0001], (b) [1\bar{1}00], and (c) [1\bar{1}20] planes, where bold and gray spheres denote O and Al atoms, respectively [69].

Equation 4.1 indicates that lattice mismatch between InN and sapphire is ~35%; however, the actual mismatch is ~25%. When InN epilayer is grown on nitridized sapphire substrate, the epitaxial relationship between InN and \(\alpha\)-Al\(_2\)O\(_3\) substrate was found to be [1010]\(_{\text{InN}}\) // [1020]\(_{\text{Al}_2\text{O}_3}\). This is mainly due to InN basal plane rotates by ~30° with respect to the \(c\)-plane of sapphire during the growth [70]. In other words, epitaxial growth of InN on sapphire substrate is governed by \(Al-O\) ionic bonding, one-third aluminum site vacancies result in a 30° in-plane rotation of the InN lattice with respect to sapphire plane [71]. Recent researches have revealed
that sapphire substrate surface pretreatment and insert in intermediate buffer layer between sapphire substrate and InN epilayer can significantly improve the film quality. Nitridization of sapphire substrate surface significantly improves the crystalline quality of InN as a result of the AlN buffer layer formation [72–74]. The improvement of InN film quality by the formation of an AlN buffer layer is due to the fact that AlN has the same lattice structure as InN and the lattice mismatch is reduced from ~25% for InN/sapphire to 13% for InN/AlN/sapphire [70]. InN epitaxial films grown on sapphire substrate are generally hexagonal. However, there are few researches formation of mixed hexagonal and cubic structures at low growth temperature between 375 and 450 °C [75].

Since epitaxial growth of GaN is the most well established among the group III-nitrides, GaN template is the second most common substrate utilized for the epitaxial growth of InN epilayer. The highest mobility and lowest carrier concentration of 2050 cm²/Vs and 3.49 × 10¹⁷ cm⁻³, respectively, in the MBE grown InN on MOCVD grown GaN template [76]. Due to the intrinsic asymmetry of the tetrahedral bonding in the wurtzite GaN material, polarity of the GaN template has also significant role in the growth process. High-quality InN films have been grown on an N-polar GaN template by rf-MBE [77]. Besides V/III ratio, surface polarity of GaN template is responsible for the indium-island formation on the InN growth [78].

Si is also a suitable substrate material for InN due to smaller lattice mismatch compared with the commonly used insulating sapphire substrate; 8% for InN(0001)/Si(111) and 25% for InN(0001)/α-Al₂O₃(0001). In the 90s, Si was widely used as a substrate but the film quality was very poor [86]. The biggest challenge in the growth of InN epilayer is formation of an amorphous SiNx layer on the Si-surface because of the unintentional nitridization on the substrate during the growth [72]. The Si substrate surface becomes nitride at a low growth
temperature of ~400 °C and growth at a temperature lower 400 °C are found to be polycrystalline due to reduced migration of the deposited indium and nitrogen radicals [41]. Finally, several other materials have also been utilized as a substrate for the epitaxial growth of InN. These include GaAs, InAs, GaP, InP, MgAl₂O₄, LiGaO₂, and glass [79–81].

4.4. Summary

All the above discussion has been concerned with nucleation and growth of InN epilayers on a perfect substrate and ideal epitaxial process. Although all growth techniques exhibit advantages and disadvantages simultaneously, the optimum one can be chosen under the given constraints and challenges. We, here, have focused on InN epitaxial growth either directly on sapphire (0001) substrates or on MOCVD-grown GaN/sapphire (0001) templates, which is discussed in detail in Chapter 5.
4.5. References


[31] M. Alevli, Growth and characterization of Indium Nitride layers grown by High-pressure Chemical Vapor deposition, (Ph. D. Thesis-Georgia State University, Atlanta, 2008).


CHAPTER 5

PHYSICAL PROPERTIES OF INDIUM NITRIDES GROWN BY HPCVD

In order to understand physical properties of InN material, nondestructive structural and optical characterizations were performed for InN epilayers grown by High-Pressure Chemical Vapor Deposition. InN layers studied in this research were characterized by X-ray diffraction, Raman scattering spectroscopy as well as IR reflection spectroscopy since these techniques are the three most utilized characterizations due to their nondestructive characteristic.

X-ray diffraction measurements were performed by utilizing a Philips X’Pert PRO MPD X-ray diffractometer equipped with monochromatic Cu-K\(_{\alpha1}\) (\(\lambda = 1.540598\) Å) source. For all XRD measurements, a triple axis (TrAx) configuration was used for 2\(\theta\)-\(\omega\) scans normal to \(c\)-plane of an InN material, where 2\(\theta\) refers to an angle between incident and diffracted beams and \(\omega\) refers to an angle between incident beam and thin film surface. Typically, XRD peak shape is assumed to be either Lorentzian or Gaussian; therefore, convolution of a Lorentz profile and a Gaussian profile, which is a PseudoVoigt profile, utilized through this thesis to determine 2\(\theta\) diffraction center and full-width at half maximum (FWHM) of the Bragg reflexes. The lattice constant, \(c\), of InN is calculated by plugging 2\(\theta\) value of InN (0 0 0 2) Bragg reflex into Eq. 3.26 and experimental finding is compared with reported value of 5.703 Å, though it is scattered in the range from 5.701 to 5.708 Å, listed in Table 3.17. Besides 2\(\theta\)-\(\omega\) scans, for some InN epilayers, \(\omega\)-scans were performed, where detector remains stationary and the sample is rotated about a \(\omega\) angle, to understand better dislocation-induced tilt/twist between InN layer and underlying substrate. Diffraction peaks are broadened by parameters related to XRD instrument
as well as by parameters related to InN layer. Thus, simplified method is used to estimate crystallite size and in-plane strain on InN layer from Eqs. 3.29 and 3.30, respectively.

Raman spectroscopy was applied to analyze bonding and local-range ordering of InN layers. The custom-configured Raman spectrometer uses a liquid N\textsubscript{2}-cooled multichannel charge-coupled (CCD) camera and a McPherson double subtractive monochromator in combination with a single 2m monochromator system to record inelastic Raman scattering. Diode-pumped solid-state (DPSS) laser light using an excitation energy of 2.33 eV (532 nm) was utilized to excite spectra with micro-Raman illumination stage. All Raman measurements were performed in back scattering geometry along the c-plane at room temperature. Lorentzian and Gaussian line profiles were utilized to calculate vibrational frequencies (positions) and linewidths (FWHMs) of $E_2$(high) and $A_1$(LO) modes, respectively. Since $E_2$(high) mode is a nonpolar mode, which does not interact with Coulomb forces (see page 50), it is correlated with FWHM of InN (0 0 0 2) Bragg reflex to understand long-range and short-range crystalline orderings in InN layers. Also, force constants of $E_2$(high) and $A_1$(LO) vibrational modes are calculated from Eq. 3.4 to investigate compressive and tensile force induced during the growth. Symmetric and asymmetric broadening mechanisms of these were investigated to understand cross sectional InN layer information.

For IR reflection spectroscopy, a Perkin-Elmer 2000 system was utilized. IR reflection spectra acquired in the near-normal incidence (~8°) configuration in a spectral range between 400 and 8000 cm\textsuperscript{-1} were analyzed using a multilayer stack model [1]. The fitting results, provided optoelectronic information of InN layer, were utilized to determine epilayer thickness, longitudinal-optic (LO) and transverse-optic (TO) phonon frequencies, electron mobility, $\mu$, and free carrier concentration, $n_e$, of InN layer. The dielectric function of InN layer are modeled
using a classical dielectric function for damped harmonic oscillators in combination with a Drude-Lorentz model, which blends coupled contributions of plasma oscillations by classical Drude model and phonons by Lorentzian type oscillator model, described in section 3.2.2. Extracted longitudinal-optic and transverse-optic phonons corresponds to $A_1$(LO) and $E_1$(TO) vibrational modes, respectively. However, they are still represented LO and TO phonons to remain compatible with common nomenclature of IR spectroscopy terminology. Hence they are correlated with Raman $A_1$(LO) and $E_1$(TO) frequencies to understand phonon dynamic and plasmon-phonon coupling effect better.

The surface morphology of InN epilayers was analyzed using a XE 100 Park Atomic Force Microscope (AFM) system working in noncontact mode. The AFM tip used in AFM experiments had a resonance frequency of 300 kHz and a spring constant of 45 N/m. Although only one set of InN epilayers discussed in here have AFM results, AFM analysis is still kept to demonstrate that grain sizes estimated from InN (0 0 0 2) Bragg reflex are in excellent agreement with measured grain sizes from AFM.

In following, this chapter presents ex-situ characterizations to analyze structural and optical properties and to optimize growth parameters of InN layers grown by HPCVD technique and with emphasizes on X-ray diffraction, Raman scattering spectroscopy, as well as IR reflection spectroscopy. Due to nondestructive characteristics and being sibling techniques, X-ray diffraction together with Raman scattering and Raman scattering together with IR reflection analyses are cross-correlated to obtain structural and optical properties, respectively. As described in detail in Chapter 4, the effect of varying one crucial growth parameter at a time on the structural and optical properties of InN epilayer are discussed in five subchapters. The rest of this chapter is organized as follows; the effects of reactor pressure, V/III molar ratio,
trimethylindium-ammonia and ammonia-trimethylindium precursor separations, substrate material influence, and mass transport distance along the flow direction on InN layers are discussed in detail.

5.1. Effect of Growth Pressure

The HPCVD system utilized in this study is the same as that described in detail in section 4.2.4. InN layers investigated here were grown on GaN/sapphire (0001) templates in a pressure range from 1 to 15 bar by HPCVD. The carrier gas flow was adjusted according to a growth pressure such that overall flow velocity within the reactor zone to keep constant. The identical growth pattern was followed for all samples, depicted in Fig. 5.1. InN nucleation procedure started with a heat-up sequence where gas-phase and substrate temperatures were slowly increased under a nitrogen carrier-gas flow (denoted by first step in Fig. 5.1). Then nitridization of a substrate was begun by seeding substrate with nitrogen radicals, while reactor temperature was being ramped up (denoted by second step). Afterwards, InN growth at a nucleation temperature, which was kept lower than the steady-state growth temperature to decrease the mobility of indium-adatoms at surface, was started (denoted by third step). Finally, temperatures were ramped up to growth temperatures to consume excess indium left from the previous sequence. After reaching a steady-state growth temperature, epitaxial growth process was continued 90 minutes for all samples.

In HPCVD system, two substrates can be loaded into reactor zone (see Fig. 4.8) at upper and lower side of inner reactor and both of which can be independently heated. Substrate temperature was varied from 714 to 854 °C; accordingly, the opposite heater, on the top side of
reactor, was varied between 540 and 740 °C to control gas-phase reaction process, which are listed in Table 5.1.

Since significant variation in the growth pressure might influence internal pressure and thermal expansion induced during the InN growth, remaining of the growth parameters were kept at identical conditions to investigate this effect for all InN layers. The ammonia (NH₃) to trimethylindium (TMI) molar ratio (i.e., V/III ratio) was set to 7494 and ammonia and trimethylindium injection times were set to 800 and 2000 ms, respectively. Precursor separations from the end of trimethylindium to the beginning of ammonia and from the end of ammonia to the beginning of trimethylindium were set to 1142 and 900 ms, respectively.

Figure 5.1 Schematic representation of growth pattern to optimize growth parameters. Values are taken from Ref 2.
Table 5.1  Growth parameters of InN layers grown on GaN/sapphire (0001) templates at various pressures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Total flow (slm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas-phase</td>
<td>Substrate</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>1.0</td>
<td>540</td>
<td>714</td>
</tr>
<tr>
<td>b</td>
<td>2.5</td>
<td>540</td>
<td>714</td>
</tr>
<tr>
<td>c</td>
<td>5.1</td>
<td>570</td>
<td>751</td>
</tr>
<tr>
<td>d</td>
<td>10</td>
<td>590</td>
<td>781</td>
</tr>
<tr>
<td>e</td>
<td>15</td>
<td>740</td>
<td>854</td>
</tr>
</tbody>
</table>

5.1.1. Structural and Optical Analysis

Figures 5.2a–e show XRD (2θ-ω)-scans of InN layers grown on GaN/sapphire (0001) templates at growth pressures of 1.0, 2.5, 5.1, 10, and 15 bar, respectively. As depicted in Figs. 5.2a–e, XRD Bragg reflexes with 2θ values at 31.34° and 34.58° correspond to unstrained diffractions of hexagonal and single phases of InN (0 0 0 2) and GaN (0 0 0 2) Bragg reflexes, respectively. Although the FWHM of GaN (0 0 0 2) Bragg reflexes is almost constant for all samples, which is 250 arcsec, the diffraction peak center of InN (0 0 0 2) Bragg reflex slightly shifts from unstrained diffraction value of 31.34° and significantly broadens, as growth pressure varies. Diffraction peak center and FWHM values of InN (0 0 0 2) Bragg reflex were evaluated to determine c-lattice constant, grain size, and mechanical stress along the in-plane direction (or onto c-plane) of InN layers.

Figures 5.3a and 5.3b depict the structural properties obtained from the analysis of InN (0 0 0 2) (2θ-ω) Bragg reflex. The left side of Fig. 5.3a shows the FWHM values of the InN (0 0 0
2) Bragg reflex and the right side of it shows $c$-lattice constant as a function of growth pressure. It is seen in Fig. 5.3a that the FWHM value increases with increasing growth pressure up to 5 bar and decreases afterwards for growth pressures above 5 bar. The FWHM minimum of 376 arcsec, which is observed for a growth pressure of 1.0 bar, indicates optimized growth parameters for this growth pressure. Growth pressures above 2.5 bar exhibit high FWHM values in the range of 600–750 arcsec, which might be due the V/III molar ratio and between trimethylindium and ammonia separation times. The reduction of V/III ratio at higher growth pressures as well as higher growth temperatures is required due to improved cracking efficiency of an ammonia precursor, shown in Fig. 4.7 [2]. Although the carrier gas flow was adjusted according to the growth pressure such that the overall flow velocity within the reactor zone to keep constant, increased growth temperatures also lead to optimization requirement for precursor pulse separations. The effect of V/III ratio and the effect of precursor pulse separation are investigated in sections 5.2 and 5.3, respectively.
Figure 5.2 X-ray diffraction (2θ-ω)-scans of InN layers grown on GaN/sapphire (0001) templates at growth pressures of (a) 1.0, (b) 2.5, (c) 5.1, (d) 10, and (e) 15 bar, respectively.
Calculated $c$-lattice constant value decreases with increasing growth pressure up to 5 bar and increases to a theoretically accepted value of 5.703 Å for 10 bar InN layer. As growth pressure is further increased from 10 to 15 bar, $c$-lattice constant value decreases to 5.697 Å. Although the change in $c$-lattice constant value from 5.7024 to 5.6947 Å might seem to be insignificant, $c$-lattice constant is typically precise to a few numbers in $10^{-4}$ Å in $(2\theta-\omega)$-scan measurement [3]. The FWHMs of InN layers grown with 1 and 2.5 bar exhibit relatively lower values than others, they also exhibit significantly low $c$-lattice constant values. The main reasons affect lattice parameters in the group III-nitrides are deformation potential, dopant size, residual strain, and thermal expansion coefficient [3]. These factors are discussed together with short-range ordering.

The left side of Fig. 5.3b shows the estimated grain size from the InN (0 0 0 2) Bragg reflex and the right side of it shows estimated in-plane strain on the $c$-plane as a function of growth pressure. It is seen in Fig. 5.3b that the grain size significantly decreases from 82 to 41 nm with increasing growth pressure up to 5 bar and slightly increases to 47 nm afterwards for growth pressures above 5 bar. The estimated in-plane strain on the $c$-plane shows an inverse tendency with the grain size as a function of growth pressure. The structural properties extracted from XRD $(2\theta-\omega)$ together with Raman and IR analyses for InN layers grown at various pressures are summarized in Table 5.2.

Although thick epitaxial films assumed to have less strain, the correlation of in-plane strain on the $c$-plane and InN layer thickness acquired from IR analysis exhibit the same tendency as a function of growth pressure. Therefore, the generation and diffusion of point defects might provide extra strain contribution as InN layer thickness increases, which were observed in HVPE-grown GaN layers [4].
Figure 5.3 Growth pressure dependence of X-ray diffraction ($2\theta$-$\omega$) analysis. (a) FWHM (squares, left axis) and $c$-lattice constant (circles, right axis) of InN layers grown on GaN as a function of growth pressure. (b) Grain size (squares, left scale) and in-plane strain (circles, right scale) of InN layers grown on GaN/sapphire (0001) templates as a function of growth pressure.
Figures 5.4a–e show Raman spectra of InN layers grown on GaN/sapphire (0001) templates at growth pressures of 1.0, 2.5, 5.1, 10, and 15 bar, respectively. It is seen in Figures 5.4a–e that Raman spectra are significantly influenced by growth pressure. At growth pressures of 1.0, 2.5 and 15 bar, both $E_2$(high) and $A_1$(LO) vibrational modes are prominent in the Raman spectra; however, these two modes are observed as a weak and broad peaks in the Raman spectra of InN layers grown at growth pressures of 5.1 and 10 bar. In all Raman spectra, in addition to InN vibrational modes, $E_2$(high) vibrational mode of underlying GaN/sapphire (0001) template is also observed.

The representative Raman spectra of InN layers grown on GaN/sapphire (0001) templates in the vicinity of $E_2$(high) mode for various growth pressures are shown in Fig. 5.5a and Fig. 5.5b depicts vibrational properties obtained from $E_2$(high) mode. The left side of Fig. 5.5b shows FWHM values of the $E_2$(high) mode and the right side of it shows spectral mode center of the $E_2$(high) mode. It is seen in Fig. 5.5b that the FWHM value increases with increasing growth pressure up to 5.1 bar and significantly decreases afterwards for up to growth pressure of 10 bar. The FWHM minimum of 10.1 cm$^{-1}$, which is observed for a growth pressure of 1.0 bar, as with XRD analysis indicates fairly-optimized growth parameters for this growth pressure. The $E_2$(high) mode frequency shows an inverse tendency with its linewidth (FWHM) as a function of growth pressure. Although theoretically calculated frequency of $E_2$(high) mode is scattered in the range 485–492 cm$^{-1}$, experimentally observed frequency of it is reported in the range from 488 to 495 cm$^{-1}$, listed in Table 3.8. The principal reason for this blue shifting is that unit cell in the wurtzite structure might be compressed due to hydrostatic pressure or due to thermal expansion of unit lattice which dominates over the relaxed indium nitride bond length (i.e force constant) [5].
Figure 5.4 Raman spectra of InN layers grown on GaN/sapphire (0001) templates at growth pressures of (a) 1.0, (b) 2.5, (c) 5.1, (d) 10, and (e) 15 bar, respectively.
It is profound to state once again that keeping the all growth parameters constant and varying only growth pressure; accordingly, growth temperature was to understand the effect of internal pressure and thermal expansion induced during the InN growth to evaluate by \textit{ex-situ} characterization techniques. If low V/III ratio and short precursor separation were chosen, the trend would be optimized for higher growth pressures.

Estimated force constant of $E_2$(high) mode decreases from 175.85 to 174.91 N·m$^{-1}$ for growth pressure in the range of 1–5 bar and it increases up to 175.49 N·m$^{-1}$ for further increased growth pressures. Typically, the $E_2$(high) mode is associated with vibrations of nitrogen atoms, illustrated in Figs. 3.8 and it is regarded as a representative of the band characteristic of wurtzite structure [6]. Therefore, growth pressure dependence of the $E_2$(high)-FWHM exhibits consistent tendency with FWHM, $c$-lattice constant, grain size, and in-plane strain of the InN layers obtained from XRD InN (0 0 0 2) (2$\theta$-\(\omega\)) Bragg reflex as a function of growth pressure.

The representative Raman spectra of InN layers grown on GaN/sapphire (0001) templates in the vicinity of $A_1$(LO) mode for various growth pressures are shown in Fig. 5.6a and Fig. 5.6b depicts vibrational properties obtained from $A_1$(LO) mode. The left side of Fig. 5.6b shows FWHM values of the $A_1$(LO) mode and the right side of it shows spectral mode center of the $A_1$(LO) mode. It is seen in Fig. 5.5b that the FWHM value increases with increasing growth pressure up to 2.5 bar, exhibiting local maximum value of 20.5 cm$^{-1}$ and significantly decreases afterwards for up to growth pressure of 15 bar. When best fit was being plotted, FWHM and mode frequency values of $A_1$(LO) mode for InN layer grown at 5 bar pressure was disregarded due to its infinitesimal FWHM value which is not scientific.
Figure 5.5  Growth pressure dependence of $E_2$(high) phonon mode. (a) Measured Raman spectra of InN layer grown on GaN/sapphire (0001) templates at growth pressure in the 1–15 bar range. (b) FWHM (squares, left axis) and frequency (circles, right axis) of InN layer grown on GaN/sapphire (0001) templates as a function of growth pressure.
The $A_1$(LO) mode frequency also shows an inverse tendency with its linewidth (FWHM) as a function of growth pressure. Although theoretically calculated and experimental frequencies of $A_1$(LO) mode is reported in the range 586–589 cm$^{-1}$ and 586–590 cm$^{-1}$, respectively (see Table 3.8), our findings are 1 to 1.6 cm$^{-1}$ are higher than experimentally reported frequencies. The shift of $A_1$(LO) mode towards high frequencies, i.e., blueshifting, could be due to some defects like nitrogen vacancies and/or indium interstitials [7]. Due to highest oxygen affinity of indium atom among the group III elements, surface or bulk layer passivation by interstitial oxygen atoms might contribute to upward shifting of $A_1$(LO) phonon frequency, which was reported for $n$-doped InP epilayers grown on silicon (001) substrate [8].

The growth pressure dependence of the $E_2$(high)-FWHM exhibits consistent tendency with $A_1$(LO)-FWHM; accordingly, growth pressure dependence on the band structure of wurtzite structure and on the optical phonon characteristic are correlated. The physical properties extracted from XRD analysis of InN (0002) Bragg reflex and Raman analyses from $E_2$(high) and $A_1$(LO) modes are listed in Table 5.2. The correlation of these data with the optoelectronic properties extracted from IR reflection spectroscopy be investigated next to understand better optical properties.

Infrared (IR) reflection spectra acquired in the spectral range between 400 and 6500 cm$^{-1}$ are analyzed using a multilayer stack model described in Ref. 1. The fitting results provide information on the InN layer structure to determine layer thickness, electron mobility, $\mu$, and longitudinal-optic (LO) and transverse-optic (TO) phonon frequencies, as well as free carrier concentration, $n_e$, of InN layers grown on GaN/sapphire templates, summarized in Table 5.2.
Figure 5.6  Growth pressure dependence of $A_1$(LO) phonon mode. (a) Measured Raman spectra of InN layer grown on GaN/sapphire at growth pressure in the 1–15 bar range. (b) FWHM (squares, left axis) and frequency (circles, right axis) of InN layers grown on GaN/sapphire as a function of growth pressure.
Figures 5.7a and 5.7b and Figs. 5.8a and 5.8b depict optoelectronic properties obtained from the analysis of IR reflection spectroscopy. The left side of Fig. 5.7a shows thickness and the right side of it shows free carrier concentration of InN layers grown on GaN/sapphire (0001) templates as a function of growth pressure. It is seen in Fig. 5.7a that InN layer thickness increases with increasing growth pressure up to 5.1 bar and decreases afterwards for growth pressure up to 10 bar and remains almost constant for further increased growth pressure. The suppressed InN Raman features for the growth pressures of 10 and 15 bar samples can be explained due to low InN layer thickness, which is ~110 nm. On the contrary, InN layer grown at 5.1 bar pressure also exhibit suppressed InN Raman features, shown in Fig. 5.4, it, though, has a 250 nm layer thickness. Hence, to understand better or verify this discrepancy further investigation of it required. As depicted in Fig. 5.7a, IR reflection analysis reveals that free carrier concentration, \( n_e \), decreases with increasing InN layer thickness and lowest free carrier concentration of \( 1.49 \times 10^{18} \text{ cm}^{-3} \) obtained for InN layer grown at 5 bar pressure.

The left side of Fig. 5.7b shows thickness and the right side of it shows electron mobility of InN layers grown on GaN/sapphire (0001) templates as a function of growth pressure. As shown in Fig. 5.7b, IR reflection analysis reveals that electron mobility, \( \mu \), also decreases with increasing InN layer thickness. The electron mobility of InN layers grown on GaN/sapphire (0001) templates are in the range 150–190 cm\(^2\)V\(^{-1}\)s\(^{-1}\) except for the sample grown at 5 bar pressure, which shows a significant low value of 45 cm\(^2\)V\(^{-1}\)s\(^{-1}\).

Cross correlations of InN layer thickness with \( n_e \) and \( \mu \) exhibit that as InN layer thickness increases, both \( n_e \) and \( \mu \) of InN layer decreases, shown in Figs. 5.7a and 5.7b. However, reported experimental tendency between thickness and \( \mu \) of InN layer is directly proportional [9,10].
Figure 5.7 Growth pressure dependence of IR reflection analysis. (a) Thickness (squares, left axis) and free carrier concentration (circles, right axis) of InN layers grown on GaN/sapphire (0001) as a function of growth pressure. (b) Thickness (squares, left axis) and mobility (circles, right axis) of InN layers grown on GaN/sapphire (0001) as a function of growth pressure.
The left side of Fig. 5.8a shows longitudinal-optic (LO) phonon frequency and the right side of it shows free carrier concentration, \(n_e\), of InN layers grown on GaN/sapphire (0001) templates as a function of growth pressure. It is seen in Fig. 5.8a that LO phonon frequency almost remains constant at \(\approx 590\) cm\(^{-1}\) as a function of growth pressure except InN layer grown at a growth pressure of 2.5 bar, which indicates a very low LO phonon frequency estimated at 574 cm\(^{-1}\).

Since incident EM wave impinging on a InN layer with its \(c\)-axis perpendicular to the both magnetic field and the incident radiation of InN layer surface, LO and TO phonons extracted from IR reflection analysis corresponds to \(A_1(LO)\) and \(E_1(TO)\) vibrational modes, respectively, for IR reflection spectroscopy, shown in Fig. 3.17a. Therefore, it is important to cross correlate \(A_1(LO)\) vibrational frequencies obtained from Raman and IR spectroscopies and they exhibit similar tendency as a function growth pressure. Accordingly, Raman \(A_1(LO)\) frequency values are in excellent agreement with IR \(A_1(LO)\) phonon frequency values except very low LO phonon frequency of 2.5 bar sample.

In general, IR vibrational frequencies, spectroscopically, are 2–5 cm\(^{-1}\) higher than Raman vibrational frequencies. However, our results exhibit that Raman \(A_1(LO)\) frequencies are 1–1.6 cm\(^{-1}\) higher than IR frequencies, listed in Table 5.2. Higher frequency shifting of \(A_1(LO)\) frequency results in increase in free carrier concentration for GaN material in the range of 1–100 \(\times 10^{17}\) cm\(^{-3}\), given by the following relation [11]:

\[
\begin{align*}
    n_e &= 1.1 \times (\nu_{LO} - 736)^{0.764} \times 10^{17} \text{ cm}^{-3}, \\
\end{align*}
\]

where \(n_e\) is a free carrier concentration of GaN layer and \(\nu_{LO}\) is a observed LO phonon frequency.
Although such a relation for InN material has not been established yet due to its high free carrier concentration, it is profound to express that free carrier concentration and LO phonon frequency are directly proportional to each other, which is in excellent agreement with our results, shown in Fig. 5.8a.

The left side of Fig. 5.8b shows transverse-optic (TO) phonon frequency and the right side of it shows free electron mobility, \( \mu \), of InN layers grown on GaN/sapphire (0001) templates as a function of growth pressure. It is seen in Fig. 5.8b that TO phonon frequency decreases with increasing growth pressure up to 2.5 bar and increases afterwards to 477 cm\(^{-1} \) for a growth pressure 5 bar, with leveling almost constant for higher growth pressures. Although lattice vibrations generating LO and TO phonons are orthogonal to each other, the identical tendency of these as a function growth pressure is not well understood yet.
Figure 5.8 Growth pressure dependence of IR reflection analysis. (a) LO frequency (squares, left axis) and free carrier concentration (circles, right axis) of InN layers grown on GaN/sapphire (0001) template as a function of growth pressure. (b) TO frequency (squares, left axis) and mobility (circles, right axis) of InN layers grown on GaN/sapphire (0001) template as a function of growth pressure.
Efficient growth temperature calculated from the influence of gas-phase temperature on the substrate temperature as a function of growth pressure is shown in Fig. 5.9. The optimum growth temperatures, listed in Table 5.1, for each reactor pressure were established based on the preliminary structural and optical characterizations of the InN layers by XRD, Raman, and IR spectroscopies. As shown in Fig. 5.9, the optimum growth temperature increases linearly by about 6.6 °C per bar; therefore, the HPCVD approach enables an increase on the InN growth temperature more than 100 °C if the growth pressure is increased from atmospheric pressure to 15 bar. Accordingly, InN epitaxial growth temperature as a function of growth pressure in HPCVD technique can be formulated by the following relation:

$$T = 766 + 6.6 \times p,$$

(5.2)

where T is a growth temperature and p is a growth pressure, in degree Celsius and bar, respectively.

Figure 5.9  Epitaxial growth temperature of InN layer grown on GaN/sapphire (0001) templates by HPCVD as a function of growth pressure.
Table 5.2  Summary of the structural, optical, and optoelectronic properties obtained from XRD (2θ-ω)-scan, Raman scattering, and IR reflection analyses of InN layers grown on GaN/sapphire (0001) templates at various growth pressures.

<table>
<thead>
<tr>
<th>Growth pressure (bar)</th>
<th>1.0</th>
<th>2.5</th>
<th>5.1</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
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<td>XRD</td>
<td></td>
<td></td>
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<td>$\beta_2$ (arcsec)</td>
<td>376</td>
<td>435</td>
<td>749</td>
<td>621</td>
<td>648</td>
</tr>
<tr>
<td>Lattice constant, $c$ (Å)</td>
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<td>5.695</td>
<td>5.6913</td>
<td>5.7024</td>
<td>5.6971</td>
</tr>
<tr>
<td>Grain size (nm)</td>
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<td>71</td>
<td>41</td>
<td>49</td>
<td>47</td>
</tr>
<tr>
<td>Strain ($10^{-4}$)</td>
<td>4.39</td>
<td>5.09</td>
<td>8.75</td>
<td>7.25</td>
<td>7.57</td>
</tr>
<tr>
<td>Raman</td>
<td></td>
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<td></td>
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<tr>
<td>$E_2$(high) FWHM (cm$^{-1}$)</td>
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<td>19.05</td>
<td>27.77</td>
<td>14.99</td>
<td>15.56</td>
</tr>
<tr>
<td>$E_2$(high) frequency (cm$^{-1}$)</td>
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<td>487.7</td>
<td>487.6</td>
<td>488.4</td>
<td>488.5</td>
</tr>
<tr>
<td>$A_1$(LO) FWHM (cm$^{-1}$)</td>
<td>16.93</td>
<td>20.47</td>
<td>14.50</td>
<td>17.64</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>193</td>
<td>175</td>
<td>250</td>
<td>109</td>
<td>115</td>
</tr>
<tr>
<td>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>180</td>
<td>160</td>
<td>45</td>
<td>190</td>
<td>155</td>
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<td>LO phonon frequency (cm$^{-1}$)</td>
<td>591</td>
<td>574</td>
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<tr>
<td>TO phonon frequency (cm$^{-1}$)</td>
<td>479</td>
<td>475</td>
<td>477</td>
<td>477</td>
<td>476</td>
</tr>
<tr>
<td>$N_e$ ($10^{19}$ cm$^{-3}$)</td>
<td>5.58</td>
<td>5.65</td>
<td>1.49</td>
<td>7.87</td>
<td>7.1</td>
</tr>
</tbody>
</table>

5.1.2. Summary

In summary, the effect of growth pressure on the structural, optical, and optoelectronic properties of InN layers grown at super-atmospheric pressure in the range of 1 to 15 bar have been investigated by XRD, Raman scattering, and IR reflection spectroscopies. It is profound to state that keeping all growth parameters constant and varying only growth pressure (accordingly, growth temperature) was to understand the effect of internal pressure and thermal expansion induced during the InN growth to evaluate by ex-situ characterization techniques. If low V/III
ratio and shorter precursor separation were chosen, the FWHM trends would have a different tendency as a function of growth pressure.

The results show that structural properties are strongly influenced by the growth pressure. Raman $E_2$(high) and XRD InN (0 0 0 2) Bragg reflex exhibit FWHM values in the range 10–27 cm$^{-1}$ and 376–749 arcsec, respectively. The in-plane strain on the basal plane and strain on the $c$-direction exhibit different tendencies; therefore, InN has different relaxation chemistries on the $c$-direction and basal plane. This might be due to generation and diffusion of point defects as InN growth progresses. This might be also due to reduction of efficient heating as InN layer thicknesses increases.

Experimentally acquired $E_2$(high) mode frequency values are higher than these obtained from the conventional low-temperature growth techniques, which indicates that InN wurtzite structure might be compressed due to a hydrostatic pressure during the growth or a thermal contraction during the annealing process. Therefore, either or both processes dominate over a relaxed indium nitride dative bond length, causing compressed hexagonal structure.

Free carrier concentration and carrier mobility exhibit consistent decreasing tendencies as InN epilayer thickness increases. This might be due a reduced influence of surface charge accumulation as InN epilayer thickness increases. $A_1$(LO) phonon frequencies obtained from Raman scattering and IR reflection spectroscopies also exhibit consistent tendencies as function of growth pressure; however, $A_1$(LO) frequencies obtained from Raman scattering are higher than these obtained from IR reflection. Finally, optimum growth temperature, determined from the long-range and short-range ordering results, increases linearly by 6.6 °C/bar; therefore, the HPCVD approach enables an increase 100 °C InN growth temperature, if growth pressure is increased from atmospheric to 15 bar.
5.2. Effect of V/III Precursor Ratio

Group V/III molar precursor ratio is one of the most crucial growth parameters influencing InN layer quality, discussed in details in section 4.3. InN layers studied here were grown on sapphire (0001) substrates in the V/III molar ratio range from 900 to 3600 by HPCVD. The intended V/III ratio was adjusted by varying metal organic flow of trimethylindium (TMI) precursor and flow of ammonia (NH₃) precursor was kept constant at 1.2 slm regardless of TMI flow. The identical growth pattern, described in section 5.1, was utilized for all samples. In order to investigate influence of V/III ratio on physical properties of InN epilayers, remaining of the growth parameters were kept constant. The growth pressure was set to 8 bar with a total carrier gas flow of 5.7 slm and substrate and gas-phase temperatures were set to 870 and 670 °C, respectively. The ammonia and trimethylindium injection times were set to 800 and 2000 ms, respectively. Precursor separations from the end of trimethylindium to the beginning of ammonia and from the end of ammonia to the beginning of trimethylindium were set to 1643 and 358 ms, respectively. The steady-state growth process for InN deposition was continued for 3 hours.

5.2.1. Structural and Optical Analysis

Figures 5.10a–f show XRD (2θ-ω)-scans of InN layers grown on sapphire (0001) substrates with V/III molar precursor ratios of 900, 1200, 1800, 2411, 3000, and 3600, respectively. As depicted in Figures 5.10a–f, XRD Bragg reflexes with 2θ values at 31.34° and 33.15° correspond to unstrained diffractions of hexagonal phase InN (0 0 0 2) and InN (1 0 1 1) Bragg reflexes, respectively. The XRD Bragg reflex at 33.15° is mislabeled as In (101) or InN (0 1 1 1) in some studies; however, correct labeling of it should be InN (1 0 1 1) in four-index and InN (1 0 1) in three-index notations, listed in Table 3.18. Indexing was verified with JCPDS data.
of ZnO material due to unavailability of high-quality polycrystalline InN material. Diffraction peak center and FWHM values of InN (0 0 0 2) Bragg reflex were evaluated to determine c-lattice constant, grain size, and mechanical stress along the in-plane direction of InN layers.

Figure 5.10 X-ray diffraction ($2\theta$-$\omega$)-scans of InN layers grown on sapphire (0001) substrates with V/III ratios of (a) 900, (b) 1200, (c) 1800, (d) 2400, (e) 3000, and (f) 3600, respectively.
Figures 5.11a and 5.11b depict the structural properties obtained from the analysis of InN (0 0 0 2) Bragg reflex. The left side of Fig. 5.11a shows the FWHM values of the InN (0 0 0 2) Bragg reflex and the right side of it shows c-lattice constant as a function of V/III molar ratio. It is seen in Fig. 5.11a that the FWHM value increases with increasing V/III ratio up to 1800 and significantly decreases afterwards for V/III ratio of 2400. At V/III ratios above 2400, the FWHM value increases with increasing V/III molar ratio. The FWHM minimum for InN (0 0 0 2) Bragg reflex of 210 arcsec, which is obtained for a group V/III molar ratio of 2400, indicates well-optimized growth parameters for this V/III molar ratio.

Calculated c-lattice constant value follows the same trend with FWHM of InN (0 0 0 2) Bragg reflex as a function of V/III ratio, which is described in previous paragraph. The same trends for FWHM and c-lattice constant values indicate that in-plane relaxation of InN layer is observed as layer-by-layer relaxation progresses during the InN epitaxial growth process. The FWHM and c-lattice constant values are in the range 210–420 arcsec and 5.7046–5.7092 Å, respectively. This finding also gives clue about formation of interstitial defects and structural voids, and they are more likely to be incorporated along the in-plane direction (a-plane in this case) rather than c-plane, which is known as polarization (spontaneous and/or piezoelectric field) induced growth in group III nitrides [12]. The c-lattice constant value of 5.7046 Å for a group V/III ratio of 2400 are in excellent agreement with the unstrained value of 5.7030 Å, which is also good indication of low residual strain in the InN layer and low thermal expansion generated during the epitaxial growth process [2].

The left side of Fig. 5.11b shows the estimated grain size from the InN (0 0 0 2) Bragg reflex and the right side of it shows estimated in-plane strain on the c-plane as a function of V/III molar ratio. It is seen in the Fig. 5.11b that the grain size decreases with increasing V/III ratio up
to 1800 and significantly increases afterwards for V/III ratio of 2400. At V/III ratios above 2400, the grain size decreases with increasing V/III molar ratio. The estimated in-plane strain on the c-plane shows an inverse tendency with the grain size as a function of V/III ratio. The structural properties extracted from XRD (2θ-ω)-scan together with Raman scattering and IR reflection analyses for InN layers grown on sapphire (0001) substrates with various V/III ratios are summarized in Table 5.3. Detailed discussion of the grain size and in-plane strain is investigated with AFM analysis next.

Figures 5.12a–f show Raman spectra of InN layers grown on sapphire (0001) substrates with V/III ratios of 900, 1200, 1800, 2400, 300, and 3600, respectively. It is seen in Figs. 5.12a–f that $E_2$(high) mode is slightly influenced by V/III molar ratio; however, $A_1$(LO) modes for V/III ratios of 900 and 1200 exhibit asymmetric broadening towards lower frequencies.
Figure 5.11 V/III ratio dependence of X-ray diffraction (2θ-ω) analysis. (a) FWHM (squares, left axis) and c lattice constant (circles, right axis) of InN layers grown on sapphire (0001) as a function of V/III ratio. (b) Grain size (squares, left scale) and in-plane strain (circles, right scale) of InN layers grown on sapphire (0001) as a function of V/III ratio.
Figure 5.12 Raman spectra of InN layers grown on sapphire with V/III ratio of (a) 900, (b) 1200, (c) 1800, (d) 2400, (e) 3000, and (f) 3600, respectively.
The representative Raman spectra of InN layers grown on sapphire (0001) templates in the vicinity of $E_2$(high) mode for various V/III molar ratios are shown in Fig. 5.13a and Fig. 5.13b depicts vibrational properties obtained from $E_2$(high) mode. In Raman spectrum, for all V/III ratios, the $E_2$(high) mode displays a visibly symmetric and prominent Lorentzian line shape. Since the $E_2$(high) mode is typically associated with vibrations of nitrogen atoms, illustrated in Fig. 3.8, and it is regarded as a representative of the band characteristic of wurtzite structure [6], symmetric and Lorentzian line shape is a good indication of local ordering (or microscopic crystallinity) of InN layers.

The left side of Fig. 5.13b shows FWHM values of the $E_2$(high) mode and the right side of it shows spectral mode center of the $E_2$(high) mode. It is seen in Fig. 5.13b that the FWHM value decreases with increasing V/III molar ratio up to 2400 and increases afterwards for further increased V/III molar ratios. The FWHM minimum of 7.5 cm$^{-1}$, which is observed for a V/III ratio of 2400, as with the FWHM minimum of 210 arcsec obtained from InN (0 0 0 2) $(2\theta-\omega)$-scan in X-ray diffraction indicates the best combination of the growth parameters for this V/III molar ratio as well as for 8 bar growth pressure.

It is also seen in Fig. 5.13b that the $E_2$(high) mode frequency almost remains constant at 485 cm$^{-1}$ as a function of V/III molar ratio. Although the FWHM of $E_2$(high) mode evidently changes with varying V/III ratio, constant frequency of it with varying V/III ratio may indicate that minor microscopic ordering improvement in InN layer has a negligible influence on the $E_2$(high) indium nitride bond length (or force constant).
Figure 5.13  V/III ratio dependence of $E_2$(high) phonon mode. (a) Measured Raman spectra of InN layers grown on sapphire (0001) substrates with V/III ratio in the 900-3600 range. (b) FWHM (squares, left axis) and frequency (circles, right axis) of InN layers grown on sapphire (0001) substrates as a function of V/III ratio.
The representative Raman spectra of InN layers grown on sapphire (0001) substrates in the vicinity of \( A_1(LO) \) mode for various V/III molar ratios are shown in Fig. 5.14a and Fig. 5.14b depicts vibrational properties obtained from \( A_1(LO) \) mode. In Raman spectrum, for all V/III ratios, the \( A_1(LO) \) mode displays a visibly symmetric and prominent Gaussian line shape except for InN layers grown with 900 and 1200 V/III molar ratios. They exhibit asymmetric broadening and frequency shifting towards higher reciprocal frequencies, i.e., blue shifting. The blue shifting of the \( A_1(LO) \) mode is in generally due to interstitial oxygen incorporation [8] and/or increase in free carrier concentration, which is given by the Eq. 5.1 [11]. At the same time, the blue shifting of the \( A_1(LO) \) mode from its relaxed frequency can be due to a polar phonon and plasmon coupling mechanism in InN material system, which is known as attractive electron-phonon-induced interaction minus the repulsive Coulomb interaction [13]. Accordingly, longitudinal-optic phonon-plasmon coupling in polar semiconductors is given by the following relation [14].

\[
\omega_{\pm} \approx \frac{1}{2} \left[ (\omega_{LO}^2 + \omega_p^2) \pm \sqrt{((\omega_{LO}^2 + \omega_p^2)^2 - 4 \times \omega_p^2 \times \omega_{TO}^2)} \right],
\]

where \( \omega_p, \omega_{LO}, \) and \( \omega_{TO} \) are plasma, longitudinal-optic phonon, and transverse-optical phonon frequencies, respectively. Taking \( \omega_p = 715 \text{ cm}^{-1}, \omega_{LO} = 600 \text{ cm}^{-1}, \) and \( \omega_{TO} = 475 \text{ cm}^{-1}, \) we can estimate longitudinal-optic phonon-plasmon coupled modes. Accordingly, the corresponding \( \omega_– \) and \( \omega_+ \) modes should appear in the in 425–450 cm\(^{-1}\) and 950–1300 cm\(^{-1}\), respectively. Although it is not easy to say that asymmetric broadening for V/III ratios of 900 and 1200 are due to coupling effect, low plasmon frequencies of these, listed in Table 5.3, exhibit significant differences with respect to remaining InN layers.
Figure 5.14 V/III ratio dependence of $A_1$(LO) phonon mode. (a) Measured Raman spectra of InN layers grown on sapphire (0001) substrates with V/III ratio in the 900-3600 range. (b) FWHM (squares, left axis) and frequency (circles, right axis) of InN layers grown on sapphire (0001) substrates as a function of V/III ratio.
The left side of Fig. 5.14b shows FWHM values of the $A_1$(LO) mode and the right side of it shows spectral mode center of the $A_1$(LO) mode. It is seen in Fig. 5.14b that the FWHM value decreases with increasing V/III molar ratio up to 2400, exhibiting local minimum value of 16.4 cm$^-1$ and increases afterwards for further increased V/III ratios. The $A_1$(LO) mode frequency also shows an direct proportionality with its linewidth (FWHM) as a function of V/III ratio. Since, V/III ratio of 2400 exhibit both lowest $A_1$(LO) mode frequency and lowest linewidth, broadening of the $A_1$(LO) mode is directly related to the red shifting of it. In order to understand better the asymmetric broadening mechanism of the $A_1$(LO) mode for V/III ratios of 900 and 1200, the phonon response in the infrared region is cross correlated with IR reflection results.

Figures 5.15a and 5.15b and Figs. 5.16a and 5.16b depict optoelectronic properties obtained from the analysis of IR reflection spectroscopy. The left side of Fig. 5.15a shows thickness and the right side of it shows free carrier concentration of InN layers grown on sapphire (0001) substrates as a function of V/III ratio. It is seen in the Fig. 5.15a that InN layer thickness increases with increasing V/III molar ratio up to 2400, and slightly decreases afterwards for further increased V/III molar ratio. The asymmetric broadening of the $A_1$(LO) mode for V/III molar ratios of 900 and 1200 can be also explained due to relatively thin InN layer thickness of ~100 nm.

As depicted in Fig. 5.15a, IR reflection analysis reveals that free carrier concentration, $n_e$, decreases with increasing InN layer thickness and lowest free carrier concentration of $1.7 \times 10^{18}$ cm$^-3$ obtained for a V/III ratio of 2400. It is important to note a profound principle in the phonon dynamic that wave vectors in the range 500–600 cm$^-1$ and 600–700 cm$^-1$ may result in anharmonic phonon decay in InN [15]. Although growth technique and parameters are crucial factors, which influence structural and optical relaxation of InN material, the experimental data
analyzed here indicate that thickness of the InN layer should be larger than 150 nm to avoid asymmetric broadening due to anharmonic decay channel. The free carrier concentration values obtained for V/III ratio series in HPCVD, listed in Table 5.3, are still high compared to recent reported free carrier concentration of $5.6 \times 10^{17}$ cm$^{-3}$ for InN epilayers grown on GaN by plasma-assisted molecular beam epitaxy (PAMBE) [9].

The left side of Fig. 5.15b shows thickness and the right side of it shows electron mobility of InN layers grown on sapphire (0001) substrates as a function of V/III ratio. As shown in Fig. 5.15b, IR reflection analysis reveals that electron mobility, $\mu$, increases with increasing InN layer thickness. The electron mobility of InN layers grown on sapphire (0001) substrates are in the range 64–1020 cm$^2$V$^{-1}$s$^{-1}$. The InN layer grown with V/III ratio of 900 exhibits significantly low electron mobility of 64 cm$^2$V$^{-1}$s$^{-1}$, which also gives clue about asymmetric broadening of $A_1$(LO) mode. The thickest InN layer of 360 nm exhibits highest electron mobility of 1020 cm$^2$V$^{-1}$s$^{-1}$ and lowest free carrier concentration of $1.7 \times 10^{18}$. These findings are competitive to recent reported InN layer grown on GaN/sapphire (0001) template by MOCVD with a V/III ratio of 18000, a carrier mobility of 1300 cm$^2$V$^{-1}$s$^{-1}$ and free carrier concentration of $4.6 \times 10^{18}$ cm$^{-3}$ [10].

Cross correlations of InN layer thickness with free carrier concentration and carrier mobility exhibit that as InN layer thickness increases, free carrier concentration of InN layer decreases and carrier mobility of InN layer increases, depicted in Figs. 5.15a and 5.15b, which agrees well with reported experimental tendencies [9,10]. This might be due to structural relaxation and/or reduced influence of the surface charge accumulation as InN film thicknesses increases.
Figure 5.15 V/III ratio dependence of IR reflection analysis. (a) Thickness (squares, left axis) and free carrier concentration (circles, right axis) of InN layers grown on sapphire (0001) as a function of V/III ratio. (b) Thickness (squares, left axis) and mobility (circles, right axis) of InN layers grown on sapphire (0001) as a function of V/III ratio.
Although we here only discuss V/III molar ratio in the range 900–3600, the V/III ratios above 3600 exhibit significant turn over for structural and optical properties. Accordingly, access NH\(^+\) and related precursor fragments might alter surface chemistry, incorporation of impurity, and formation of extended defects in the InN epilayers due to high V/III molar ratio, which is above 3000 at a growth pressure of 8 bar [16].

The left side of Fig. 5.16a shows longitudinal-optic (LO) phonon frequency and the right side of it shows free carrier concentration, \(n_c\), of InN layers grown on sapphire (0001) substrates as a function of V/III ratio. It is seen in Fig. 5.16a that LO phonon frequency decreases with increasing V/III molar ratio up to 2400 and significantly increases afterwards for further increased V/III ratio. However, at 2400 V/III ratio, LO phonon frequency calculated as 567 cm\(^{-1}\), which indicates quite low value with respect to LO phonon frequency of remaining V/III ratios as well as reported LO phonon frequency of ~590 cm\(^{-1}\). It is clear that the correlation of longitudinal-optic phonon frequency with free carrier concentration is directly proportional, with each other, which also verifies the relation between longitudinal-optic phonon frequency and free carrier concentration, given in Eq. 5.1.

Furthermore, the correlation of \(A_1(LO)\) phonon frequencies obtained from Raman scattering and IR reflection exhibit almost the same tendency as a function of V/III molar ratio. The \(A_1(LO)\) frequencies obtained from Raman scattering are higher than these obtained from IR reflection for InN layers grown with V/III ratio up to 2400; on the contrary, for V/III ratios above 2400, \(A_1(LO)\) frequency values obtained from IR reflection are higher than these obtained from Raman scattering. This finding might also indicate that NH\(^+\) and related precursor fragments incorporation due to relatively high V/III.
The left side of Fig. 5.16b shows transverse-optic (TO) phonon frequency and the right side of it shows free electron mobility, $\mu$, of InN layers grown on sapphire (0001) substrates as a function of V/III molar ratio. It is seen in Fig. 5.16b that TO phonon frequency wildly oscillates with increasing V/III ratio and shows significant variation in the range 477–495 cm$^{-1}$ except for the V/III ratio of 2400, which exhibit even higher value of 533 cm$^{-1}$. Although the transverse-optical phonon frequencies are substantially higher than the theoretical value of 472 cm$^{-1}$, the similar trend of TO phonon frequency and mobility as a function of V/III ratio give indications about cation (indium) vacancies.

Since $E_1$(TO) vibrational mode wags along the $c$-plane of wurtzite structre, shown in Fig. 3.8, and carrier mobilities also mostly move on the surface accumulation layer of the InN material, having similar tendency as a function of V/III molar ratio might indicate formation of the cation vacancies during growth [17]. Khan et al. have reported that the same behavior for the free carrier concentration and mobility for the bulk InN layer grown on AlN/sapphire templates [10].

Figures 5.17a–f show representative 10 μm × 10 μm AFM images of the InN layers grown on sapphire (0001) substrates with V/III molar ratios of 900, 1200, 1800, 2411, 3000, and 3600, respectively. In all cases, the InN films are homogeneous, without any crack, rather dense and exhibit almost complete coverage of the epilayers; however, the growth pattern likely to be a columnar growth type rather than layer by layer growth (or 2D-like). This growth is not perfectly columnar since the hexagonal columns are located on the top of non-geometric grains, which indicates that the growth was redirected from 2D to columnar growth during the growth progression.
Figure 5.16  V/III ratio dependence of IR reflection analysis. (a) LO phonon frequency (squares, left axis) and free carrier concentration (circles, right axis) of InN layers grown on sapphire (0001) as a function of V/III ratio. (b) TO phonon frequency (squares, left axis) and mobility (circles, right axis) of InN layers grown on sapphire (0001) as a function of V/III ratio.
Figure 5.17 AFM images of a 10 μm × 10 μm scan area of InN layers grown on sapphire (0001) substrates with V/III ratios of (a) 900, (b) 1200, (c) 1800, (d) 2400, (e) 3000, and (f) 3600, respectively.
In Fig. 5.18, growth deviation of the InN crystallites from $c$-axes are presented in oblique view of the AFM image. Since XRD ($2\theta$-ω)-scan reveals that two Bragg reflexes are present in the InN layer grown on sapphire (0001), we can utilize relative intensity of tilted facets. In order to estimate relative intensity, tilted facet intensity divided by the most intense peak, which is InN (0 0 0 2) here, and then converted to a percentage. The estimated percentage of InN (1 0 1 1) phase are found in the range 1.7–12% and the InN layers having larger grain sizes exhibit greater percentage of InN (1 0 1 1) phase.

Figure 5.18  An AFM image of InN columnar growth indicating tilt axis of the columns.

Figures 5.19a and 5.19b depict the surface morphologies obtained from the statistical analyses of AFM and XRD, respectively. The left side of Fig. 5.19a shows grain size and the right side of it shows surface roughness of InN layers grown on sapphire (0001) substrates as a function of the V/III molar ratio. It is seen in Fig. 5.19a that the average grain size and surface roughness slightly decrease with increasing V/III precursor ratio up to 1800, exhibiting local minimums for both at 1800 V/III ratio and significantly increase up to V/III ratio of 2400. As
V/III molar ratio is further increases from 2400 to 3600, the average grain size significantly decreases and surface roughness slightly decreases. The decreases in the average grain size and in the surface roughness towards lower and higher V/III ratios suggest an increase in extended defects, which might be due to decreased amount of surface voids. However, we think that the increase in both grain size and surface roughness at once is not due to degradation of InN layer but more likely due to surface effect.

The left side of Fig. 5.19b shows calculated grain size from AFM and the right side of it shows grain size estimated from XRD InN layers grown on sapphire (0001) substrates as a function of the V/III molar ratio. It is seen in Fig. 5.19b that AFM and XRD analyses exhibit similar trend as a function of V/III ratio. It is crucial to correlate long range ordering (XRD) and surface morphology (AFM) results to understand surface voids and degradation of the InN layers. At 2400 group V/III molar precursor ratio, InN layer exhibits the largest grain area and grain size with the lowest lattice strain but the roughest surface. We think that roughest surface is resulted due to high percentage of InN (1 0 1 1) phase.

The grain area obtained from AFM analysis constitutes 2 dimensional information and the grain size estimated from XRD scan is a 1 dimensional line scan, therefore, the relation between two grain sizes can be given as:

\[ A \approx \alpha \pi r^2, \quad (5.4) \]

where \( A \) is a grain area obtained from AFM and \( r \) is a grain size estimated from XRD analysis. The coefficient \( \alpha \) is calculated in the range 12–13 for all V/III ratios except for V/III ratios 900 and 1200. For these two V/III molar ratios, the coefficient gets smaller to ~3, which is still might be due to low thicknesses of these two InN layers.
Figure 5.19  V/III ratio dependence of AFM and XRD analyses. (a) AFM grain size (squares, left axis) and surface roughness (circles, right axis) of InN layers grown on sapphire as a function of V/III ratio. (b) AFM grain size (squares, left axis) and XRD grain size (circles, right axis) of InN layers grown on sapphire as a function of V/III ratio.
Table 5.3  Summary of the structural, optical, and optoelectronic properties as well as surface morphologies obtained from XRD (2θ-ω)-scan, Raman scattering, IR reflection, and AFM analyses of InN layers grown on sapphire (0001) substrates with various V/III ratios.

<table>
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<tr>
<th></th>
<th>V/III Ratio</th>
<th>900</th>
<th>1200</th>
<th>1800</th>
<th>2411</th>
<th>3000</th>
<th>3600</th>
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<td></td>
<td></td>
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<tr>
<td>β2θ (arcsec)</td>
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<td>287</td>
<td>353</td>
<td>420</td>
<td>210</td>
<td>321</td>
<td>399</td>
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<tr>
<td>Lattice constant, c (Å)</td>
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<td>5.7064</td>
<td>5.7092</td>
<td>5.7046</td>
<td>5.7071</td>
<td>5.7079</td>
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<td>Grain size (nm)</td>
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<td>81.7</td>
<td>64.1</td>
<td>94.4</td>
<td>74.6</td>
<td>70.6</td>
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<tr>
<td>Strain (10⁻⁴)</td>
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<td>4.4</td>
<td>5.6</td>
<td>3.8</td>
<td>4.8</td>
<td>5.1</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>E₂(high) FWHM (cm⁻¹)</td>
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<td>8.40</td>
<td>8.20</td>
<td>7.53</td>
<td>7.90</td>
<td>7.99</td>
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<td>A₁(LO) FWHM (cm⁻¹)</td>
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<td>1.0</td>
<td>0.17</td>
<td>1.8</td>
<td>1.2</td>
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<td></td>
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<td>Ave. grain area (10⁻² μm²)</td>
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<td>1.9</td>
<td>8.5</td>
<td>5.8</td>
<td>4.6</td>
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<td>Surface roughness (nm)</td>
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<td>42</td>
<td>41</td>
<td>72</td>
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5.2.2. Summary

In summary, the effect of group V/III molar precursor ratio on the structural, optical, and optoelectronic properties of InN layers grown on sapphire (0001) substrates with various V/III ratio in the range of 900 to 3600 have been investigated by XRD, Raman scattering, and IR reflection spectroscopies. The results show that the structural and optical properties of InN
epilayers vary strongly with different V/III ratios. An optimum in the structural properties is observed for a group V/III precursor ratio of 2400, where $E_2$(high) and InN (0 0 2) Bragg reflex exhibited lowest FWHM values of 7.53 cm$^{-1}$ and 210 arcsec, respectively, with an estimated grain size of 95 nm and an in-plane strain component of $3.8 \times 10^{-4}$. The calculated epilayer thickness for this V/III ratio was 360 nm (i.e., growth rate of 120 nm/hr), with a free carrier concentration of $1.7 \times 10^{18}$ cm$^{-3}$ and a carrier mobility of 1020 cm$^2$V$^{-1}$s$^{-1}$.

Furthermore, the optical analysis indicates that with varying group V/III precursor ratio, the nonpolar phonon frequency of $E_2$(high) mode remains constant; whereas, the polar phonon branches of transverse-optic (TO) and longitudinal-optic (LO) phonons are significantly shifted. As InN epilayer thickness increases, free carrier concentration of InN layers decreases and carrier mobility of InN layers increases. The multilayer stack analysis also reveals that free carrier concentration and longitudinal-optic phonon frequency exhibit consistent tendencies; while, carrier mobility and transverse-optical phonon frequency exhibit consistent tendencies as a function of V/III ratio.

In addition to structural and optical analyses, surface morphologies of AFM as a function of V/III molar ratio exhibits consistent tendency with grain size estimated from XRD. At 2400 group V/III molar ratio, InN layer exhibits the largest grain area with the lowest lattice strain but the roughest surface. We think that roughest surface is resulted due to high percentage of InN (1 0 1 1) phase. Finally, the grain areas measured from AFM and grain sizes estimated from XRD verify the simplified model, given in Eq. 5.4 with a correction factor of ~10.
5.3. Effect of Precursor Pulse Separation

Precursor pulse separation is also an important growth parameter in HPCVD approach, which utilizes pressure dependency of surface reaction chemistry to stabilize surface radicals at high growth pressures. Therefore, a unique pulsed injection scheme was embedded into a HPCVD growth technique to separate precursors of trimethylindium (TMI) and ammonia (NH₃) temporarily in a high-pressure nitrogen gas stream, illustrated in Fig. 5.20. This approach allows controlling gas phase chemistry and enables to trace surface chemistry. In Fig. 5.20, steady-state growth of InN epilayer was depicted for a constant injection cycle. Two sets of InN layers grown either directly on sapphire substrates or on GaN/sapphire templates at 15 bar growth pressure were investigated for various precursor pulse separations in this study.

For InN layers grown directly on sapphire (0001) substrates, precursor pulse separation from end of TMI to beginning of NH₃ (denoted by S₁) was varied from 800 to 1800 ms and accordingly precursor separation from end of NH₃ to beginning of TMI (denoted by S₂) was varied from 2400 to 1400 ms, keeping the overall cycle duration constant. The V/III ratio was set to 2252 and the flows of ammonia and trimethylindium precursors were kept constant at 600 and 0.26 sscm, respectively, with a total carrier gas flow of 12 slm. Gas-phase and substrate temperatures were adjusted at 751 and 865 °C, respectively, and epitaxial growth process was continued for 3 hours, listed in Table 5.4.

For the InN layers grown on c-plane GaN/sapphire (0001) templates, precursor pulse separation from end of TMI to beginning of NH₃ (denoted by S₁) was kept constant at 1643 ms and precursor separation from end of NH₃ to beginning of TMI (denoted by S₂) was varied from 308 to 558 ms, adjusting the overall cycle duration accordingly. The V/III ratio was set to 2854
and flows of ammonia and trimethylindium precursors were kept constant at 1300 and 1.4 sscm, respectively, with a total carrier gas flow of 11.5 slm. Gas-phase and substrate temperatures were adjusted at 796 and 865 °C, respectively, and epitaxial growth process was continued for 3 hours, listed in Table 5.4.

The optimized growth parameters of InN layers grown on c-plane sapphire (0001) substrates and c-plane GaN/sapphire (0001) templates are obtained from the results of the effect of growth pressure and the effect of V/III molar ratio, which are described in detail in sections 5.1 and 5.2, respectively.

Figure 5.20 Schematic illustration of HPCVD pulsed-injection sequence employed for InN epitaxial growth by trimethylindium and ammonia precursors [2].
Table 5.4 Growth parameters of InN layers grown with various precursor separations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Temperatures (°C)</th>
<th>V/III ratio</th>
<th>Flows (sscm)</th>
<th>Separations (ms)</th>
<th>Total cycle (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gas-phase</td>
<td>Substrate</td>
<td>Total</td>
<td>NH₃</td>
</tr>
<tr>
<td>a</td>
<td>Sapphire</td>
<td>751</td>
<td>865</td>
<td>2252</td>
<td>12000</td>
<td>600</td>
</tr>
<tr>
<td>b</td>
<td>Sapphire</td>
<td>751</td>
<td>865</td>
<td>2252</td>
<td>12000</td>
<td>600</td>
</tr>
<tr>
<td>c</td>
<td>Sapphire</td>
<td>751</td>
<td>865</td>
<td>2252</td>
<td>12000</td>
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</tr>
<tr>
<td>d</td>
<td>Sapphire</td>
<td>751</td>
<td>865</td>
<td>2252</td>
<td>12000</td>
<td>600</td>
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<tr>
<td>e</td>
<td>Sapphire</td>
<td>751</td>
<td>865</td>
<td>2252</td>
<td>12000</td>
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<td>Sapphire</td>
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<td>2252</td>
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</tr>
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<td>865</td>
<td>2854</td>
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<td>865</td>
<td>2854</td>
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</tr>
<tr>
<td>d</td>
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<td>865</td>
<td>2854</td>
<td>11500</td>
<td>1300</td>
</tr>
<tr>
<td>e</td>
<td>GaN/Sapp.</td>
<td>796</td>
<td>865</td>
<td>2854</td>
<td>11500</td>
<td>1300</td>
</tr>
<tr>
<td>f</td>
<td>GaN/Sapp.</td>
<td>796</td>
<td>865</td>
<td>2854</td>
<td>11500</td>
<td>1300</td>
</tr>
</tbody>
</table>
5.3.1. Influence of TMI–NH₃ Pulse Separation

Figures 5.21a–f show XRD (2θ-ω)-scans of InN layers grown on c-plane sapphire (0001) substrates with S₁ separations of 800, 1000, 1200, 1400, 1600, and 1600 ms, respectively. As depicted in Figs. 5.21a–f, XRD Bragg reflexes with 2θ values at 31.34° and ~33° correspond to unstrained diffraction of hexagonal phase InN (0 0 0 2) and In (1 0 1) adlayer, respectively. The diffraction peak centers of InN (0 0 0 2) and In (1 0 1) Bragg reflexes clearly shifts towards lower or higher 2θ values and line shape of In (1 0 1) Bragg reflex is significantly influenced, as S₁ separation varies. Diffraction peak center and FWHM values of the InN (0 0 0 2) Bragg reflex were evaluated to determine c-lattice constant, grain size and mechanical stress along the in-plane direction (or onto c-plane) of the InN layers.

Figures 5.22a and 5.22b depict the structural properties obtained from the analysis of InN (0 0 0 2) Bragg reflex. The left side of Fig. 5.22a shows the FWHM values of the InN (0 0 0 2) Bragg reflex and the right side of it shows c-lattice constant as a function of S₁ precursor separation. It is seen in Fig. 5.22a that the FWHM value decrease with increasing S₁ separation from 800 to 1400 ms, exhibiting a local minimum at 1400 ms with a FWHM of 590 arcsec. As S₁ pulse separation is further increases from 1400 to 1800 ms, the FWHM value increases. The FWHM minimum of 590 arcsec for a S₁ separation of ~1400 ms indicates optimized parameters. The S₁ separations above or below 1400 ms exhibits high FWHM values in the range 750–930 arcsec, which can be due to substantial impact on the growth parameters of temperature and V/III ratio caused by significant variation in the S₁ precursor pulse separation.

Calculated c-lattice constant value decreases with increasing S₁ separation up to 1200 ms, reaching to a theoretically accepted value of 5.7030 Å for 1200 S₁ separation. As S₁ separation is
further increases to 1800 ms, $c$-lattice constant increases to 5.7071 Å. The overall tendencies of calculated $c$-lattice constant value and FWHM of InN (0 0 0 2) Bragg reflex are similar as a function of $S_1$ separation with local minimums observed at 1200 and 1400 ms, respectively.

Figure 5.21 X-ray diffraction ($2\theta$-$\omega$)-scans of InN layers grown on sapphire (0001) substrates with $S_1$ separations of (a) 800, (b) 1000, (c) 1200, (d) 1400, (e) 1600, and (f) 1800 ms, respectively.
Similar to growth pressure samples, which are discussed in details in Chapter 5.1, S₁ separation samples exhibit significant fluctuations between FWHM of InN (0 0 0 2) Bragg reflex and c-lattice constant; on the other hand, the V/III ratio samples’ these values exhibit perfect agreement with each other. Since the FWHM values of InN (0 0 0 2) Bragg reflex for V/III ratio series are in the range of 200–400 arcsec, interplanar relaxation along the c-axis of InN layer, which lead to small fluctuations as a function V/III molar ratio. The InN (0 0 0 2) Bragg reflex values of growth pressure and S₁ separation series are in the range of 500–950 arcsec; therefore, long-range ordering exhibits small influence on the interplanar relaxation along the c-axis of InN layer during the growth.

A plausible explanation for this can be localized deformation along the grain boundaries, which is known as slip band channels [18]. Although the total force needed to enlarge of all the atoms along the c-axis of a crystal is very large, movements of the dislocations allow atoms in a crystal plane to slip one another at a much lower force [19]. Due to lowest energy is required to move along the densest planes of atoms, dislocations enforce lowest energy direction of alignment within a grain of the material. This results in slip that occurs along parallel planes within the grain and known as slip bands. These parallel slip planes were experimentally observed in GaN layers grown on sapphire (0001) substrates [19,20].

The left side of Fig. 5.22b shows the estimated grain size from the InN (0 0 0 2) Bragg reflex and the right side of it shows estimated in-plane strain on the c-plane as a function of S₁ precursor separation. It is seen in Fig. 5.22b that the grain size increases with increasing S₁ separation up to 1400 ms and decreases afterwards for further increasing S₁ separation. The estimated in-plane strain on the c-plane shows an inverse tendency with the grain size as a function S₁ separation.
Figure 5.22 $S_1$ precursor separation dependence of X-ray diffraction ($2\theta$-\omega) analysis. (a) FWHM (squares, left axis) and $c$ lattice constant (circles, right axis) of InN layers grown on sapphire (0001) substrates as a function of $S_1$ separation. (b) Grain size (squares, left axis) and in-plane strain (circles, right axis) grown on sapphire (0001) substrates as a function of $S_1$ separation.
5.3.2. Influence of NH₃–TMI Pulse Separation

Figures 5.23a–f show XRD (2θ-ω)-scans of the InN layers grown on GaN/sapphire (0001) templates with S₂ separations of 308, 358, 408, 458, 508, and 558 ms, respectively. As depicted in Fig. 5.23, XRD Bragg reflexes with 2θ values about 31.34° and 34.58° correspond to unstrained diffractions of hexagonal phases of InN (0 0 0 2) and GaN (0 0 0 2) Bragg reflexes, respectively. Only InN layer grown with S₂ separation of 308 ms exhibit Bragg reflex at 33° corresponds to diffraction of Indium-adlayer of (101) plane. It is seen in Fig. 5.23 that diffraction intensity of InN (0 0 0 2) Bragg reflex significantly decreases above 408 ms S₂ separation. Diffraction peak center and FWHM values of the InN (0 0 0 2) Bragg reflex were evaluated to determine c-lattice constant, grain size and mechanical stress along the in-plane direction (or onto c-plane) of the InN layers.

Figures 5.24a and 5.24b depict the structural properties obtained from the analysis of InN (0 0 0 2) Bragg reflex. The left side of Fig. 5.24a shows the FWHM values of the InN (0 0 0 2) Bragg reflex and the right side of it shows c-lattice constant as a function of S₂ precursor separation. It is seen in Fig. 5.24a that the FWHM value decreases with increasing S₂ separation up to 358 ms with a FWHM of 221 arcsec and increases afterwards for S₂ separation up to 508 ms. As S₂ pulse separation is further increases, the FWHM value decreases to 199 arcsec. However, small FWHM value of InN (0 0 0 2) Bragg reflex for S₂ separation of 558 ms is more likely due to a weak diffraction intensity of it.

Calculated c-lattice constant value remains constant with increasing S₂ separation up to 408 ms and significantly increases afterwards to 5.7023 Å. As S₂ separation is further increases, c-lattice constant value decreases again. Although the FWHM value of InN (0 0 0 2) Bragg
reflex for S₂ separation of 358 ms is one of the lowest values, relatively small c-lattice constant value of it is contradictory, which is not understood yet.

Figure 5.23 X-ray diffraction (2θ-ω)-scans of InN layers grown on GaN/sapphire (0001) substrates with S₂ separations of (a) 308, (b) 358, (c) 408, (d) 458, (e) 508, and (f) 558 ms, respectively.
The left side of Fig. 5.24b shows the estimated grain size from the InN (0 0 0 2) Bragg reflex and right side of it shows estimated in-plane strain on the c-plane as a function of S2 precursor separation. It is seen in Fig. 5.24b that the grain size increases from 105 to 140 nm with increasing S2 separation up to 358 ms and decreases afterwards for up to 508 ms S2 separation. As S2 precursor pulse separation is further increases from 508 to 558 ms, the grain size significantly increases again. The estimated grain sizes are in the range 100–155 nm and they are the second largest grain sizes grown by HPCVD technique. The estimated in-plane strain on the c-plane shows an inverse tendency with the grain size as a function S2 precursor separation; accordingly, they are the second lowest strain values grown by HPCVD.

The cross correlations of the structural results obtained for InN layers grown on GaN/sapphire (0001) templates for the effect of growth pressure series, which is discussed in Chapter 5.1, and grown on sapphire (0001) substrates for the effect of V/III ratio series, which is discussed in Chapter 5.2, with this series are very informative. Two InN layers, exhibiting similar InN (0 0 0 2) FWHMs, are compared with each other, InN layer grown on GaN/sapphire (0001) template exhibits lower in-plane strain and larger grain size but shorter c-lattice constant than the InN layer grown on sapphire (0001) substrates. Therefore, this influence is investigated as a separate subchapter in next.

Initial assessment of the InN layers grown on GaN/sapphire (0001) substrates for various S2 precursor pulse separation indicates that InN layers grown with S2 separations of 308, 358, and 408 ms exhibit better structural properties. Therefore, higher order XRD (2θ-ω)-scan and corresponding ω-scans (rocking curve) of these InN layers were performed to understand the influence of dislocation-induced tilt/twist between InN layer and underlying GaN/sapphire (0001) substrate.
Figure 5.24 S\textsubscript{2} separation dependence of X-ray diffraction (2\(\theta\)-\(\omega\)) analysis. (a) FWHM (squares, left axis) and c lattice constant (circles, right axis) of InN layers grown on GaN/sapphire (0001) as a function of S\textsubscript{2} separation. (b) Grain size (squares, left axis) and in-plane strain (circles, right axis) of InN layers grown on GaN/sapphire (0001) substrates as a function of S\textsubscript{2} separation.
Figures 5.25a–c and Figs. 5.25d–f show XRD (2θ-ω)-scans of InN layers grown on GaN/sapphire (0001) templates along the [0 0 0 l] and [1 0 1 3] directions with S₂ precursor pulse separations of 308, 358, and 408 ms, respectively and the insets show corresponding X-ray rocking curve scans. The line shape, FWHM, and 2θ Bragg reflex cross correlations between on axis (i.e. growth axis) and off axis X-ray diffraction scans enlighten crucial information on the structural properties of InN layers and on the interface as well. It is seen in Figs. 5.25a–c that the line shapes of diffraction peaks of InN (0 0 0 2) and GaN (0 0 0 2) are Lorentzian profile. The line shape of GaN (1 0 1 3) diffraction is also Lorentzian; however, that of InN (1 0 1 3) diffraction is a Gaussian profile. Hence, it is clear that long-range ordering in the GaN/sapphire (0001) template exhibits symmetric expansion from growth axis to off growth axis; whereas, long-range ordering in InN layer exhibits asymmetric expansion of the Bragg planes, which causes deformation in a hexagonal structure of InN material. The finding also helps to explain why InN layers grown on sapphire (0001) substrates exhibit InN (1 0 1 1) Bragg reflex even when X-ray diffraction scan performed on the [0 0 0 l] direction.

Figures 5.26a–d depict the structural properties obtained from the analysis of InN (0 0 0 2) and InN (1 0 1 3) Bragg reflexes, listed in Table 5.5. The left sides of Figs. 5.26a and 5.26c show the FWHM values of the InN (0 0 0 2) and InN (1 0 1 3) Bragg reflexes and the right sides of these show c-lattice constant and 2d spacing as a function of S₂ separation, respectively. It is seen in Fig. 5.26a that the FWHM value decreases with increasing S₂ separation from 308 to 358 ms and increases afterwards for further increasing S₂ separation along the [0 0 0 l] direction. Accordingly, the FWHM value decreases with increasing S₂ separation from 308 to 408 ms along the [1 0 1 3] direction, shown in Fig. 5.26c.
The calculated $c$-lattice constant value remains constant as a function of $S_2$ separation along the [0 0 0 l] direction and calculated 2$d$ spacing value decreases with increasing $S_2$ separation from 308 to 358 ms and increases afterwards for higher $S_2$ separations along the [1 0 1 3] direction. Besides line shape analyses, it is clear that wurtzite lattice expansion of InN layer between [0 0 0 l] and [1 0 1 3] directions as a function of $S_2$ separation is asymmetric. In order to investigate this effect, we express a linear lattice expansion relation between [0 0 0 l] and [1 0 1 3] directions, given by the following expression:

$$\alpha_i = \left( \frac{f_i - f_f}{f_i} \right),$$  \hspace{1cm} (5.5)

where $\alpha_i$ is a lattice expansion, in arbitrary number, $f_i$ and $f_f$ are FWHM values of [0 0 0 l] and [1 0 1 3] directions, respectively. As Eq. 5.5 is used to find lattice expansions for GaN and InN layers, results indicate expansion coefficients of 4.7170 and 4.3484, respectively. Therefore, the expansion difference between InN layer and underlying GaN/sapphire (0001) template exerts an extra force on the InN structure, in which deformation or tilting begins from an ideal wurtzite structure. The left sides of Figs 5.26b and 5.26d show the estimated grain sizes of the InN (0 0 0 2) and InN (1 0 1 3) Bragg reflexes and the right sides of them shows estimated in-plane strain on the (0 0 0 2) and (1 0 1 3) planes as a function of $S_2$ separation, respectively. It is seen in Fig. 5.26b that the grain size increases with increasing $S_2$ separation from 308 to 358 ms and decreases afterwards for further increased $S_2$ separation along the [0 0 0 l] direction. Accordingly, the grain size decreases with increasing $S_2$ separation from 308 to 408 ms along the [1 0 1 3] direction, shown in Fig. 5.26d. The estimated in plane strains along the (0 0 0 l) plane and (1 0 1 3) plane show an inverse tendency with the grain size as a function of $S_2$ separation.
Figure 5.25 XRD (2θ-ω)-scans of InN layers grown on GaN/sapphire (0001) along the [0 0 0 2] and [1 0 1 3] directions with S₂ separations of (a) and (d) 308, (b) and (e) 358, and (c) and (f) 408 ms, respectively. Insets show corresponding rocking curve scans.
Figure 5.26 $S_2$ precursor separation dependence of XRD ($2\theta$-$\omega$) analysis. FWHM (squares, left axis) and lattice constant, $c$-lattice constant (circles, right axis) of InN layers as a function of $S_2$ separation along the (a) [0 0 0 2] and (c) [1 0 $\bar{1}$ 3] directions. Grain size (squares, left axis) and in-plane strain (circles, right axis) of InN layers as a function of $S_2$ separation along the (b) [0 0 0 2] and (d) [1 0 $\bar{1}$ 3] directions, respectively.
The wurtzite crystal structure is non-centrosymmetric and has a polar axis along the [0 0 0 1], along with spontaneous polarization fields occur, shown in Fig. 3.10 [21]. Semipolar orientations include the r-plane (1 0 ě 2) or other planes (1 0 ě 1), (1 0 ě 3), and (1 1 ě 2) [22,23]. Therefore, the correlation of (0 0 0 2) and (1 0 ě 3) planes also reveals correlation of polar and semipolar planes, which is an indication of spontaneous polarization. It is profound to express that lateral microstrain broadening does not affect the symmetric reflections, since these planes have no lateral component [3]. Accordingly, rocking curves are obtained in the symmetric and asymmetric geometry on the planes (0 0 0 2) and (0 0 1 3) planes, respectively.

Figures 5.27a and 5.27b depict the structural properties obtained from the analysis of InN (0 0 0 2) and InN (1 0 ě 3) ω-scan, respectively and they are summarized in Table 5.5. The left side of Fig. 5.27a–b show ω-scan FWHM values and the right side of them show intensity of ω-scans. It is seen in the figures that FWHM values decrease with increasing S2 separation up to 358 ms and increase afterwards for a S2 separation of 408 ms. The RC intensities shows an inverse tendency with FWHM values. Since edge dislocations do not distort the (0 0 0 l) planes [24], the different tendencies of (2θ-ω)-scan and the similar tendencies of ω-scan along the (0 0 0 2) and (0 0 ě 3) planes might indicate edge dislocations are generated in the InN layers as a function of S2 separation. A symmetric and relatively narrow rocking curve FWHMs is an indication of good epitaxial alignment of InN layers on the GaN/sapphire (0001) templates with an optimum observed at a S2 separation of 358 ms.
Figure 5.27  $S_2$ separation dependence of XRD $\omega$-RC analysis. FWHM (squares, left axis) and peak intensity (circles, right axis) of InN layers grown GaN/sapphire (0001) templates along the (a) $(0 \ 0 \ 0 \ 2)$ and (b) $(1 \ 0 \ \bar{1} \ 3)$ planes as a function of $S_2$ separation, respectively.
Table 5.5 Summary of the structural properties obtained from XRD $\omega$- and $(2\theta$-$\omega)$-scans analyses of InN layers along the $(0002)$ and $(10\bar{1}3)$ planes.

<table>
<thead>
<tr>
<th>$S_2$ separation</th>
<th>Angle $\omega$ (°)</th>
<th>308</th>
<th>358</th>
<th>408</th>
<th>308</th>
<th>358</th>
<th>408</th>
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</thead>
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<td>$\omega$-RC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Angle $\omega$ (°)</td>
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<td>15.7071</td>
<td>15.6884</td>
<td>14.2857</td>
<td>14.2912</td>
<td>14.2790</td>
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<tr>
<td>$\beta_\omega$ (arcsec)</td>
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<td>2463</td>
<td>1510</td>
<td>1210</td>
<td>1406</td>
<td></td>
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<td>3758</td>
<td>564</td>
<td>556</td>
<td>265</td>
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<td>5276</td>
<td>4598</td>
<td>1112</td>
<td>1378</td>
<td>574</td>
<td></td>
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<tr>
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<td>31.3856</td>
<td>31.3854</td>
<td>25.6208</td>
<td>25.6681</td>
<td>25.6255</td>
</tr>
<tr>
<td>$\beta_{2\theta}$ (arcsec)</td>
<td>292</td>
<td>221</td>
<td>241</td>
<td>1293</td>
<td>1182</td>
<td>1125</td>
<td></td>
</tr>
<tr>
<td>Lattice constant, c (Å)</td>
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<td>5.6958</td>
<td>5.6958</td>
<td>6.8915</td>
<td>6.8788</td>
<td>6.8902</td>
<td></td>
</tr>
<tr>
<td>Grain size (nm)</td>
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<td>140</td>
<td>128</td>
<td>23.6</td>
<td>25.8</td>
<td>27</td>
<td></td>
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<tr>
<td>Strain ($10^{-4}$)</td>
<td>3.42</td>
<td>2.58</td>
<td>2.82</td>
<td>15</td>
<td>13.5</td>
<td>13</td>
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Figures 5.28a–f show Raman spectra of InN layers grown on GaN/sapphire (0001) templates with $S_2$ precursor separations of 308, 358, 408, 458, 508, and 558 ms, respectively. It is seen in Figs. 5.28a–f that all InN layers grown with various $S_2$ separations exhibit prominent $E_2$(high) and $A_1$(LO) vibrational modes. The InN layers grown with 308, 358, and 408 ms $S_2$ separation also exhibit two weak signals, which are observed at 445 and 472 cm$^{-1}$ and assigned to $A_1$(TO) and $E_1$(TO) modes, respectively. Raman selection rules dictate that along the $z(x, y + x, x)\bar{z}$ back-scattering geometry these two modes are forbidden, listed in Table 3.7. Since XRD $(2\theta$-$\omega$)-scan do not indicates any tilting, the appearance of these two Raman modes are more likely due to instrumental factor in Raman spectroscopy. However, appearance of them in the meantime are considerable to correlate them with longitudinal-optic and transverse-optic phonons obtained from IR reflection spectroscopy.
Figure 5.28 Raman spectra of InN layers grown on GaN/sapphire (0001) templates with $S_2$ separations of (a) 308, (b) 358, (c) 408, (d) 458, (e) 508, and (f) 558 ms, respectively.
The representative Raman spectra of InN layers grown on GaN/sapphire (0001) templates in the vicinity of $E_2$(high) mode for various $S_2$ separations are shown in Fig. 5.29a and Fig. 5.29b depicts vibrational properties obtained from $E_2$(high) mode. It is seen in Fig. 5.29a that Raman spectrum with $S_2$ separations above 458 ms becomes weaker and broader and also Lorentzian line profile for these $S_2$ separations disappear. The left side of Fig. 5.29b shows FWHM values of the $E_2$(high) mode and the right side of it shows spectral mode center of it. It is seen in Fig. 5.29b that the FWHM value increases with increasing $S_2$ separation up to 508 ms and significantly increases for $S_2$ separation from 508 to 558 ms. The significant upheveal in the short-range ordering of InN layer expose a upper limit for $S_2$ parameter for a InN growth at 15 bar.

The $E_2$(high) FWHM minimum of $\sim 8.36$ cm$^{-1}$ and InN (0 0 0 2) Bragg reflex FWHM of 221 arcsec for $S_2$ separation of 358 ms indicate an optimized growth parameters. The $E_2$(high) mode frequency increases with increasing $S_2$ separation from 308 to 358 ms and almost remains constant afterwards up to 508 ms. As the $S_2$ separation is further increased from 508 to 558 ms, the $E_2$(high) mode frequency significantly increases again. Although InN (0 0 0 2) Bragg reflex FWHM for $S_2$ separation exhibits lowest FWHM value, $E_2$(high) FWHM of it indicates very broad linewidth, which is not fully understood yet. Since $E_2$(high) phonon mode is sensitive to the strain in the wurtzite structure along the $c$-plane, discussed in details in section 3.2.1.1, the variation in phonon frequency with the $S_2$ separation, which is attributed to the lattice strain induced by the $S_2$ separation can be evaluated using the empirical formula given below [25].

$$\nu = 50\varepsilon + \nu_0,$$ \hspace{1cm} (5.6)

where $\nu$ and $\nu_0$ are strained and relaxed $E_2$(high) phonon frequencies, respectively, and $\varepsilon$ is given in%. 

Figure 5.29  $S_2$ separation dependence of $E_2$(high) phonon mode. (a) Measured Raman spectra of InN layers grown on GaN/sapphire (0001) templates with various $S_2$ separation in the range of 308–558 ms. (b) FWHM (squares, left axis) and frequency (circles, right axis) of InN layers grown on GaN/sapphire (0001) templates as a function of $S_2$ separation.
The 1.2 cm$^{-1}$ frequency shift of the Raman $E_2$(high) mode for $S_2$ separation from 308 to 558 ms corresponds to an estimated lattice strain of $2.4 \times 10^{-2} \varepsilon$ (in %) (or $2.4 \times 10^{-4} \varepsilon$). Accordingly, the estimated in-plane strain increase on the $c$-plane due to a given $S_2$ separation is a $1.1 \times 10^{-4} \varepsilon$. These findings reveals that long- and short-range ordering results obtained from the analyses of InN (0 0 0 2) Bragg reflex and Raman $E_2$(high) mode, respectively, are perfectly correlated with each other. The differences, however, are more likely related with microscopic ordering and long-range relaxation. Although microscopic ordering is generally believed to be mainspring of long-range ordering, contradictions are always observed in the InN growth process (see section 5.1).

The representative Raman spectra of InN layers grown on GaN/sapphire (0001) templates in the vicinity of $A_1$(LO) mode for various $S_2$ precursor separations are shown in Fig. 5.30a and Fig. 5.30b depicts vibrational properties obtained from $A_1$(LO) mode. Raman spectra indicate that $A_1$(LO) mode exhibits red shifting and asymmetric broadening for $S_2$ precursor separations above 408 ms. It is seen in Fig. 5.30b that the FWHM value increases with increasing $S_2$ separation from 308 to 358 ms and decreases afterwards up to 458 ms $S_2$ separation. As $S_2$ separation is further increases, the $A_1$(LO) FWHM increases again. Although $S_2$ separation of 458 ms exhibits relatively high InN (0 0 0 2) Bragg reflex and Raman $E_2$(high) FWHM values compared to 358 ms, the significantly low $A_1$(LO) FWHM of it is more likely due to the weak Raman $A_1$(LO) feature, which resulted low statistical value. It is also seen in Fig. 5.30b that the $A_1$(LO) mode frequency decreases from 590 to 586 cm$^{-1}$ as a function of $S_2$ precursor separation. The Raman $A_1$(LO) mode frequency be discussed in more detail in next part together with longitudinal optic and free carrier concentration.
Figure 5.30  $S_2$ separation dependence of $A_1$(LO) phonon mode. (a) Measured Raman spectra of InN layers grown on GaN/sapphire (0001) templates with various $S_2$ separation in the range of 308–558 ms. (b) FWHM (squares, left axis) and frequency (circles, right axis) of InN layers grown on GaN/sapphire (0001) templates as a function of $S_2$ separation.
Figures 5.31a and 5.31b and Figs. 5.32a and 5.32b depict optoelectronic properties obtained from the analysis of IR reflection spectroscopy. The left side of Fig. 5.31a shows thickness and the right side of it shows free carrier concentration of InN layers grown on GaN/sapphire (0001) templates as a function of S₂ precursor separation. It is seen in Fig. 5.31a that InN layer thickness decreases with increasing S₂ separation up to 458 ms and increases afterwards for S₂ separations above 458 ms. The weak Raman A₁(LO) mode feature might be due to relatively low thickness of InN layer grown with 458 ms S₂ separation.

As depicted in Fig. 5.31a, IR reflection analysis reveals that free carrier concentration, nₑ, decreases with increasing S₂ separation in the range of 308–408 ms and significantly increases for S₂ separation of 458 ms, which also explains the significant weakening and asymmetric broadening of the A₁(LO) vibrational mode from 408 to 458 ms S₂ separation. As S₂ precursor separation is further increases, the calculated free carrier concentration decreases again. It is important to note that InN layer thickness exhibits similar tendency with free carrier concentration for low S₂ separations (i.e. 308–408 ms); however, it exhibits inverse tendency with nₑ for high S₂ separation (i.e. 458–558 ms). InN layers investigated for growth pressure and V/III ratio dependency revealed inverse correlation between epilayer thickness and nₑ; therefore, the similar tendency of them is not fully understood.

The left side of Fig. 5.31b shows thickness and the right side of it shows electron mobility of InN layers grown on GaN/sapphire (0001) templates as a function of S₂ precursor separation. As shown in Fig. 5.31b, IR reflection analysis also reveals that electron mobility, μ, decreases with increasing S₂ separation in the range of 308–358 ms and significantly increases for S₂ separation of 458 ms. As S₂ precursor separation is further increases, the calculated electron mobility again.
Cross correlations of thickness, free carrier concentration, and electron mobility reveal crucial optoelectronic properties of the InN layers grown on GaN/sapphire (0001) templates. The effect of growth pressure series exhibits linear correlation between free carrier concentration and electron mobility as a function of layer thickness (see Fig. 5.7); on the other hand, the effect of V/III ratio series exhibits reciprocal tendency between them as a function of layer thickness (see Fig. 5.15). Accordingly, this series indicates linear tendency between $n_e$ and $\mu$ as a function of layer thickness.

The estimated $n_e$ values for growth pressure series are $\sim 5 \times 10^{19}$ cm$^{-3}$, for V/III series are $1.5 \times 10^{19}$ cm$^{-3}$, and for $S_2$ separation series $2 \times 10^{19}$ cm$^{-3}$. Accordingly, the estimated $\mu$ values for growth pressure series are $\sim 200$ cm$^2$V$^{-1}$s$^{-1}$, for V/III series are $\sim 500$ cm$^2$V$^{-1}$s$^{-1}$, and for $S_2$ separation series $\sim 200$ cm$^2$V$^{-1}$s$^{-1}$. Therefore, besides structural improvements in the InN layers, there exists optical and/or optoelectronic factors, which totally alter optoelectronic tendencies of the InN material regardless of the short- and long-range ordering influence.

To illustrate, InN layers grown with $S_2$ separations of 408 and 458 ms exhibit free carrier concentrations of $2.01 \times 10^{19}$ and $1.98 \times 10^{19}$ cm$^{-3}$ and $A_1$(LO) phonon frequencies of 590.1 and 586.1 cm$^{-1}$, respectively. As noted previously, the Eq. 5.1 indicates linear tendency between free carrier concentration and $A_1$(LO) phonon frequency in the range of $1-100 \times 10^{17}$ cm$^{-3}$. However, as observed in this series the tendency is lost due to high free carrier concentration of the InN layers.
Figure 5.31 $S_2$ precursor separation dependence of IR reflection analysis. (a) Thickness (squares, left axis) and free carrier concentration (circles, right axis) of InN layers grown on GaN/sapphire (0001) substrates as a function of $S_2$ separation. (b) Thickness (squares, left axis) and mobility (circles, right axis) of InN layers grown on GaN/sapphire (0001) substrates as a function of $S_2$ separation.
The left side of Fig. 5.32a shows longitudinal-optic (LO) phonon frequency and the right side of it shows free carrier concentration, \( n_e \), of InN layers grown on GaN/sapphire (0001) templates as a function of \( S_2 \) precursor separation. It is seen in Fig. 5.32a that LO phonon frequency decreases with increasing \( S_2 \) separation in the range of 308–408 ms and significantly increases for \( S_2 \) separation of 458 ms, which also explains the significant weakening and asymmetric broadening of the Raman \( A_1(LO) \) vibrational mode from 408 to 458 ms \( S_2 \) separation. As \( S_2 \) precursor separation is further increases, the calculated LO decreases again. Unlike Raman \( A_1(LO) \) phonon frequency, longitudinal-optic phonon frequency obtained from IR reflection analysis exhibits perfect agreement with the free carrier concentration. As noted previously, LO phonon extracted from IR reflection analysis is a IR \( A_1(LO) \) vibrational mode, shown in Fig. 3.17. Since IR-fitting-reflection high-frequency dielectric function, given in Eq. 3.19, includes the contribution from all the interband transitions to dielectric function [26], the discrepancy observed between Raman and IR \( A_1(LO) \) modes could be due to the electronic or interband contribution on the IR reflection.

The left side of Fig. 5.32b shows transverse-optic (TO) phonon frequency and the right side of it shows electron mobility, \( \mu \), of InN layers grown on GaN/sapphire (0001) templates as a function of \( S_2 \) precursor separation. It is seen in Fig. 5.32b that TO phonon frequency exhibits almost similar behavior together with LO phonon frequency, \( n_e \), \( \mu \), and thickness of InN layers as a function of \( S_2 \) precursor separation. Although requisite parameters of InN layer are not available at present, the similar tendencies of all parameters obtained from IR reflection spectroscopy indicate strong influence on them due to electronic and interband contribution on the InN multi-layer stack model.
Figure 5.32 $S_2$ precursor separation dependence of IR reflection analysis. (a) LO frequency (squares, left axis) and free carrier concentration (circles, right axis) of InN layers grown on GaN/sapphire (0001) substrates as a function of $S_2$ separation. (b) TO frequency (squares, left axis) and mobility (circles, right axis) of InN layers grown on GaN/sapphire (0001) substrates as a function of $S_2$ separation.
Table 5.6  Summary of the structural, optical, and optoelectronic properties obtained from XRD (2θ-ω)-scan, Raman scattering, and IR reflection analyses of InN layers grown on GaN/sapphire (0001) templates with various S_2 precursor separations.

<table>
<thead>
<tr>
<th>S_2 precursor separation (ms)</th>
<th>308</th>
<th>358</th>
<th>408</th>
<th>458</th>
<th>508</th>
<th>558</th>
</tr>
</thead>
<tbody>
<tr>
<td>β_20 (arcsec)</td>
<td>292</td>
<td>221</td>
<td>241</td>
<td>245</td>
<td>301</td>
<td>199</td>
</tr>
<tr>
<td>Lattice constant, c (Å)</td>
<td>5.6959</td>
<td>5.6958</td>
<td>5.6958</td>
<td>5.7023</td>
<td>5.6995</td>
<td>5.6972</td>
</tr>
<tr>
<td>Grain size (nm)</td>
<td>105</td>
<td>140</td>
<td>128</td>
<td>126</td>
<td>102</td>
<td>155</td>
</tr>
<tr>
<td>Strain (10^-4)</td>
<td>3.42</td>
<td>2.58</td>
<td>2.82</td>
<td>2.87</td>
<td>3.52</td>
<td>2.33</td>
</tr>
<tr>
<td>E_2(high) FWHM (cm^-1)</td>
<td>8.47</td>
<td>8.36</td>
<td>9.06</td>
<td>9.20</td>
<td>9.08</td>
<td>13.31</td>
</tr>
<tr>
<td>E_2(high) frequency (cm^-1)</td>
<td>486.0</td>
<td>487.0</td>
<td>487.0</td>
<td>486.5</td>
<td>487.0</td>
<td>487.8</td>
</tr>
<tr>
<td>A_1(LO) FWHM (cm^-1)</td>
<td>15.6</td>
<td>16.9</td>
<td>16.1</td>
<td>13.7</td>
<td>16.8</td>
<td>18.8</td>
</tr>
<tr>
<td>A_1(LO) frequency (cm^-1)</td>
<td>590.1</td>
<td>589.1</td>
<td>590.1</td>
<td>588.0</td>
<td>586.9</td>
<td>586.1</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>442</td>
<td>320</td>
<td>276</td>
<td>197</td>
<td>327</td>
<td>300</td>
</tr>
<tr>
<td>Mobility (cm^2V^-1s^-1)</td>
<td>260</td>
<td>250</td>
<td>200</td>
<td>290</td>
<td>160</td>
<td>170</td>
</tr>
<tr>
<td>LO phonon frequency (cm^-1)</td>
<td>594</td>
<td>581</td>
<td>579</td>
<td>590</td>
<td>587</td>
<td>583</td>
</tr>
<tr>
<td>TO phonon frequency (cm^-1)</td>
<td>480</td>
<td>477</td>
<td>477</td>
<td>477</td>
<td>485</td>
<td>484</td>
</tr>
<tr>
<td>N_e (10^19 cm^-3)</td>
<td>2.69</td>
<td>2.47</td>
<td>2.01</td>
<td>4.84</td>
<td>2.79</td>
<td>1.98</td>
</tr>
</tbody>
</table>

5.3.3. Summary

In summary, the effect of precursor pulse separations on the structural and optoelectronic properties of InN layers grown either directly on c-plane sapphire (0001) substrates or on MOCVD grown c-plane GaN/sapphire (0001) templates have been investigated by XRD, Raman scattering, and IR reflection spectroscopies. For InN layers grown directly on c-plane sapphire (0001) substrates, the results reveal that XRD InN (0 0 0 2) Bragg reflex exhibited lowest FWHM value of 575 arcsec with an estimated grain size of 52 nm and an in-plane strain
component of $6.4 \times 10^{-4}$ for 1400 ms $S_1$ precursor separation. For this $S_1$ precursor separation, the calculated $c$-lattice constant is completely relaxed; therefore, for optimization of $S_2$ precursor separation, the $S_1$ precursor separation was fixed at 1643.

For InN layers grown on $c$-plane GaN/sapphire (0001) templates, the results reveal that an optimum in the long-range and short-range crystalline orderings of InN layers is observed for a $S_2$ precursor separation of 358 ms, in which $E_2$(high) mode and InN (0 0 0 2) Bragg reflex exhibit lowest FWHM values of 8.3 cm$^{-1}$ and 220 arcsec, respectively. For this $S_2$ separation, the estimated grain size of 140 nm, an in-plane strain of $2.58 \times 10^{-4}$, $n_e$ of $2.1 \times 10^{19}$ cm$^{-3}$, and thickness of 320 nm were observed. However, $c$-lattice is highly compressed for this $S_2$ separation.

The $c$-plane (0 0 0 2) and side cut plane (1 0 $\bar{1}$ 3) of InN layer exhibit inconsistent lattice relaxation tendencies with increasing $S_2$ precursor separation. This reveals that there are different relaxation chemistries for various planes of InN material, exhibiting asymmetric wurtzite structure. The lattice expansion values of InN and GaN are calculated to be 4.3484 and 4.7170, respectively; therefore, anisotropy of InN layer is greater than that of GaN template. This might cause compressive stain in InN-GaN interface. The lattice strain induced by $S_2$ separation, estimated from short-range crystalline ordering, i.e., $E_2$(high) mode, are in excellent agreement with the in-plane strain obtained from InN (0 0 0 2) Bragg reflex. At 358 ms $S_2$ separation, Raman results revealed that dative polar and nonpolar InN bond length is completely relaxed.

Furthermore, growth rate (accordingly thickness) decreases with increasing $S_2$ separation up to 458 ms and increases afterward. $N_e$ and $\mu$ exhibit inconsistent tendencies as a function of $S_2$ separation, which might be due to electronic and interband contributions to a multilayer stack model.
5.4. Effect of Substrate Material

Substrate material type also an important factor in the epitaxial growth process and it also imposes physical and chemical constraints on the nucleation chemistry, growth temperature, and V/III molar ratio. Two sets of InN layers grown either on c-plane sapphire (0001) substrates or c-plane GaN/sapphire (0001) templates at 7.5 bar growth pressure were investigated for a V/III ratio in the range of 1200–3600. The intended V/III ratio was adjusted by varying metal organic flow of trimethylindium (TMI) precursor and flow of ammonia (NH$_3$) precursor was kept constant at 1.2 slm regardless of TMI flow with a growth pressure of 8 bar and a total carrier gas flow of 5.7 slm. The identical growth pattern, discussed in section 5.1, was utilized with 60 and 30 seconds nitridization for sapphire (0001) substrates and GaN/sapphire (0001) templates, respectively. Nitridization of GaN/sapphire (0001) templates was set relatively lower than that of sapphire (0001) substrates due to identical crystal symmetry and compatible dangling bonds.

In order to investigate influence of substrate material type and V/III ratio on InN layer properties, remaining of the growth parameters were kept constant. All InN epilayers were grown with TMI and NH$_3$ injection times of 800 and 2000 ms, respectively. Precursor separation, acquired from the optimization of precursor separation (discussed in section 5.3), from end of TMI to beginning of NH$_3$ (denoted by S$_1$) and from end of NH$_3$ to beginning of TMI (denoted by S$_2$) were set to 1643 and 358 ms, respectively (see Fig. 5.20). The substrate temperature of InN layers grown on GaN/sapphire (0001) templates was slightly higher than sapphire (0001) substrates. However, the gas-phase temperature for sapphire grown InN epilayers was two times as high as that for GaN/sapphire grown InN epilayers. The reduced gas phase temperature was due to decrease gas-phase reactions, listed in Table 5.7.
Table 5.7  Growth parameter of InN layers investigated for the effect of substrate material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Temperatures (°C)</th>
<th>V/III ratio</th>
<th>Nitridization (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gas-phase</td>
<td>Substrate</td>
<td></td>
</tr>
<tr>
<td>Series I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>Sapphire</td>
<td>665</td>
<td>865</td>
<td>1200</td>
</tr>
<tr>
<td>b</td>
<td>Sapphire</td>
<td>665</td>
<td>865</td>
<td>3000</td>
</tr>
<tr>
<td>c</td>
<td>Sapphire</td>
<td>665</td>
<td>865</td>
<td>3600</td>
</tr>
<tr>
<td>Series II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>GaN</td>
<td>338</td>
<td>876</td>
<td>1800</td>
</tr>
<tr>
<td>e</td>
<td>GaN</td>
<td>338</td>
<td>876</td>
<td>2400</td>
</tr>
<tr>
<td>f</td>
<td>GaN</td>
<td>338</td>
<td>876</td>
<td>3600</td>
</tr>
</tbody>
</table>

5.4.1. Structural and Optical Analysis

Figures 5.33a–c and Figs. 5.33d–f show XRD (2θ-ω)-scans of InN layers grown on sapphire (0001) substrates and GaN/sapphire (0001) templates with various V/III ratios, respectively and the insets show corresponding X-ray rocking curve scans. As depicted in Figs. 5.33a–c, XRD Bragg reflexes with 2θ values at 31.34°, 33.14°, and 32.90°, and correspond to unstrained diffractions of hexagonal phase of InN (0 0 0 2), InN (1 0 1 1), and In (1 0 1) adlayer, respectively. Accordingly, XRD Bragg reflexes with 2θ values at 31.34°, and 34.58°, and 32.90°, correspond to unstrained diffractions of hexagonal phase of InN (0 0 0 2), GaN (0 0 0 2), and In (1 0 1) adlayer, respectively, shown in Figs. 5.33d–f. The XRD scans reveal that InN layers grown on sapphire (0001) substrates exhibit InN (1 0 1 1) due to tilted InN epitaxial growth, shown in Fig. 5.18. In addition, InN thin films grown on sapphire (0001) substrates show more prominent In (1 0 1) adlayer, which is responsible for achieving atomically smooth surfaces [27], than that on GaN/sapphire (0001) templates.
Figure 5.33 XRD ($2\theta$-$\omega$)-scans of InN layers grown either on GaN/sapphire (0001) templates with V/III ratios of (a) 1200, (b) 3000, and (c) 3600 or on sapphire (0001) substrates with V/III ratios of (d) 1800, (e) 2400, and (f) 3600, respectively. Insets show corresponding rocking curve scans.
Figures 5.34a–d depict the structural properties extracted from the analysis of InN (0 0 0 2) ($2\theta$-ω)-scan and ω-scan, respectively. The left side of Figs. 5.34a and 5.34c show the FWHM values of the InN (0 0 0 2) Bragg reflex and the right side of these show $c$-lattice constant of InN layers grown either on sapphire (0001) substrates or on GaN/sapphire (0001) templates, respectively, as a function of V/III ratio. It is seen in Fig. 5.34a that the FWHM value decreases with increasing V/III ratio from 1200 to 3000 and increases afterwards for higher V/III ratio. The FWHM minimum of 179 arcsec, which is obtained for a group V/III ratio of 3000, indicates optimized growth parameters of InN grown on sapphire (0001) substrate. Accordingly, as depicted in Figs. 5.34c that the FWHM value decreases with increasing V/III ratio from 1800 to 3600. The FWHM minimum of 225 arcsec, which is obtained for a group V/III ratio of 3600, reveals that growth parameters of InN layer grown on GaN/sapphire (0001) templates can be further optimized (see Table 5.6).

Calculated $c$-lattice constant value of InN layers grown on various substrates follow the same trend with FWHM value as a function of V/III ratio. Figures 5.34a and 5.34c indicate that FWHM and $c$-lattice constant exhibit linear tendency for each sample sets, revealing $c$-plane relation with long-range ordering improvement. Although requisite parameters of InN layer expansion generally given as a function of temperature, it can be also adjusted to investigate as a function long-range ordering due to optimized growth temperature, V/III ratio, and $S_1$ and $S_2$ pulse separations, discussed in Chapters 5.1–5.3.

\[
c = \alpha (\beta - \beta_0) + c_0,
\]  

(5.7)

where $c_0$ and $c$ are minimum and maximum $c$-lattice values; accordingly, $\beta_0$ and $\beta$ are corresponding FWHMs, respectively. The results indicates that the lattice expansion along the $c$-lattice axis is calculated as $5.08 \times 10^{-5}$ and $7.86 \times 10^{-5}$ Å·arcsec$^{-1}$ for InN layers grown on
sapphire (0001) substrates and on GaN/sapphire (0001) templates, respectively. The obtained experimental lattice expansion values in excellent agreement with the reported thermal expansion coefficient of $4 \times 10^{-6} \text{ K}^{-1}$ [28].

The left side of Figs. 5.34b and 5.34d show the estimated grain size from the InN (0 0 0 2) Bragg reflex and the right side of these show estimated in-plane strain on the c-plane of InN layers grown either on sapphire (0001) substrates or on GaN/sapphire (0001) templates, respectively, as a function of V/III ratio. It is seen in Fig. 5.34b that the grain size decreases with increasing V/III ratio from 1200 to 3000 and decreases afterwards for higher V/III ratio for InN layers grown on sapphire (0001) substrates. Accordingly, as depicted in Fig. 5.34d that the grain size increases with increasing V/III ratio from 1800 to 3600 for InN layers grown on GaN/sapphire (0001) templates. The correlation of in-plane grain size expansion per unit c-lattice expansion reveals a symmetric/asymmetric expansion of the InN wurtzite base to its height. The modified Eq. 5.7 indicates a wurtzite base expansion per its height expansion of $0.11 \times 10^6$ and $0.60 \times 10^6$ for InN layers grown on sapphire (0001) substrates and on GaN/sapphire (0001) templates, respectively. The result indicate high restoring force are present on InN layer grown on GaN/sapphire (0001) templates, than these on sapphire (0001) substrates; accordingly, InN (1 0 1 1) Bragg reflex, which is observed for all InN layers grown on sapphire (0001) substrates, is easily generated on sapphire (0001) substrates. Also Figs. 5.34b and 5.34d exhibit that in-plane strain on the c-plane shows an inverse tendency with the grain size as a function of V/III ratio.
Figure 5.34  Substrate material and V/III ratio dependencies of XRD (2θ-ω)-scan analysis. FWHM (left axis) and c lattice constant (right axis) of InN layers grown on (a) sapphire (0001) and (c) GaN/sapphire (0001) as a function of V/III ratio. Grain size (left axis) and in-plane strain (right axis) of InN layers grown on (b) sapphire (0001) and (d) GaN/sapphire (0001) as a function of V/III ratio.
Figures 5.35a and 5.35b depict the structural properties obtained from the analysis of InN layers grown either on sapphire (0001) substrates or on GaN/sapphire (0001) templates, respectively, as a function of V/III ratio. The left side of Figs. 5.35a and 5.35b show $\omega$-scan FWHM values and the right side of them show intensity of $\omega$-scans. It is seen in the figures that FWHM values obtained from $\omega$-scans follow the same trend with FWHM values obtained from $(2\theta-\omega)$-scans. Since edge dislocations do not distort the (0 0 0 l) planes [24], the symmetric tendencies of $\omega$-scans and $(2\theta-\omega)$-scans exhibit lateral dislocation densities. Symmetric and relatively narrow rocking curve FWHM values of InN layers on the GaN/sapphire (0001) templates are an indication of better epitaxial alignment between InN layers and underlying substrate material than sapphire (0001) substrates. The structural properties extracted from XRD $\omega$- and $(2\theta-\omega)$-scans indicate that the influence of V/III ratio on the InN layers grown on sapphire (0001) substrates is greater than that of GaN/sapphire (0001) templates, summarized in Table 5.8.

Figures 5.36a–c and Figs. 5.36d–f show Raman spectra of InN layers grown either on sapphire (0001) substrates or on GaN/sapphire (0001) templates with various V/III ratios, respectively. Figures 5.36a–f exhibit vibrational modes at ~487.5 and ~589 cm$^{-1}$ assigned as $E_2$(high) and $A_1$(LO) vibrations, respectively. In addition to group symmetrically allowed modes of $E_2$(high) and $A_1$(LO) vibrations, two weak and broad vibrations are observed at ~440 and ~470 cm$^{-1}$ assigned as $A_1$(TO) and $E_1$(TO), respectively. It is also seen in Figs. 5.36a–f that InN layers grown on sapphire (0001) substrates indicate stronger group theoretically forbidden $A_1$(TO) and $E_1$(TO) phonon modes than on GaN/sapphire (0001) templates. The vibration assigned as $\beta$ is discussed with $A_1$(LO) in following.
Figure 5.35 Substrate material and V/III ratio dependencies of XRD $\omega$-RC analysis. FWHM (squares, left axis) and peak intensity (circles, right axis) of InN epilayers grown on (a) sapphire (0001) substrates and (b) GaN/sapphire (0001) templates as a function of V/III molar ratio, respectively.
Figure 5.36 Raman spectra of InN layers grown either on sapphire (0001) substrates with V/III ratios of (a) 1200, (b) 3000, and (c) 3600 or on GaN/sapphire (0001) templates with V/III ratios of (d) 1800, (e) 2400, and (f) 3600, respectively.
The representative Raman spectra of InN layers grown either on sapphire (0001) substrates or on GaN/sapphire (0001) templates in the vicinity of \(E_2\text{(high)}\) phonon mode with various V/III ratios are shown in Figs. 5.37a and 5.37c, respectively, and Figs. 5.37b and 5.37d depict corresponding vibrational properties obtained from \(E_2\text{(high)}\) modes. \(E_2\text{(high)}\) phonon frequency of InN layers grown on sapphire (0001) substrate is \(\sim 1\) cm\(^{-1}\) higher than these grown on GaN/sapphire (0001) templates. Accordingly, calculated \(E_2\text{(high)}\) force constant, given in Eq. 3.4, of InN layers grown on sapphire (0001) substrates and GaN/sapphire (0001) templates are 175.32 and 174.64 N\(\cdot\)m\(^{-1}\), respectively.

The left side of Figs. 5.37b and 5.37d show FWHM value of the \(E_2\text{(high)}\) mode and the right side of these show \(E_2\text{(high)}\) vibrational frequency of InN layers grown on sapphire (0001) substrates and GaN/sapphire (0001) templates, respectively. It is seen in Fig. 5.37b that the FWHM value of InN layers grown on sapphire (0001) substrates increases with increasing V/III ratio. Accordingly, the FWHM value InN layers grown on GaN/sapphire (0001) templates increases with increasing V/III ratio from 1800 to 2400 and decreases afterwards for V/III ratio above 2400 V/III ratio. The FWHM minimum of 5.14 cm\(^{-1}\) is observed for InN layers grown on sapphire (0001) substrates with a V/III ratio of 1200; accordingly, the FWHM minimum of 4.79 cm\(^{-1}\) is observed for InN layers grown on GaN/sapphire (0001) templates with a V/III ratio of 3600. Cross correlation of long-range ordering with local-crystallinity of InN layers grown on different substrate material exhibits nonlinear tendency. To illustrate, the long-range ordering of InN layer grown on sapphire (0001) substrates reveals a FWHM minimum at 3000 V/III ratio; however, short-range ordering of it indicates a FWHM minimum at 1200 V/III ratio. Accordingly, the long- and short-range ordering of InN layer grown on GaN/sapphire (0001) templates substrates reveals a FWHMs minimum at 3600 V/III ratio.
Figure 5.37 Substrate material and V/III ratio dependencies of $E_2$(high) phonon mode. Measured Raman spectra of InN layers grown on (a) sapphire (0001) and (b) GaN/sapphire(0001) with V/III ratio in 1200–3600 range. FWHM (left axis) and frequency (right axis) of $E_2$(high) mode of InN layers grown on (c) sapphire (0001) and (d) GaN/sapphire (0001) as a function of V/III ratio, respectively.
The frequency of $E_2$(high) mode shows an inverse tendency with the FWHM value of it below 2400 V/III ratio and similar tendency above 2400 V/III ratio. Additionally, both long- and short-range ordering results reveal that InN layers grown on sapphire (0001) substrates are affected more than InN layers grown on GaN/sapphire (0001) templates.

The representative Raman spectra of InN layers grown either on sapphire (0001) substrates or on GaN/sapphire (0001) templates in the vicinity of $A_1$(LO) phonon mode with various V/III ratios are shown in Figs. 5.38a and 5.38c, respectively, and Figs. 5.38b and 5.38d depict corresponding vibrational properties obtained from $A_1$(LO) modes. $A_1$(LO) phonon frequency of InN layers grown on sapphire (0001) substrate is ~2 cm$^{-1}$ higher than these grown on GaN/sapphire (0001) templates. Accordingly, calculated $A_1$(LO) force constant, given in Eq. 3.4, of InN layers grown on sapphire (0001) substrates and GaN/sapphire (0001) templates are 256.86 and 254.79 N·m$^{-1}$, respectively.

The left side of Figs. 5.38b and 5.38d show FWHM value of the $A_1$(LO) mode and the right side of these show $A_1$(LO) vibrational frequency of InN layers grown on sapphire (0001) substrates and GaN/sapphire (0001) templates, respectively. It is seen in Fig. 5.38b that the FWHM value of InN layers grown on sapphire (0001) substrates decreases with increasing up to 3000 V/III ratio and significantly increases afterwards for V/III ratio above 3000. Accordingly, the FWHM value InN layers grown on GaN/sapphire (0001) templates increases with increasing V/III ratio from 1800 to 2400 and decreases afterwards for V/III ratio above 2400 V/III ratio. The FWHMs minimums of 14.2 and 17.5 cm$^{-1}$ are observed for InN layers grown on sapphire (0001) substrates with a V/III ratio of 1200 and grown on GaN/sapphire (0001) templates with a V/III ratio of 3600, respectively.
Figure 5.38 Substrate material and V/III ratio dependencies of $A_1$(LO) phonon mode. Measured Raman spectra of InN layers grown on (a) sapphire (0001) and (b) GaN/sapphire (0001) with V/III ratio in the 1200–3600 range. FWHM (left axis) and frequency (right axis) of $A_1$(LO) mode of InN layers grown on (c) sapphire (0001) and (d) GaN/sapphire as a function of V/III ratio, respectively.
Since polar $A_1$-$E_1$ mode splitting with pressure, temperature, and so on evidences an increase in the crystal anisotropy in wurtzite group III-nitrides, phonon ratios of these modes is proportional to the structural anisotropy of a given structure [29].

$$\frac{[\omega_{E_1(\text{TO})} - \omega_{A_1(\text{TO})}]}{\omega_{E_1(\text{TO})}} = s\Delta(c/a),$$ (5.8)

where $\Delta(c/a)$ is a deviation of the $c/a$ ratio from its ideal value (1.633), i.e. $\Delta(c/a) = c/a - 1.633$; accordingly, $s$ is a correction parameter, estimated to be in the range of $-3.14$ and $-3.65$ for wurtzite InN material [30,31].

The left side of Figs. 5.39a and 5.39b show the $[\omega_{E_1(\text{TO})} - \omega_{A_1(\text{TO})}]/\omega_{E_1(\text{TO})}$ phonon frequency ratio and the right side of these show LO-TO splitting of $A_1$ mode of InN layers grown on sapphire (0001) substrates and on GaN/sapphire (0001) templates as a function of V/III ratio. It is seen in Fig. 5.39a that the crystal anisotropy $\Delta(c/a)$ of InN layers grown on sapphire (0001) substrates decreases with increasing up to 3000 V/III ratio and significantly increases afterwards for V/III ratio above 3000. Accordingly, the crystal anisotropy $\Delta(c/a)$ of InN layers grown on GaN/sapphire (0001) templates increases with increasing V/III ratio from 1800 to 2400 and decreases afterwards for V/III ratio above 2400 V/III ratio. The LO-TO splitting of $A_1$ mode show the same tendency with crystal anisotropy $\Delta(c/a)$ as a function of V/III ratio.

There seems to be nonlinear increase in the crystal anisotropy with V/III ratio, which results in nonlinear increase in LO-TO splitting of $A_1$ mode. In addition, correlation of the crystal anisotropy with long- and short-range ordering also exhibit nonlinear tendency, which also reveals physical and/or chemical variations on the nucleation chemistry of InN layers grown either on sapphire (0001) substrates or on GaN/sapphire (0001) templates.
Figure 5.39 Substrate material and V/III ratio dependencies of polar phonon frequencies. The \[\frac{\omega_{E_{1}(TO)} - \omega_{A_{1}(TO)}}{\omega_{E_{1}(TO)}}\] phonon frequency ratio (squares, left axis) and LO-TO (A\textsubscript{1}) splitting (circles, right axis) of InN layers grown (a) on sapphire (0001) substrates and (b) on GaN/sapphire (0001) templates as a function of V/III ratio, respectively.
The deformation of the InN wurtzite structure by alteration of the $c/a$ ratio, $u$ value, is given by [32].

$$u = \frac{1}{3} \frac{a^2}{c^2} + \frac{1}{4}.$$  

(5.9)

Although $a$ and $c$ lattice constants are generally obtained from the XRD ($2\theta$-$\omega$)-scan, we still can utilize $c/a$ ratio estimated from the polar phonon frequency ratio, with an $s$ value of $-3.5$. The estimated $c/a$ and $u$ values of the InN layers grown by HPCVD, listed in Table 5.8, are higher and lower than the MOCVD and MBE grown InN layers, respectively [33–35].

InN layers grown on sapphire (0001) substrate and on GaN/sapphire (0001) templates exhibit InN (0 0 0 2) Bragg reflexes linewidth minimums of 179 and 225 arcsec and $c/a$ ratios of 1.6158 and 1.6142, respectively. Since $c$ lattice constant of these two samples can be regarded as unstrained (see Fig. 5.34a and c), InN layer grown on sapphire (0001) substrate indicate shorter $a$ lattice constant than InN layer grown on GaN/sapphire (0001) templates, which explains very well observed InN (1 0 1 1) Bragg reflex for InN layers grown on sapphire (0001) substrates.

Figures 5.40a–d and Figs. 5.41a–d depict optoelectronic properties obtained from the analysis of IR reflection spectroscopy. The left side of Figs. 5.40a and 5.40c show thicknesses and the right side of these show free carrier concentration of InN layers grown either directly on sapphire (0001) substrates or on GaN/sapphire (0001) templates as a function of V/III molar ratio, respectively. It is seen in Fig. 5.40a that InN layer thickness increases with increasing V/III ratio. Accordingly, it is seen in Fig. 5.40c that InN layer thickness increases with increasing V/III ratio up to 2400 and decreases afterwards for further increasing V/III ratio. IR reflection analyses also reveal that free carrier concentration, $n_e$, shows an inverse tendency with the InN layer thickness. Results also reveals that two thick InN layers grown either on sapphire (0001)
substrates or on GaN/sapphire (0001) templates with thicknesses of 333 and 300 nm exhibit free carrier concentrations of $1.2 \times 10^{19}$ and $3.9 \times 10^{19}$ cm$^{-3}$, respectively. Likewise, free carrier concentration of the InN layers grown on GaN/sapphire (0001) templates are at least twice as high as that of the InN layers grown on sapphire (0001) substrates, which also agrees with previous results listed in Table 5.2 and Table 5.3.

The left side of Fig. 5.40b and d show thicknesses and the right side of these show carrier mobility of InN layers grown either directly on sapphire (0001) substrates or on GaN/sapphire (0001) templates as a function of V/III molar ratio, respectively. It is seen in Fig. 5.40b that there seems to be nonlinear increase in the carrier mobility with epilayer thickness of InN directly grown on sapphire (0001) substrates; on the contrary, there is a linear increase in the carrier mobility with epilayer thickness of InN grown on GaN/sapphire (0001) templates, depicted in Fig. 5.40d. Although carrier mobility values of InN layers exhibit significant variation, the InN samples grown directly on sapphire (0001) substrates usually reveals at least twice as high as that of the InN samples grown on MOCVD grown GaN/sapphire (0001) templates.
Figure 5.40 Substrate material and V/III ratio dependencies of IR reflection analysis. Thickness and $n_e$ of InN layers grown (a) directly on sapphire (0001) substrates and (c) on GaN/sapphire (0001) templates as a function of V/III ratio. Thickness and $\mu$ of InN layers grown (b) directly on sapphire (0001) substrates and (d) on GaN/sapphire (0001) templates as a function of V/III ratio.
The left side of Figs. 5.41a and 5.41c show longitudinal-optic (LO) phonon frequency and the right side of these show free carrier concentration of InN layers grown either directly on sapphire (0001) substrates or on GaN/sapphire (0001) templates as a function of V/III molar ratio, respectively. It is seen in Figs. 5.41a and 5.41c that there seems to be linear increase in the LO phonon frequency with free carrier concentration of the InN layers. With increasing V/III ratio, the LO phonon frequency of the InN layers grown directly on sapphire (0001) substrates increases to a maximum value of 593 cm\(^{-1}\) and slightly decreases afterwards. However, with increasing V/III ratio, the LO phonon frequency of the InN layers grown on MOCVD-grown GaN/sapphire (0001) templates decreases to a minimum value of 585 cm\(^{-1}\) and increases afterwards. The LO phonon frequency and free carrier concentration of the InN layers grown directly on sapphire (0001) substrates exhibit inverse tendency with each other as a function of V/III ratio; however, these of InN layers grown on GaN/sapphire (0001) templates exhibit similar tendency with each other as a function of V/III ratio.

The left side of Figs. 5.41b and 5.41d show transverse-optic (LO) phonon frequency and the right side of these show free carrier mobility, \(\mu\), of InN layers grown either directly on sapphire (0001) substrates or on GaN/sapphire (0001) templates as a function of V/III molar ratio, respectively. As depicted in Figs.5.41b and 5.41d, the correlation of TO phonon frequency with carrier mobility exhibit similar tendency for InN layers grown either directly on sapphire (0001) substrates or on MOCVD-grown GaN/sapphire (0001) templates. The cross correlations of LO phonon-\(n_e\) with TO phonon-\(\mu\) reveals that coupling of TO phonon-\(\mu\) is stronger than LO phonon-\(n_e\) coupling regardless of the substrate material type, if optimum V/III ratio regime is chosen. This finding also sheds a light onto coupling LO phonon with free carrier concentration should have an extra requisite parameter.
Figure 5.41 Substrate material and V/III ratio dependencies of IR reflection analysis. LO phonon frequency (left axis) and carrier concentration (right axis) of InN layers grown on (a) sapphire and (c) GaN as a function of V/III ratio. TO phonon frequency (left axis) and mobility (right axis) of InN layers grown on (b) sapphire and (d) GaN as a function of V/III ratio.
Table 5.8  Summary of the structural, optical, and optoelectronic properties obtained from XRD, Raman scattering, and IR reflection analyses of InN layers grown on different substrates with various V/III ratios.

<table>
<thead>
<tr>
<th>Material and V/III ratio</th>
<th>Sapphire</th>
<th>GaN/sapphire</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1200</td>
<td>3000</td>
</tr>
<tr>
<td>XRD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{20}$ (arcsec)</td>
<td>303</td>
<td>179</td>
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<tr>
<td>Lattice constant, $c$ (Å)</td>
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</tr>
<tr>
<td>Grain size (nm)</td>
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<td>172</td>
</tr>
<tr>
<td>Strain ($10^{-4}$)</td>
<td>3.55</td>
<td>2.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raman</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_1$(TO) FWHM (cm$^{-1}$)</td>
<td>8.52</td>
<td>7.27</td>
</tr>
<tr>
<td>$A_1$(TO) frequency (cm$^{-1}$)</td>
<td>443.68</td>
<td>444.22</td>
</tr>
<tr>
<td>$E_1$(TO) FWHM (cm$^{-1}$)</td>
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<td>7.78</td>
</tr>
<tr>
<td>$E_1$(TO) frequency (cm$^{-1}$)</td>
<td>473.41</td>
<td>472.66</td>
</tr>
<tr>
<td>$E_2$(high) FWHM (cm$^{-1}$)</td>
<td>5.14</td>
<td>6.18</td>
</tr>
<tr>
<td>$E_2$(high) frequency (cm$^{-1}$)</td>
<td>488.06</td>
<td>487.97</td>
</tr>
<tr>
<td>$A_1$(LO) FWHM (cm$^{-1}$)</td>
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<td>590.88</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.6150</td>
<td>1.6158</td>
</tr>
<tr>
<td>$u$</td>
<td>0.3779</td>
<td>0.3776</td>
</tr>
<tr>
<td>IR reflection</td>
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<td></td>
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<tr>
<td>Thickness (nm)</td>
<td>111</td>
<td>324</td>
</tr>
<tr>
<td>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</td>
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<td>230</td>
</tr>
<tr>
<td>LO phonon frequency (cm$^{-1}$)</td>
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<tr>
<td>$N_e$ ($10^{19}$ cm$^{-3}$)</td>
<td>3.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>
5.4.2. Summary

In summary, the effect of substrate material and V/III molar ratio on the structural and optoelectronic properties of InN epilayers have been investigated by XRD, Raman scattering, and IR reflection spectroscopies. Structural properties of InN epilayers grown directly on sapphire (0001) substrates or on GaN/sapphire (0001) templates indicate optimum V/III ratios of 3000 and 3600, respectively.

For these V/III ratios, XRD results exhibit that the lowest InN (0 0 0 2) Bragg reflex FWHM values of 179 and 225 arcsec are obtained for sapphire substrates grown InN epilayers and GaN/sapphire templates grown InN epilayers, respectively. Raman scattering results reveals that the lowest $E_2$(high) mode FWHM values of 6.18 and 4.79 cm$^{-1}$ are obtained sapphire substrates grown InN epilayers and GaN/sapphire templates grown InN epilayers, respectively. Therefore, InN layers grown on different substrate materials exhibit different growth parameter for optimization of the physical properties.

However, InN layers grown directly on sapphire (0001) substrates exhibit hexagonal tilting due to underlying substrate material influence. Sapphire substrates grown InN epilayers exhibit tensile strain on $c$-lattice constant and compressive force on nonpolar InN dative bond. However, GaN/sapphire templates grown InN epilayers exhibit compressive strain on $c$-lattice constant and tensile force on nonpolar InN dative bond. The structural results also indicate that lattice expansion along the $c$-lattice axis is obtained $5.08 \times 10^{-5}$ and $7.86 \times 10^{-5}$ Å·arcsec$^{-1}$ for InN layers grown on sapphire (0001) substrates and on GaN/sapphire (0001) templates, respectively. In addition, Short-range crystal anisotropy of sapphire substrates grown InN epilayers is lower than that of GaN/sapphire templates grown InN epilayers.
IR reflection results reveal that two thick InN layers grown either directly on sapphire (0001) substrates or on GaN/sapphire (0001) templates with thicknesses of 333 and 300 nm exhibit free carrier concentrations of $1.2 \times 10^{19}$ and $3.9 \times 10^{19}$ cm$^{-3}$, respectively. Likewise, free carrier concentration of the InN layers grown on GaN/sapphire (0001) templates are at least twice as high as that of the InN layers grown on sapphire (0001) substrates, which also agrees with previous results.

Longitudinal-optic phonon frequency and free carrier concentration exhibit inverse tendencies as a function of V/III ratio for sapphire grown InN epilayers; however, these exhibit consistent tendencies as a function of V/III for GaN template grown InN epilayers. Transverse-optic phonon frequency and electron mobility exhibit inverse tendencies as a function of V/III ratio for InN epilayers regardless of its substrate material. For the best long-range and short-range crystal orderings, carrier mobility of InN epilayers is almost equal regardless of substrate type.

### 5.5. Effect of Mass Transport

Since HPCVD can be regarded as superatmospheric MOCVD, growth rate dependency of growth temperature for MOCVD process, illustrated schematically in Fig. 4.4, can be utilized to investigate mass transport efficiency along the flow direction for HPCVD technique. HPCVD growth system consists of a horizontal flow channel reactor, in which carrier-gas flow over a substrate surface generates a boundary layer of thickness, $\delta$. In the boundary layer, carrier-gas flow-velocity is parallel to the substrate and reactant radicals are depleted from the carrier-gas stream. Although growth in the mass transport limited regime is a nonequilibrium process, for simplicity InN epitaxial growth only along the carrier flow direction is investigated.
InN epilayer investigated here was grown with TMI and NH\textsubscript{3} injection times of 800 and 2000 ms, respectively. Precursor separation, acquired from the optimization of precursor pulse separation (discussed in section 5.3), from end of TMI to beginning of NH\textsubscript{3} (denoted by S\textsubscript{1}) and from end of NH\textsubscript{3} to beginning of TMI (denoted by S\textsubscript{2}) were set to 1643 and 358 ms, respectively (see Fig. 5.20). The reactor pressure was set to 8 bar with a total carrier gas flow of 5.5 slm. Ammonia and TMI flow rates were kept constant at 1200 sscm and 44.64 μmol/min and V/III ratio was set to 1200 molar ratio.

The schematic illustration of InN epilayer investigated in this study is sketched in Figs. 5.42a and 5.42b. The investigated spots correspond to 2, 7, 12, 17, and 22 mm from the inlet distance on the flow direction. Due to spatial proximity of neighboring spots, only \textit{a}, \textit{c}, and \textit{e} spots could be probed by X-ray beam.

![Figure 5.42](image-url)  
(a) Schematic illustration and (b) real image of InN layer investigated for the effect of mass transport along the flow direction.
5.5.1. Structural and Optical Analysis

Figures 5.43a–c show XRD (2θ-ω)-scans of InN layer grown on sapphire (0001) substrate at distances along the flow direction of 2, 12, and 22 mm, respectively. As depicted in Figs. 5.43a–c, XRD Bragg reflexes with 2θ values at 31.33°, 33.15°, and 41.68° correspond to unstrained diffractions of hexagonal phases of InN (0 0 0 2), InN (1 0 1 1), and α-sapphire (0 0 0 6), respectively. Bragg diffraction at 38.38°, denoted with γ, is only observed at the center of the sample; however, the appearance of it is not understood.

Figure 5.43 X-ray diffraction (2θ-ω)-scans of InN layer grown on sapphire (0001) substrate at distances along the flow direction of (a) 2, (b) 12, and (c) 22 mm, respectively.
Figures 5.44a and 5.44b depict the structural properties obtained from the analysis of InN (0 0 0 2) Bragg reflex. The left side of Fig. 5.44a shows the FWHM values of the InN (0 0 0 2) Bragg reflex and the right side of it shows c-lattice constant as a function of distance along the flow direction. It is seen in Fig. 5.44a that the FWHM value increases with increasing distance from 2 to 12 mm, exhibiting local minimum of 138 arcsec at 12 mm and increases afterwards for distances above 12 mm. The FWHM value of 138 arcsec is one of the lowest reported InN (0 0 0 2) Bragg reflexes. At an inlet and center spot of sample, the lattice constant, c, of InN is calculated from the value of 2θ diffraction angle to be 5.7032 Å, which is excellent agreement with the reported values (see Table 3.17). However, at an outlet spot of the sample, i.e. 22 mm, the lattice constant slightly increases to 5.7040 Å, which is still quite close to reported value.

The left side of Fig. 5.44b shows the estimated grain size from the InN (0 0 0 2) Bragg reflex and the right side of it shows estimated in-plane strain on the c-plane as a function of distance along the flow direction. It is seen in Fig. 5.44b that the grain size significantly increases from 2 to 12 mm distance, exhibiting maximum grain size of 224 nm and decreases afterwards for further increased distances. The estimated in-plane strain on the c-plane shows an inverse tendency with the grain size as a function of distance along the flow direction. The structural properties extracted from XRD (2θ-ω)-scan together with Raman scattering and IR reflection analysis for various distances along the flow direction are summarized in Table 5.9.

The representative Raman spectra of InN layer grown on sapphire (0001) substrate in the vicinity of $E_2$(high) phonon mode for various distances along the flow direction are shown in Figs. 5.45a and 5.45b depicts vibrational properties obtained from $E_2$(high) mode. The left side of Fig. 5.45b shows FWHM values of the $E_2$(high) mode and the right side of it shows spectral frequency of the $E_2$(high) mode. It is seen in Fig. 5.45a that Raman spectra of InN layers
acquired at distances of 2, 7, and 12 mm along the flow direction show similar spectrum. However, Raman spectra acquired at distances of 17 and 22 mm exhibit weak mode intensities and asymmetric broadening. Figure 5.45b depicts that the FWHM value of $E_2$(high) mode increases with increasing distance on the flow direction from 2 to 7 mm, showing a local maximum FWHM value of 12.16 cm$^{-1}$ and decreases afterwards. At distances along the flow direction above 12 mm, the FWHM value increases with increasing distance along the flow direction.
Figure 5.44 Distance along the flow direction dependence of X-ray diffraction ($2\theta$-$\omega$) analysis. (a) FWHM (squares, left axis) and $c$ lattice constant (circles, right axis) as a function of distance along the flow direction. (b) Grain size (squares, left scale) and in-plane strain (circles, right scale) as a function of distance along the flow direction.
The $E_2$(high) phonon frequency shows an inverse tendency with FWHM of $E_2$(high) mode as a function of distance along the flow direction. For the best long-range and short-range orderings, obtained at the center of a thin film, InN dative bond is slightly blueshifted, i.e., slight compressive strain is present. The long-range ordering obtained from XRD exhibits FWHM of 138 arcsec, the lowest value obtained in this research, while short-range ordering obtained from Raman scattering spectroscopy exhibits 10.47 cm\(^{-1}\). In V/III ratio series, (discussed in detail in section 5.2) $E_2$(high) FWHM down to 7.5 cm\(^{-1}\) is obtained. This discrepancy between long-range and short-range orderings might be due to decay channel of $E_2$(high) vibrational mode.

The decay channel for $E_2$(high) phonon requires higher-order (four phonon) process to explain strong anharmonic effects [36]. Dominant four-phonon process involves a zone-center phonon and pairs of opposite wavevector phonons at the symmetry points [15]. Therefore, asymmetric decays of pair phonons more likely to be the main reason for $E_2$(high) phonon broadening, which might add extra constraint even in a well-ordered lattice. The decay channel of $E_2$(High) phonon is given by the following relation [15]:

$$E_2\text{(high)} \rightarrow E_2\text{(low)} + \text{TO}(A – H) – \text{TA}(A – H),$$ (5.10)

where $\omega(E_2\text{low}) = 84$ cm\(^{-1}\), $\omega(\text{TO}) = 495$ cm\(^{-1}\), and $\omega(\text{TA}) = 91$ cm\(^{-1}\).

Although Domenech et al. [15] stated four possible decay channels for $E_2$(high) phonon, because InN epilayer investigated in this study exhibits reasonably good mobility and free carrier concentration values, the remaining three channels are unlikely.
Figure 5.45 Distance along the flow direction dependence of $E_2$(high) phonon mode. (a) Measured Raman spectra of InN layer grown on sapphire (0001) at along the flow direction distance in the 2–22 mm range. (b) FWHM (squares, left axis) and frequency (circles, right axis) of InN layer grown on sapphire (0001) as a function of distance along the flow direction.
The representative Raman spectra of InN layer grown on sapphire in the vicinity of $A_1$(LO) phonon mode for various distances along the flow direction are shown in Figs. 5.46a and Fig. 5.46b depicts vibrational properties obtained from $A_1$(LO) mode. At distances along the flow direction of 2, 7, and 12 mm, $A_1$(LO) vibrational mode exhibit symmetric Gaussian distribution; however, it exhibit asymmetric broadening towards and redshifting at distances of 17 and 22 mm. The redshifting of $A_1$(LO) mode could be due to point defects and vacancies, which generates tensile force on the polar dative dative bond [8].

The left side of Fig. 5.46b shows FWHM values of the $A_1$(LO) mode and the right side of it shows phonon frequency of the $A_1$(LO) mode. It is seen in Fig. 5.46b that the FWHM value increases with increasing distance from 2 to 7 mm and decreases afterwards from 7 to 12 mm, exhibiting local minimum value of 18.50 cm$^{-1}$. As distance along the flow direction increases, FWHM of $A_1$(LO) mode increases again. The $A_1$(LO) phonon frequency shows an inverse tendency with FWHM of $A_1$(LO) mode as a function of distance along the flow direction.

It is interesting to cross correlate $E_2$(high) and $A_1$(LO) phonon behaviors with each other to underrated nonpolar and polar characteristics. The identical tendencies of $E_2$(high) and $A_1$(LO) indicate that long-range Coulombic influence on the polar $A_1$(LO) mode is minimum, which might be related well-improved long-range crystalline ordering. At the center of InN thin film, $A_1$(LO) phonon frequency is slightly blueshifted, which also indicates point defects and vacancies, which generates tensile force on the polar dative bond [8].
Figure 5.46 Distance along the flow direction dependence of $A_1$(LO) phonon mode. (a) Measured Raman spectra of InN layer grown on sapphire (0001) at along the flow direction distance in the 2–22 mm range. (b) FWHM (squares, left axis) and frequency (circles, right axis) of InN layer grown on sapphire (0001) as a function of distance along the flow direction.
Figures 5.47a and 5.47b and Figs. 5.48a and 5.48b depict optoelectronic properties obtained from the analysis of IR reflection spectroscopy. The left side of Fig. 5.47a shows thickness and the right side of it shows free carrier concentration of InN layer grown on sapphire (0001) substrate as a function of distance along the flow direction. It is seen in Fig. 5.47a that InN layer thickness decreases with increasing distance along the flow direction. As depicted in Fig. 5.47a, IR reflection analysis reveals that free carrier concentration increases with increasing distance along the flow direction. The significant increase of the free carrier concentration from $1.91 \times 10^{18}$ to $2.96 \times 10^{18}$ cm$^{-3}$ for increase of the distance along the flow direction from 17 to 22 mm is related to significant decrease of InN layer thickness from 275 to 110 nm. Asymmetric broadening of $A_1$(LO) mode for distance along the flow direction of 22 mm can be also explained due to relatively thin InN layer thickness, in which the influence of surface charge accumulation of InN increases on the thin epilayer. The free carrier concentration values reported in this study of InN layer are one of the lowest values for HPCVD grown InN epilayers.

The left side of Fig. 5.47b shows thickness and the right side of it shows carrier mobility of InN layer grown on sapphire (0001) substrate as a function of distance along the flow direction. It is seen in Fig. 5.47b that as InN layer thickness decreases, carrier mobility of InN layer wildly oscillates. Except the center spot, various spots InN layer exhibit mobility values above $1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. At distances along the flow direction of 7 and 17 mm exhibit mobility of $\sim 5200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is even higher than theoretical value of $4400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Since repetitive analyses indicated the same values, it is unlikely to be resulted from experimental or fitting error; however, the main reason is still unknown.
Figure 5.47 Distance along the flow direction dependence of IR reflection analysis. (a) Thickness (squares, left axis) and free carrier concentration (circles, right axis) and (b) Thickness (squares, left axis) and mobility (circles, right axis) of InN layer grown on sapphire (0001) substrate as a function of distance along the flow direction, respectively.
The left side of Fig. 5.48a shows longitudinal-optic (LO) phonon frequency and the right side of it shows free carrier concentration, \( n_e \), of InN layer grown on sapphire (0001) substrate as a function of distance along the flow direction. It is seen in Fig. 5.48a that LO phonon frequency remains constant with increasing distance along the from direction up to 17 mm and significantly increases afterwards for further increased distance along the flow direction. For all spots investigated here exhibit very low longitudinal-optic phonon frequency values (~568 cm\(^{-1}\)) except the flow distance of 22 mm, which exhibits longitudinal-optic phonon frequency of 592 cm\(^{-1}\), in excellent agreement with the reported LO frequencies and experimentally observed Raman \( A_1(LO) \) mode frequency. The correlation of longitudinal-optic phonon frequency with free carrier concentration exhibits the same tendency as a function of distance along the flow direction. As Eq. 5.1 is utilized to obtain free carrier concentration from LO phonon frequency, there is a one-order magnitude difference between calculated (2.72 \( \times \) 10\(^{17}\)) and obtained (2.96 \( \times \) 10\(^{18}\)) free carrier concentrations. Since multiplier of Eq. 5.1 is derived from experimental results for GaN epilayers, that for InN material can be also modified if further investigations indicate similar accuracies. This might be due to indicate coupling between them.

The left side of Fig. 5.48b shows transverse-optic (LO) phonon frequency and the right side of it shows carrier mobility, \( \mu \), of InN layer grown on sapphire (0001) substrate as a function of distance along the flow direction. It is seen in Fig. 5.48b that TO phonon frequency remains constant with increasing distance along the from direction up to 17 mm and significantly decreases afterwards for further increased distance along the flow direction. Interestingly, for all spots exhibit very high longitudinal-optic phonon frequency values (~530 cm\(^{-1}\)) except the flow distance of 22 mm, which exhibits longitudinal-optic phonon frequency of 475 cm\(^{-1}\), in excellent agreement with reported values.
Figure 5.48 Distance along the flow axis dependence of IR reflection analysis. (a) LO phonon frequency (squares, left axis) and free carrier concentration (circles, right axis) and (b) TO phonon frequency (squares, left axis) and mobility (circles, right axis) of InN layer grown on sapphire (0001) substrate as a function of distance along the flow direction, respectively.
The inverse tendencies of LO and TO phonons as a function of distance along the flow direction are not understood yet. The correlation of transverse-optic phonon frequency together with mobility is difficult to interpret due to wild oscillating values of carrier mobility as a function of distance along the flow direction. The growth conditions stated in an introductory paragraph clearly indicates that sufficient indium and nitrogen radicals are available regardless of the spatial distribution. Therefore, significant variation in the long-range and short-range orderings is more likely due to gas flow or temperature distribution on the growth surface of InN layer. A schematic sketch of temperature distribution during the growth is shown in Fig. 5.49. Since tantalum metal-plate was placed underneath of sapphire substrate, heat distribution at the bottom of sapphire substrate is evenly distributed. However, temperature profile on the growth surface may not be equal due to different sweeping effect of cold precursors at different distances along the flow direction. Therefore, we estimate that temperature ordering along the flow direction is $T_c > T_c > T_a$. As InN epilayer thickness increases, this influence increases as well. Therefore, significant changes on the physical properties of InN epilayers above 300 nm thickness might be due to decrease in growth surface temperature by carrier gas sweeping effect.

Figure 5.49  A schematic sketch of growth temperature distribution along the flow direction.
Table 5.9 Summary of the structural, optical, and optoelectronic properties obtained from XRD (2θ-ω)-scan, Raman scattering, and IR reflection analyses of InN layer grown on sapphire (0001) substrate at various distances along the flow direction.

<table>
<thead>
<tr>
<th>Distance along the flow direction</th>
<th>2 mm</th>
<th>7 mm</th>
<th>12 mm</th>
<th>17 mm</th>
<th>22 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β2θ (arcsec)</td>
<td>167</td>
<td>138</td>
<td>201</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice constant, c (Å)</td>
<td>5.7032</td>
<td>5.7032</td>
<td>5.7040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grain size (nm)</td>
<td>184</td>
<td>224</td>
<td>153</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strain (10^{-4})</td>
<td>1.96</td>
<td>1.61</td>
<td>2.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raman</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E2(high) FWHM (cm^{-1})</td>
<td>11.22</td>
<td>12.16</td>
<td>10.47</td>
<td>13.69</td>
<td>16.96</td>
</tr>
<tr>
<td>E2(high) frequency (cm^{-1})</td>
<td>488.33</td>
<td>487.83</td>
<td>488.96</td>
<td>488.61</td>
<td>487.08</td>
</tr>
<tr>
<td>A1(LO) FWHM (cm^{-1})</td>
<td>18.71</td>
<td>21.31</td>
<td>18.50</td>
<td>19.15</td>
<td>23.83</td>
</tr>
<tr>
<td>A1(LO) frequency (cm^{-1})</td>
<td>591.07</td>
<td>589.85</td>
<td>591.63</td>
<td>591.49</td>
<td>587.88</td>
</tr>
<tr>
<td>IR reflection</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>338</td>
<td>370</td>
<td>243</td>
<td>276</td>
<td>110</td>
</tr>
<tr>
<td>Growth rate (nm/min)</td>
<td>112</td>
<td>123</td>
<td>81</td>
<td>92</td>
<td>36</td>
</tr>
<tr>
<td>Mobility (cm^2 V^{-1} s^{-1})</td>
<td>1690</td>
<td>5190</td>
<td>230</td>
<td>5180</td>
<td>940</td>
</tr>
<tr>
<td>LO phonon frequency (cm^{-1})</td>
<td>567</td>
<td>566</td>
<td>569</td>
<td>567</td>
<td>592</td>
</tr>
<tr>
<td>TO phonon frequency (cm^{-1})</td>
<td>533</td>
<td>530</td>
<td>528</td>
<td>531</td>
<td>475</td>
</tr>
<tr>
<td>Ne (10^{18} cm^{-3})</td>
<td>1.77</td>
<td>1.81</td>
<td>1.98</td>
<td>1.91</td>
<td>2.96</td>
</tr>
</tbody>
</table>

5.5.2. Summary

In summary, the effect of efficient mass transport distance along the flow direction on the structural and optoelectronic properties of InN layer have been investigated by XRD, Raman scattering, and IR reflection spectroscopies. The improved structural properties of InN layer is observed for a flow distance of 12 mm, i.e., center spot, where FWHM values of InN (0 0 0 2) Bragg reflex and E2(high) vibrational mode are 138 arcsec and 10.47 cm^{-1}, respectively. Although much lower E2(high) FWHM values were observed for the series of V/III ratio,
FWHM value of 138 arcsec for InN (0 0 0 2) Bragg reflex was the lowest FWHM among the any InN layer discussed in here. Accordingly, estimated grain size of 224 nm and in-plane strain of $1.61 \times 10^{-4}$ was the maximum and minimum values obtained as well, respectively.

Furthermore, Raman scattering results indicate that dependencies of $E_2$(high) and $A_1$(LO) phonon frequencies as a function of distance along the flow direction are inversely correlated with linewidths of these. Therefore, vibrational bond strength is inversely correlated with InN epilayer quality. The lowest FWHM values of $E_2$(high) and $A_1$(LO) modes were observed for flow distance of 12 mm. Calculated InN layer thickness almost linearly decreases with increasing flow distance. The calculated epilayer thickness for this flow distance was 243 nm (i.e., growth rate of 81 nm/hr), with a free carrier concentration of $1.98 \times 10^{18}$ cm$^{-3}$.

The wild fluctuation in carrier mobility value made difficult to interpret mobility results as a function of distance along the flow direction; however, some spots on the sample indicate very high mobility value of $\sim 5185$ cm$^2$V$^{-1}$s$^{-1}$. Longitudinal-optic and transverse-optic phonon frequencies exhibit constant values for all spots discussed here except outlet spot. Low longitudinal-optic and high transverse-optic phonon frequency values are still not well understood. Finally, structural and optical results indicate that growth surface might have an uneven temperature distribution. As InN epilayer thickness increases, this influence increases as well. Therefore, significant changes on the physical properties of InN epilayers above 300 nm thickness might be due to decrease in growth surface temperature from the carrier gas sweeping effect.
5.6. References


CHAPTER 6

VIBRATIONAL STUDIES OF ZGP SINGLE CRYSTAL

The research in this chapter focuses on the structural and optical properties of single crystal chalcopyrite zinc germanium phosphide (ZnGeP$_2$ also denoted as ZGP) along (001), (110), and (110) crystalline planes by Raman scattering and infrared (IR) reflection spectroscopies. Zinc germanium phosphide single crystal grown by Vertical Bridgman method with dimensions of 5 mm by 5 mm by 20 mm were cut and polished along (001), (110), and (110) crystalline faces from the annealed ingots. Detailed discussions of the growth procedure of bulk ZGP crystal are given in Refs. 1 and 2. Here, local ordering and optical properties of the ZGP single crystal are studied by Raman scattering and infrared (IR) reflection spectroscopies.

All Raman measurements were performed in back scattering geometry along the (001), (110), and (110) crystalline faces. The Raman spectrometer, equipped liquid $N_2$-cooled multichannel charge-coupled (CCD) camera, consists of a McPherson double subtractive monochromator and a single two-meter monochromator system. Diode-pumped solid-state (DPSS) laser light using excitation energy of 2.33 eV (532 nm) was used to excite the spectra with micro-Raman illumination stage. Standard optical elements were used to control incident and scattered polarizations for polarized Raman measurements. Standard Lorentzian line shape fitting mechanisms were employed to calculate Raman peak center, intensity, and linewidth analyses of the vibrational modes.
A Perkin-Elmer 2000 system was utilized for IR reflection measurements performed in the frequency range of 90 and 450 cm\(^{-1}\) in a near normal incidence geometry (~8°). Infrared reflection measurement was also performed under s-polarized, p-polarized, and 45° polarized light configuration onto c-plane of incidence. Details of the IR reflection spectroscopy and its application in wurtzite structure were described in elsewhere [3].

In following, Raman and infrared (IR) reflection spectroscopic investigations of ZGP crystal grown by Vertical Bridgman technique are presented. The rest of the paper is organized as follows: First, a brief description of experimental methods employed in this study and then a detailed discussion of vibrational properties of ZGP. Finally, Raman scattering and IR reflection analyses along the (001), (110), and (110) crystallographic orientations are discussed.

### 6.1. Introduction

Development of nonlinear optical (NLO) materials for mid-infrared region is essential for the next generation of high-power and tunable solid-state lasers. Ternary \(ABC_2\) semiconductor crystals having chalcopyrite structure have been synthesized from group I-III-VI\(_2\) and group II-IV-V\(_2\) elements [4]. Of these, the II-IV-V\(_2\) pnictide compound of zinc germanium phosphide (ZGP) received a particular attention due to its large birefringence in near- and mid-IR region, suitable for various frequency conversion applications [5]. Since ZGP crystal possesses highest nonlinear coefficient of 75 pm/V and highest thermal conductivity of 0.35 W/Kcm among the any crystal, which is transparent and phase matching at 2 \(\mu\)m, it has been used for 2 \(\mu\)m pumped Optical Parametric Oscillators (OPOs) [6]. Likewise, bulk crystals of ZGP have been studied as coherent radiation source which is tunable in the range of 2 to 8 \(\mu\)m (in the near-IR region). The
ZGP has an anisotropic chalcopyrite lattice structure in the tetragonal crystallographic system, space group of I42m in the Hermann-Mauguin notation [4].

The ZGP crystal lacks inversion symmetry, i.e., an anisotropic material; thus, refractive index depends on the polarization direction called as birefringence [6]. Since ZGP is a transparent and a birefringent material, it exhibits characteristic phenomenon of frequency doubling [7, 8], where a pumped EM-wave generates a second wave with twice the optical frequency along the path through the nonlinear medium, known as Second-Harmonic Generation (SHG) process. Although most nonlinear optical applications are based on birefringent bulk crystals, a new physical phenomena and device functionalities can be studied and applied using advanced thin film growth technologies to fabricate electrically and optically confined birefringent heterostructures. Understanding the physical properties of confined ZGP layers and mastering their growth and optimization process may enable a new class of nonlinear, magneto-optical devices, such as Solid-State Molecular Sensors (SSMS) suitable for monitoring chemical or biological agents [9]. For the development of confined birefringent ZGP layers, it is critical to have a detailed understanding of the structural and NLO properties of bulk ZGP as well as how point and extended defects affect the nonlinearity with respect to ordinary and extraordinary crystalline axes.

Even though many studies over the last four decades established the main physical properties of the ZGP, there are still some uncertainties regarding band structure, defect related energy states affecting the sub-bandgap properties (e.g. NLO properties), and lack of thin film growth knowledge. In addition, computational defect studies [10] and band structure calculations [11] show large discrepancies in reference to experimental results, since the empirical methods neglect contributions of $d$-orbitals of the Zn-cations to the band structure. However, significant
progress has been implemented for the growth of ZGP and drawing renewed attention to it and ZGP related materials. Hence, efforts to understand linear and nonlinear optical properties of ZGP and evaluation are crucial.

6.2. Symmetry of Vibrational Modes

The ZGP crystal has a chalcopyrite structure with a space group of $I42d$ in the Hermann-Mauguin notation and $D_{2d}^{12}$ in the Schoenflies notation, shown in Fig. 6.1b. Similarity of group II-IV-V$_2$ ternary chalcopyrite compound to group III-V zinc blende material is the basis for interpretation of both structural and electronic properties of ternary materials, depicted in Fig. 6.2 [4]. The chalcopyrite structure can be derived from two zinc blende unit cells, stacked on top of each other, shown in Fig. 6.1a. One face centered cubic sublattice is populated by phosphorous atoms and other one with equal amounts of zinc and germanium in a tetragonal-ordered fashion.

Since electronic charge density (or electron affinity) of hybridized zinc and germanium atoms are different, the bond length of Zn-P bond is slightly longer than the Ge-P bond. First consequence of having two different cation-anion bond lengths, chalcopyrite structure is tetragonally distorted by the following relation:

$$u = \frac{1}{4} + \frac{(d_{\text{Zn-P}}^2 - d_{\text{Ge-P}}^2)}{d^2}.$$  \hspace{1cm} (6.1)

Where $a$ is a lattice constant in the $x$ or $y$ direction and quantity $u$ is the Wyckoff positions (i.e. distortion parameter) of the phosphorous atoms, summarized in Table 6.1.
Figure 6.1 Comparison of the crystal structure of binary zinc blende (GaP) with that of a ternary pnictide (ZGP) having the chalcopyrite structure.

Figure 6.2 Ternary ZGP chalcopyrite as analogs of binary compounds and elements.
Table 6.1 Atomic Wyckoff (lattice) positions in a chalcopyrite ZGP crystal [12].

<table>
<thead>
<tr>
<th>Atom</th>
<th>Lattice position</th>
<th>Atom</th>
<th>Lattice position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn₁</td>
<td>(0, 0, 0)</td>
<td>P₁</td>
<td>(u, ¼, ¼)</td>
</tr>
<tr>
<td>Zn₂</td>
<td>(0, ½, ¼)</td>
<td>P₂</td>
<td>(¾, u, ¾)</td>
</tr>
<tr>
<td>Ge₁</td>
<td>(½, ½, 0)</td>
<td>P₃</td>
<td>(1 - u, ¾, ½)</td>
</tr>
<tr>
<td>Ge₂</td>
<td>(½, 0, ¼)</td>
<td>P₄</td>
<td>(¼, 1 - u, ¾)</td>
</tr>
</tbody>
</table>

Second consequence of having two different cation-anion bond lengths is a deformation of the unit cell to a length $c$, which is generally different than $2a$. This tetragonal compression is characterized by the quantity $\eta = c/2a$. Experimentally obtained value of $u = 0.25816$ and $\eta = 0.98$ [13].

The character table for $D_{2d}$ point group symmetry is presented in Table 6.2. Character table indicates that symmetry elements for $D_{2d}$ point group are classified into four nondegenerate $A_1, A_2, B_1$, and $B_2$ modes and a double-degenerate $E$ mode. Spectroscopically, the character table indicates that $A_1, B_1, B_2$ and $E$ modes are polarizable so they are Raman active. Since $B_2$ and $E$ modes exhibit symmetry of translations (or possess $p$ orbitals) and their symmetry of translations behaves as $d$ orbitals, they are Raman and IR active and exhibit longitudinal and transverse splitting. Therefore, nonpolar $A_1, A_2$, and $B_1$ modes are only Raman active and polar $B_2$ and $E$ modes both Raman and IR active.

However, real ZGP crystal belongs to $D_{2d}^{12}$ space group, containing eight atoms per unit cell; thereby, possessing 28 quantized lattice motions. A detailed discussion of the group theory allowed symmetry reduction of the $D_{2d}^{12}$ space group is published in Ref. 14. The irreducible
representation of 28 phonon modes at zone center (\(\Gamma\) point) is given by the following relation [15]:

\[
\Gamma_{\text{irreducible}} = 1A_1 + 2A_2 + 3B_1 + 4B_2 + 7E. \tag{6.2}
\]

Since one \(B_2\) mode and one \(E\) mode are translationally active, remaining \(3B_2\) and \(6E\) modes are Raman active. Therefore, except spectroscopically inactive \(A_2\) mode due to nonpolarizability, Raman active vibrational modes are given by:

\[
\Gamma_{\text{Raman}} = 1A_1 + 3B_1 + 3B_2 + 6E. \tag{6.3}
\]

<table>
<thead>
<tr>
<th>(D_{2d})</th>
<th>Symmetry elements for the group</th>
<th>Spectroscopy active components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E) (2S_4) (C_2(z)) (2C'_2) (2\sigma_d)</td>
<td>Microwave</td>
</tr>
<tr>
<td>(A_1)</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>(A_2)</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>(B_1)</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>(B_2)</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>(E)</td>
<td>+2</td>
<td>0</td>
</tr>
</tbody>
</table>

Where \(E\) is an identity, \(C_n\) is a rotation by \(2\pi/n\) angle, \(\sigma_v\) is a vertical reflection plane (contains the principal axis), and \(\sigma_d\) is a diagonal reflection plane (contains the principal axis and bisect the angle between two \(C_2\) axes perpendicular to the principal axis) operators.

Modes exhibiting \(A_1\) and \(A_2\) symmetries involve only displacements of phosphorous atoms. The \(B_1\), \(B_2\), and \(E\) modes include also displacements of \(Zn\) and \(Ge\) atoms. To understand the nature of the chalcopyrite structure, it is crucial to compare chalcopyrite structure with that of
zinc blende, shown in Figs. 6.1b and 6.1a, respectively. The volume of the primitive cell of a chalcopyrite lattice is four times the volume of a zinc blende primitive cell. On the other hand, in the reciprocal space, the opposite must hold, i.e., Brillouin zone of zinc blende is four times larger than that of chalcopyrite [4, 5]. Symmetry points at \( \Gamma(0, 0, 0) \), \( X(0, 0, 2\pi/a) \), \( W^a(2\pi/a, 0, \pi/a) \), and \( W^b(0, 2\pi/a, \pi/a) \) and compatibility relationship are given as [12]:

at \( \Gamma \) point: \[ \Gamma_{15} \rightarrow B_2 + E, \] (6.4)

at \( X \) point: \[ X_1 \rightarrow A_2, X_3 \rightarrow B_1, \text{ and } X_5 \rightarrow E, \] (6.5)

at \( W_1 \) point: \[ W_1 \rightarrow A_1 + A_2, W_2 \rightarrow B_1 + B_2, W_3 \rightarrow E, \text{ and } W_4 \rightarrow E. \] (6.6)

At the \( W \) point, phonon modes lack of a distinct longitudinal or transverse character [12]. Symmetry conditions restrict eight \( W \) points to only two distinct points [16], \( W^a \) and \( W^b \); therefore, even in real chalcopyrite structure, at \( \Gamma \) point, \( B_2 \) and \( E \) vibrational modes, might have different tendencies in reference to at \( X \) and \( W \) points.

Raman tensors for a \( D_{2d} \) point group symmetry are given in Appendix A.3 [17]. Raman tensor components for strained chalcopyrite structure (\( u = 0 \), zinc blende atom positions, bond angles, and \( c = 2a \) lattice length) are listed in Appendix A. The theoretical calculations and experimental results of Raman intensity analyses for isotropic or anisotropic crystalline planes are discussed next. The allowed polarizations (selection rules) of the Raman modes in the chalcopyrite structure are presented in Table 6.3 for backscattering geometry along the investigated crystalline planes [18].
Table 6.3 Allowing polarization configurations for back scattering geometry along (110) and (110) crystal planes in an ideal chalcopyrite structure. Alternative polarizations having equivalent crystal axes are not listed.

<table>
<thead>
<tr>
<th>Face</th>
<th>Geometry</th>
<th>Allowed symmetry</th>
<th>Allowed mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>(z(x, x)\hat{z})</td>
<td>(\Gamma_1 + \Gamma_3)</td>
<td>(A_1 + B_1)</td>
</tr>
<tr>
<td></td>
<td>(z(x, y)\hat{z})</td>
<td>(\Gamma_3(LO))</td>
<td>(B_2(LO))</td>
</tr>
<tr>
<td>(110)</td>
<td>(x(y, y)\hat{x})</td>
<td>(\Gamma_1 + \Gamma_3)</td>
<td>(A_1 + B_1)</td>
</tr>
<tr>
<td></td>
<td>(x(y, z)\hat{x})</td>
<td>(\Gamma_5(TO))</td>
<td>(E(TO))</td>
</tr>
<tr>
<td></td>
<td>(x(z, z)\hat{x})</td>
<td>(\Gamma_1)</td>
<td>(A_1)</td>
</tr>
</tbody>
</table>

where \(x = (110), y = (1\bar{1}0),\) and \(z = (001)\).

6.3. Vibrational Modes

6.3.1. Raman Analysis

Optical properties of chalcopyrite ZGP single crystal have been extensively studied by Raman spectroscopy. Raman spectra acquired along (001), (110), and (1\bar{1}0) crystalline planes are shown in Fig. 6.3. In Fig. 6.3, Raman spectra exhibit a common strong vibrational line at 328 cm\(^{-1}\) with symmetry of an \(A_1\) mode and it is, spectroscopically, known as breathing mode. The spectral peak position of nonpolar \(A_1\) mode is constant along all crystalline planes and it is in excellent agreement with literature values listed in in Table 6.4. Selection rule of undistorted chalcopyrite structure, presented in Table 6.3, indicates that nonpolar \(A_1\) and \(B_1\) and polar \(B_2(LO)\) modes are allowed along (001) plane. Other allowed mode of \(B_1\) along (001) plane corresponds to vibrations of the phosphorous atoms along the \(x\) and \(y\) axes and presence of a weak \(B_1\) mode feature consistent with the backscattering geometry along the \(c\)-lattice pane is also common for other chalcopyrite and sphalerite family alloys [19, 20]. Since weak phonon modes at 248.6 and 385.7 cm\(^{-1}\) are present only along the (001) plane, they are identified as two phonon branches of
$B_1$ mode. The remaining vibrational modes centered at 358.2 and 407.3 cm$^{-1}$ are assigned two branches of $B_2$(LO) mode.

Figure 6.3  Raman spectra of chalcopyrite ZGP single crystal along (001), (110), and ($\bar{1}$10) crystalline planes. (All spectra are taken under identical conditions).

Undistorted chalcopyrite structure has two isotropic $a$ and $b$ lattice axes (or two identical lattice planes). Since the $c$-lattice axis of the real ZGP crystal is slightly distorted to the germanium atoms side, (110) and (110) crystalline planes possess slightly different lattice constants, site symmetries, and stress parameters. Since nonpolar $A_1$ mode essentially involves symmetric and equal displacements of phosphorous vibrations, Raman intensity (i.e. amplitude
of coordinate change) and Raman shift (i.e. force constant of the tetrahedrally bonded phosphorous atom) are almost constant regardless of the crystallographic orientation of the chalcopyrite structure, summarized in Table 6.5. However, two polar modes of $E$ and $B_2$ have two distinct polarizations and vibrational coordinate changes. Specifically, polar $E$ mode has antisymmetric vibration of the $Ge_1$, $Ge_2$ and $Zn_1$, $Zn_2$ atoms and they are polarized along the $x$ or $y$ direction. Whereas, $B_2$ mode has a symmetric vibration of $Ge_1$, $Ge_2$ and $Zn_1$, $Zn_2$ pairs and they are polarized along the $z$ direction [12]. Five vibrational branch of $E$(TO) mode are observed around at 142, 200, 328, 367, and 384 cm$^{-1}$ along the $(110)$ and $(110)$ crystalline planes. The spectral position of the $E$(TO) modes along the $(110)$ and $(\bar{1}10)$ planes are observed within the proximity of 0.5 cm$^{-1}$ instrumental accuracy. On the other hand, two $B_2$(TO) modes are observed at 339.8 and 398.9 cm$^{-1}$ and 341.2 and 399.8 cm$^{-1}$ along the $(110)$ and $(110)$ crystallographic planes, respectively. Table 6.4 summarizes experimentally observed and theoretically calculated vibrational frequencies of the chalcopyrite ZGP structure. The calculated and observed frequencies of the ZGP chalcopyrite in the low-frequency regime are quite close to each other; however, at mid-frequency regime, they are off by 4 cm$^{-1}$ which indicates that ionic charges accountable for the distortion has more influence on the higher frequency regimes or higher frequency modes could be strongly effected from growth condition [21].

In contrast to group theory allowed vibrational modes, spectroscopically forbidden $A_2$ nonpolar mode was also observed around 183 cm$^{-1}$ with almost equal Raman intensity (see Table 6.5). Character table (see Table 6.2) clearly indicates that $A_2$ mode has zero polarizability; therefore, it is neither in Raman nor in IR active. The activation mechanism of $A_2$ symmetry could be due to slight deviation of the dihedral bond angles from the 180° (i.e. a slight polarizability component generated in the scattering wave vector due to distortion parameter, $u$).
Ohrendorf et al. [15] and Mintarinov et. al. [12] experimentally assigned $A_2$ mode for ZnSnP$_2$ crystal at 295 and 335 cm$^{-1}$, thus, the observation of $A_2$ mode is also common for other pnictide materials but spectral peak position assignment has still ambiguity.

**Birefringence calculation from the Raman Shift**

Pinnic et al. have proposed that Raman spectroscopy could be utilized to measure hydrostatic pressure dependency as a function of $A_1$ mode’s peak position [22]. Shirakata et al. studied hydrostatic pressure dependence of Raman shift up to 6 GPa and obtained pressure coefficients of various Raman modes, which is given by the following relation [16]:

$$\omega = \omega_0 + a \times p,$$

(6.7)

where $\omega$, $\omega_0$ are the pressurized and normal Raman mode centers, respectively and $a$ is a pressure coefficient of the given Raman mode. Hence, an anisotropic lattice distortion between (110) and (110) crystalline planes could be calculated from the given relation:

$$\omega(B_{2}^{TO}(110)) - \omega(B_{2}^{TO}(110)) = a_1 \times (p(110) - p(110)).$$

(6.8)

where $a_1 = 6.25$ cm$^{-1}$/GPa. Equation 6.8 indicates 0.195 GPa anisotropic strain exist between (110) and (110) crystallographic planes. Therefore, this amount of hydrostatic pressure is generated from the bond length differences between Zn-P and Ge-P bond pairs (or optical anisotropy). Due to the lack of optical isotropy, ZGP crystal possesses birefringence. The birefringence of the ZGP crystal can be calculated from the given relation:

$$Birefringence : \frac{\text{Strain in the equivalent planes}}{\text{Total hardness}}.$$
Table 6.4 Calculated and measured Raman zone-center ($\Gamma$) phonons in chalcopyrite ZGP crystal. Compatibility with phonon symmetries in zinc blende structure is included. LO (TO) denotes longitudinal (transverse) optic, respectively.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Calculation</th>
<th>Raman measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{5ac}$</td>
<td>$E$(LO)</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>$E$(TO)</td>
<td>94</td>
</tr>
<tr>
<td>$W_{2ac}$</td>
<td>$B_1$</td>
<td>120</td>
</tr>
<tr>
<td>$W_{2ac}$</td>
<td>$B_2$(LO)</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>$B_2$(TO)</td>
<td>120</td>
</tr>
<tr>
<td>$W_{4ac}$</td>
<td>$E$(LO)</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>$E$(TO)</td>
<td>141</td>
</tr>
<tr>
<td>$X_3$</td>
<td>$A_2$</td>
<td>182.7</td>
</tr>
<tr>
<td>$W_3$</td>
<td>$E$(LO)</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>$E$(TO)</td>
<td>203</td>
</tr>
<tr>
<td>$X_3$</td>
<td>$B_1$</td>
<td>247</td>
</tr>
<tr>
<td>$W_1$</td>
<td>$A_1$</td>
<td>328</td>
</tr>
<tr>
<td>$X_{5opt}$</td>
<td>$E$(LO)</td>
<td>332</td>
</tr>
<tr>
<td></td>
<td>$E$(TO)</td>
<td>330</td>
</tr>
<tr>
<td>$W_{2opt}$</td>
<td>$B_2$(LO)</td>
<td>368</td>
</tr>
<tr>
<td></td>
<td>$B_2$(TO)</td>
<td>340</td>
</tr>
<tr>
<td>$X_{4opt}$</td>
<td>$E$(LO)</td>
<td>375</td>
</tr>
<tr>
<td></td>
<td>$E$(TO)</td>
<td>370</td>
</tr>
<tr>
<td>$\Gamma_{15}$</td>
<td>$E$(LO)</td>
<td>402</td>
</tr>
<tr>
<td></td>
<td>$E$(TO)</td>
<td>386</td>
</tr>
<tr>
<td>$W_{2opt}$</td>
<td>$B_1$</td>
<td>389</td>
</tr>
<tr>
<td>$\Gamma_{15}$</td>
<td>$B_2$(LO)</td>
<td>414</td>
</tr>
<tr>
<td></td>
<td>$B_2$(TO)</td>
<td>397</td>
</tr>
</tbody>
</table>
As Eq. 6 is employed for birefringence calculation, birefringence of the ZGP crystal is estimated as 0.033, which is excellent agreement with the reported value of 0.035 [24, 25].

The vibrational properties extracted from Raman measurement analyses of ZGP single crystal along (001), (110) and (110) crystalline planes are summarized in Table 6.5. The correlation of these data with theoretical Raman scattering intensities and phonon characteristic of vibrational modes are discussed below. Theoretical Raman scattering intensity can be calculated from the Raman tensor equation, expressed by the following equation:

\[ I_{\text{Raman}} \approx \sum |e_i \cdot R_{\text{Raman}} \cdot e_s|^2 \]  \hspace{1cm} (6.10)

\( R \) is a Raman tensor; \( \hat{e}_i \) and \( \hat{e}_s \) are polarizations of incoming and scattered light, respectively. To illustrate, if Raman scattering geometry has a polarization of both incident and scattered light along the \( \hat{z} \) direction, i.e., parallel polarization geometry, the resulting Raman intensity of \( A_1 \) mode should be,

\[
I(A_1) \approx \begin{vmatrix}
0 & 0 & [a \ 0 \ 0] \\
0 & a & 0 \\
0 & 0 & b
\end{vmatrix}^2 = b^2 \tag{6.11}
\]

However, in the alternative geometry, when only the polarization of the incident light is rotated from \( \hat{z} \) to \( \hat{y} \), i.e., perpendicular polarization geometry, the resulting Raman intensity of \( A_1 \) would be instead,

\[
I(A_1) \approx \begin{vmatrix}
0 & 1 & [a \ 0 \ 0] \\
0 & 0 & a \\
0 & 0 & b
\end{vmatrix}^2 = 0 \tag{6.12}
\]
The above example shows how Raman tensor algebra determines the symmetrically allowed vibrational modes for particular polarization geometry of interest. Since nonpolar $A_1$ tensor has only diagonal elements, the incident and scattered light must be co-polarized.

Calculated Raman scattering intensity of $A_1$ mode is $a^2$ along the (001) and $b^2$ along the (110) and ($\overline{1}$10) crystallographic planes. Experimental Raman intensities of $A_1$ mode along (110) and (110) crystalline planes are equal (see Table 6.5). However, it is interesting to compare full-width at half-maximum (FWHM) analysis of the $A_1$ mode in all planes. The smallest $A_1$ linewidth of 5.2 cm$^{-1}$ is observed along (001) plane, indicating well-ordered crystalline structure. However, $A_1$ linewidth along ($\overline{1}$10) crystalline plane is 0.8 cm$^{-1}$ greater than that of (110) plane. Table 6.5 clearly indicates that linewidth values of (110) plane are higher than those of (110) plane. Therefore, chalcopyrite ZGP growth along (001) plane (or $c$-axis) is structurally more stable (or relaxed) than the others. Since $A_1$ and $A_2$ are the only common two modes among all crystalline planes, it is informative to cross correlate vibrational properties of the $A_2$ mode along the three crystalline planes. The peak position of $A_1$ is at the same frequency for all crystalline planes and distortion activated $A_2$ mode possesses close proximity of spectral peak position, intensity, and linewidth. Thus, these slight changes indicate that mode possesses either $A_1$ or $A_2$ symmetry involves only displacements of the phosphorous atoms. Finally, the FWHM difference between (110) and (110) crystalline planes monotonically increases as the frequency increases and FWHM of high-frequency $B_2$(LO) mode along the ($\overline{1}$10) plane reaches almost twice of that along the (110) plane.
Table 6.5  Summary of the optical properties obtained from Raman analyses, spectral frequency, scattering intensity, and linewidth of the ZGP single crystal along (001), (110) and (110) crystalline planes.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency</th>
<th>Intensity</th>
<th>FWHM</th>
<th>Frequency</th>
<th>Intensity</th>
<th>FWHM</th>
<th>Frequency</th>
<th>Intensity</th>
<th>FWHM</th>
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<tr>
<td>$E$(TO)</td>
<td></td>
<td></td>
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<td>142.4</td>
<td>481</td>
<td>5.6</td>
<td>141.9</td>
<td>491</td>
<td>5</td>
</tr>
<tr>
<td>$A_2$</td>
<td>182.7</td>
<td>75</td>
<td>15.2</td>
<td>184.3</td>
<td>90</td>
<td>18.9</td>
<td>183.8</td>
<td>80</td>
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<td>$E$(TO)</td>
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<td></td>
<td></td>
<td>200</td>
<td>99</td>
<td>14.3</td>
<td>199.8</td>
<td>98</td>
<td>20.9</td>
</tr>
<tr>
<td>$B_1$</td>
<td>248.6</td>
<td>25</td>
<td>22.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_1$</td>
<td>328</td>
<td>1202</td>
<td>5.2</td>
<td>328</td>
<td>1636</td>
<td>6.1</td>
<td>328</td>
<td>1641</td>
<td>6.9</td>
</tr>
<tr>
<td>$B_2$(TO)</td>
<td></td>
<td></td>
<td></td>
<td>339.8</td>
<td>500</td>
<td>7.2</td>
<td>341.2</td>
<td>391</td>
<td>8.8</td>
</tr>
<tr>
<td>$B_2$(LO)</td>
<td>358.2</td>
<td>1012</td>
<td>4.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E$(TO)</td>
<td></td>
<td></td>
<td></td>
<td>367.3</td>
<td>807</td>
<td>4.5</td>
<td>367.2</td>
<td>445</td>
<td>5.7</td>
</tr>
<tr>
<td>$E$(TO)</td>
<td></td>
<td></td>
<td></td>
<td>384.3</td>
<td>1360</td>
<td>4.7</td>
<td>384</td>
<td>749</td>
<td>6.3</td>
</tr>
<tr>
<td>$B_1$</td>
<td>385.7</td>
<td>41</td>
<td>13.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_2$(TO)</td>
<td></td>
<td></td>
<td></td>
<td>398.9</td>
<td>973</td>
<td>5.6</td>
<td>399.8</td>
<td>1068</td>
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<tr>
<td>$B_2$(LO)</td>
<td>407.3</td>
<td>1843</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.3.2. Polarized Raman Analysis

In order to understand the effect of chalcopyrite compression along the c-lattice axis and tetrahedral distortion along the a- and b-lattice axes on the ZGP crystal, we performed polarized Raman spectroscopy and calculated Raman intensities for different vibrational modes by varying polarization angle by 15°. Figure 6.4 shows polarized Raman spectra of the ZGP crystal obtained along the (001) crystalline plane from perpendicular to parallel polarization geometry. Raman selection rules for ideal chalcopyrite structure, listed in Table 6.3, dictate that nonpolar A₁ and B₁ modes are allowed at parallel polarization geometry, i.e., z(x, x)z and polar B₂(LO) mode is allowed at perpendicular polarization geometry, i.e., z(x, y)z. In Fig. 6.4, from perpendicular to parallel polarization geometry, optical B₂(LO) mode vanishes and nonpolar B₁ mode almost disappears at perpendicular polarization geometry as expected. However, nonpolar A₁ mode exhibits different tendency. In other words, Raman intensity of the A₁ mode diminishes as the polarization angle is rotated from parallel polarization geometry to 60° and it is intensified as the polarization angle is further rotated to perpendicular polarization geometry. Since B₁ mode corresponds to vibrations of the phosphorous atoms polarized along the x and y axes, from perpendicular to parallel polarization geometry, B₁ mode is polarized along its polarizability direction. Therefore, B₁ mode exhibits the similar tendencies both in distorted and undistorted chalcopyrite structures. Although A₁ mode possesses also phosphorous vibrations, it is only polarized along the c-lattice axis. Therefore, distortion in the real chalcopyrite structure shifted minimum and maximum point in the polarizability vector. Since B₂(LO) mode possesses vibrations of Zn and Ge atom contributions in addition to P atoms, distortion in the real chalcopyrite structure didn’t influence its minimum polarizability point but shifted maximum
polarizability point to 30°. The low intensity peak at 366 cm\(^{-1}\) (denoted by \(\alpha\)) could be a polarization activated second branch of \(A_2\) mode as stated in the literature [15].

Figure 6.4 Polarization dependence of the Raman spectra of chalcopyrite ZGP crystal from perpendicular to parallel polarization geometry along (001) crystalline plane.
The experimental Raman intensities (real chalcopyrite structure) are compared with theoretically calculated Raman intensities (undistorted chalcopyrite structure) of $A_1$ and $B_2$(LO) modes in order to understand point and extended defects on the optical property, symmetry broken selection rules, and structural birefringence of ZGP crystal. Figures 6.5a and 6.5b depict the results obtained from the $A_1$ and $B_2$(LO) mode analyses along (001) crystallographic plane, respectively. The left axes in Figs. 6.5a and 6.5b show the experimental Raman intensity with the calculated Raman intensity displayed on the right axes for $A_1$ and $B_2$(LO) modes respectively as a function of polarization angle. Comparison of Figs. 6.5a and 6.5b depicts that $A_1$ and $B_2$(LO) modes of undistorted chalcopyrite structure (see right axis) exhibit the same tendency with 90° phase shift. However, those of real chalcopyrite structure (see left axis) exhibit different tendency and different phase.

$A_1$ mode in the undistorted chalcopyrite structure possesses two minimums at 0° and 180° polarization angles with a periodicity of 180°; however, $A_1$ mode in the real chalcopyrite structure has two minimums at 30° and 150° polarization angles with a periodicity of 120°. $B_2$(LO) mode in the undistorted chalcopyrite structure exhibits two minimums at 90° and 270° polarization angles with a periodicity of 180°; however, $B_2$(LO) mode in the real chalcopyrite structure exhibits two minimums at 90° and 150° polarization angels with an aperiodic tendency. Therefore, polarized Raman study indicates that (001) crystalline plane exhibits different optical polarizability for different vibrational modes. Significant polarization dependency of the $B_2$(LO) mode compared to that of $A_1$ mode is could be due the polar characteristic of the $B_2$(LO) mode.
Figure 6.5  Polarization angle dependence of the $A_1$ and $B_2$(LO) phonon modes along (001) crystallographic plane. (a) Measured intensity (blue squares, left axis) and theoretically calculated intensity (red circles, right axis) of the $A_1$ mode as a function of polarization angle. (b) Measured intensity (blue squares, left axis) and calculated intensity (red circles, right axis) of the $B_2$(LO) mode as a function of polarization angle.
Figures 6.6a and 6.6bb show polarized Raman spectra of ZGP single crystal obtained along (110) and (110) crystalline planes from parallel to perpendicular polarization geometry, respectively. In an ideal chalcopyrite structure, (110) and (110) crystalline planes are isotropic; therefore, Raman selection rules listed in Table 6.3 are identical. Raman selection rules dictate that $A_1$ mode is allowed at parallel polarization geometry and polar $E$(TO) mode is allowed at perpendicular polarization geometry. Although only $A_1$ and $E$(TO) vibrational modes are allowed in the undistorted chalcopyrite structure, $A_1$, $E$(TO), and $B_2$(TO) vibrational modes were observed in the polarized Raman spectra obtained along the (110) and (110) crystallographic planes of the real ZGP.

It is important to study the dependency of the Raman scattering intensity on the polarization angle along the (110) and (110) crystallographic planes. Raman intensity of the vibrational mode, at 328 cm$^{-1}$, remains almost constant along the (110) crystallographic plane and significantly changes along the (110) crystalline plane as polarization geometry is rotated from parallel to perpendicular polarization geometry. Since $A_1$ and $E$(TO) modes are allowed vibrational modes along the (110) crystallographic plane, the constant vibrational mode observed at 328 cm$^{-1}$ is most likely to be distortion activated mode (denoted by $\beta$), depicted in Figs. 6.6a and 6.7a. On the other hand, along the (110) crystallographic plane, the vibrational mode observed at 328 cm$^{-1}$ exhibits similar tendency of undistorted chalcopyrite $E$(TO) mode, depicted in Fig. 6.7b, with an almost 30° phase shift in between.

Also, in Figs. 6.6a and 6.6b, two $E$(TO) modes and a $B_2$(LO) mode observed at 367.5, 384.5, and 338.4 cm$^{-1}$, respectively exhibit similar dependencies on the polarization angle. However, the $B_2$(LO) mode observed at 400.3 displays distinctive differences. In other words, the $B_2$(LO) mode along the (110) crystalline plane is weak but that along the (110) plane is even
more prominent than allowed $E$(TO) vibrational mode. Therefore, Raman spectra, in Figs. 5a and 6a, show that both $B_2$(LO) modes along (110) crystalline plane and low-frequency $B_2$(LO) mode along the (1¯10) crystallographic plane can be suppressed due to polarizability. However, relatively high-frequency $B_2$(LO) mode along the (110) crystallographic plane remains prominent even if polarized Raman measurement is performed.

The vibrational properties extracted from polarized Raman spectroscopy of the ZGP single crystal along (110) and (1¯10) crystalline planes are summarized in Table 6.6. The correlation of these data indicates that Raman line shape of all polarized modes along the (110) crystalline plane exhibits symmetric Lorentzian distribution. However, along (1¯10) crystalline plane two $E$(TO) modes observed at 328 and 383 cm$^{-1}$ are symmetric and high-frequency $B_2$(TO) mode at 400.3 cm$^{-1}$ is asymmetrically broadened to lower frequency side. The linewdths of the vibrational modes in the polarized Raman spectra are ~1.5 cm$^{-1}$ broader than in the conventional Raman spectra (compare Table 6.5 and Table 6.6). Although FWHM values of the $E$(TO) and $B_2$(TO) modes along (1¯10) crystalline plane are still higher than these along (110) plane, the difference is decreased. The appearance of the distortion activated (denoted by $\alpha$ in Fig. 6.4) mode and distinctive difference in the high-frequency $B_2$(TO) mode along (110) and (1¯10) crystalline planes could be due to the common difficulty of mode separation in the chalcopyrite structure which is still controversial among the $A_1$, $B_2$, and $E$ vibrational modes [26]. Finally, unlike (001) plane which exhibits nonlinear polarizability, (110) and (1¯10) crystalline planes are likely to have linear polarizability.
Figure 6.6  Polarized Raman spectra of chalcopyrite ZGP single crystal along the (a) (110) and (b) (1̅10) crystallographic planes.
Figure 6.7 Polarization angle dependence of the phonon mode at 328 cm\(^{-1}\) (a) Measured intensity (blue squares, left axis) and theoretically calculated intensity (red circles, right axis) of the Raman mode at 328 cm\(^{-1}\) along the (110) crystallographic plane as a function of polarization angle. (b) Measured intensity (blue squares, left axis) and calculated intensity (red circles, right axis) of the \(E(\text{TO})\) mode along the (\(\bar{1}10\)) crystallographic plane as a function of polarization angle.
Table 6.6 Summary of the vibrational mode properties obtained from 45° polarized-Raman measurement analyses, spectral frequency, scattering intensity, and linewidth of the ZGP single crystal along the (110) and (1\bar{1}0) crystalline planes.

<table>
<thead>
<tr>
<th>Mode</th>
<th>(110)</th>
<th></th>
<th>(1\bar{1}0)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequency</td>
<td>Intensity</td>
<td>FWHM</td>
<td>Frequency</td>
</tr>
<tr>
<td>$\beta$ vs $E$(TO)</td>
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<td>900</td>
<td>6.85</td>
<td>328.0</td>
</tr>
<tr>
<td>$B_2$(TO)</td>
<td>338.4</td>
<td>200</td>
<td>6.92</td>
<td>340.4</td>
</tr>
<tr>
<td>$E$(TO)</td>
<td>367.5</td>
<td>4300</td>
<td>6.64</td>
<td>367.7</td>
</tr>
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<td>$E$(TO)</td>
<td>384.5</td>
<td>7450</td>
<td>5.65</td>
<td>384.8</td>
</tr>
<tr>
<td>$B_2$(TO)</td>
<td>400.3</td>
<td>750</td>
<td>6.68</td>
<td>400.4</td>
</tr>
</tbody>
</table>

6.3.3. IR Reflection Analysis

Infrared reflection spectrum acquired in normal-incidence configuration in the spectral range between 300 and 450 cm\(^{-1}\), shown in Fig. 6.8a. Since IR reflection spectroscopy and Raman spectroscopy are sibling techniques, it is important to cross correlate their results. Only $B_2$ and $E$ vibrational modes exhibit symmetry of translations, i.e., $p$ orbitals; therefore, only they are IR active. In Fig. 6.8a, infrared reflection spectrum exhibits well-separated two sharp and one broad IR modes. Minimum reflectance of the IR spectrum observed at 334, 377, and 406 cm\(^{-1}\) are assigned as three branches of $E$(LO) mode. Two sharp peaks of the IR spectrum observed at 326 and 371 cm\(^{-1}\) are assigned as two branches of $E$(TO) mode.

The $s$-, cross-, and $p$-polarized IR reflection measurements were performed to understand the nature of broad peak, shown in Fig. 6.8b. Polarized IR reflectivity measurement indicates two distinct modes within the close proximity of each other and they were assigned as $E$(TO) and $B_2$(LO) phonon modes at resolved at 388 and 395 cm\(^{-1}\), respectively. In addition, at 340 cm\(^{-1}\), a
broad and weak peak exist but it is difficult to assign as a mode, which might be due to small dipole moment of the $B_2$(LO) mode. Since it is also weak in Raman spectra, both dipole moment and polarizability are weak as well. As with Raman scattering, the IR reflection spectrum indicates that mode splitting of pnictide chalcopyrite structure is well established for the low-frequency regions. However, at high-frequency regions, mode splitting of $B_2$ and $E$ modes depends on the chalcopyrite distortion parameter, which is quite likely to be influenced by defect states and growth temperature.

Figure 6.8  IR reflectivity spectra of ZGP single crystal in a (a) unpolarized and (b) polarized scattering configuration on the (001) crystalline plane.
6.4. Summary

In summary, vibrational and optical properties of ZGP crystal on the (001), (110), and (1̅10) crystalline planes have been investigated by Raman scattering and infrared (IR) reflection spectroscopies. The experimental results were compared with the theoretical calculations to understand chalcopyrite distortion effect better. Spectral positions and vibrational symmetries of Raman active modes have been assigned for all. In addition to spectroscopically allowed vibrations of $A_1$, $2B_1$, $2B_2$(LO, TO), and $5E$(TO) modes, forbidden $A_2$ nonpolar mode was also observed due to chalcopyrite distortion ($u$).

Raman measurements showed that the $B_2$(TO) mode were observed at 339.8 and 341.2 cm$^{-1}$ along the (110) and (1̅10) crystalline planes, respectively. Also birefringence (optical anisotropy) of the ZGP crystal was calculated from the hydrostatic pressure difference of the $B_2$(LO) mode along the (110) and (110) crystalline planes and found to be 0.033, in excellent agreement with reported value of 0.035. However, low-frequency branches of $B_1$ and $B_2$(LO, TO) modes were silent in Raman scattering and IR reflection spectroscopies which might be due to weak polarizability and dipole moments of atomic vibrations.

Infrared reflection spectrum exhibited three $E$(LO, TO) mode pairs and a $B_2$(TO) mode. As with Raman scattering, the IR reflection spectrum indicates that mode splitting of pnictide chalcopyrite structure is well established for the low-frequency regions. However, at high-frequency regions, mode splitting of $B_2$ and $E$ modes depends on the chalcopyrite distortion parameter, which is likely to be influenced by defect states and growth temperature.
6.5. References


CHAPTER 7

CONCLUSIONS

In this research, the physical properties of InN layers grown by High-Pressure Chemical Vapor Deposition technique have been studied by X-ray diffraction, Raman scattering, and infrared (IR) reflection spectroscopies. X-ray diffraction together with nonpolar phonon of Raman scattering and polar phonon of Raman scattering together with IR reflection analyses were correlated in order to gain a better understanding on how growth pressure, V/III molar ratio, precursor pulse separation, substrate material, and efficient mass transport along the flow direction influence physical properties of InN epilayers, investigated separately.

The long-range crystalline ordering results show that strains on the basal plane and on the c-direction exhibit different tendencies as a function of pressure (accordingly temperature) and precursor pulse separation. Therefore, InN material has different relaxation chemistry for various planes, which results in intrinsic asymmetry of InN structure (i.e., intrinsic spontaneous polarization). This might be due to a generation and diffusion of point defects as InN growth progresses or decrease in growth surface temperature by a carrier gas sweeping effect. However, in-plane and c-direction strains exhibit consistent tendencies with V/III molar ratio in the range of 1000–3000, which might be due to well-established growth parameters in that V/III molar ratio window.

At high growth pressures, long-range and short-range crystalline orderings indicate that calculated c-lattice constant is shorter and $E_2$(high) mode frequency is higher than those obtained from conventional low-pressure growth techniques, indicating that InN wurtzite structure is
compressed either due to a hydrostatic pressure during the growth or a thermal contraction during the cooling (annealing) process. Optimum growth temperature, which is determined from the best long-range ordering, increases linearly by 6.6 °C/bar; therefore, HPCVD approach enables an increase of 100 °C growth temperature, if growth pressure is increased from atmospheric to 15 bar. The influence of varied growth parameter usually exhibit linear correlation between long-range and short-range ordering; however, the nonlinear correlation of those indicate inclination of wurtzite anisotropy towards 2D or 3D like growth mode.

Growth rate (accordingly epilayer thickness) is maximized at V/III ratio in the range of 2000–3000 molar ratio, which might be due to reduced nitrogen desorption from the growth surface or increased surface diffusion of indium atoms to find energetically favored sites on the In-lattice. However, growth rate decreases with increasing growth pressure. Interestingly, all InN epilayers investigated in this research exhibited growth rate of ~110 nm/hr (or 330 nm epilayer thickness) for the best long-range and short-range crystalline orderings, regardless of growth pressure, precursor pulse separation, and substrate material type. Structural and optical properties significantly degrade above ~310 nm epilayer thicknesses, which might indicate either a constraint on HPCVD growth technique or further optimizations of crucial growth parameters are required to increase growth rate without degrading InN material quality.

$E_2$(high) mode, a nonpolar phonon vibration, is excited only on basal plane, which is perpendicular to incoming EM wave, and the influence of long-range Columbic interaction on the $E_2$(high) phonon frequency (i.e., force constant of dative bond) is lower than that of $A_1$(LO) phonon frequency. Reasonable good quality of InN thin films revealed that strain on the dative bond of $E_2$(high) mode, induced by any growth parameters, which is estimated from short-range crystalline ordering are in excellent agreement with in-plane strain obtained from InN (0 0 0 2)
Bragg reflex. Therefore, there is consistent correlation between short-range and long-range crystalline orderings obtained from Raman $E_2$(high) mode and XRD InN (0 0 0 2) Bragg reflex, respectively. This tendency disappears when degradation chemistry dominates over a crystalline ordering due to point defects and/or extended defects.

Since $A_1$(LO) mode, a polar phonon vibration, is excited on the $c$-direction, which is parallel to incoming EM wave, the influence of long-range Columbic interaction on the $A_1$(LO) phonon frequency is significant. In other words, electrostatic force and inter-atomic force compete with each other to dominate over each other, and this domination indicates asymmetric broadening of $A_1$(LO) mode. Because Raman scattering is acquired from a certain thickness, asymmetric broadening mechanisms of $E_2$(high) and $A_1$(LO) modes indicate cross sectional ordering of InN epilayer. In general, $A_1$(LO) phonon frequency obtained from Raman scattering is higher than that obtained from IR reflection, i.e., increased cross sectional area changes dative force from compressive to tensile due to present point defects.

Free carrier concentration and carrier mobility of InN epilayers exhibit consistent (decreasing) tendencies as InN epilayer thickness increases up to $\sim$310 nm. This might be due a reduced influence of InN surface charge accumulation as epilayer thickness increases. However, there is no consistent correlation between free carrier concentration and carrier mobility above thickness of 300 nm, which might be due to generation and/or diffusion of point defects as InN epitaxial growth exceed over 300 nm epilayer thickness or decrease of growth surface temperature by a high-velocity carrier gas sweeping effect. It is clear that free carrier concentration and $A_1$(LO) phonon frequency exhibit consistent tendencies, when long-range crystalline ordering of InN material is in the range of 200–300 arcsec.
InN epilayers grown either directly on sapphire (0001) substrates or on MOCVD grown GaN/sapphire (0001) templates show that the best structural and optical properties of InN thin films are obtained with V/III ratio in the 2000–3000 range. Sapphire grown InN epilayers exhibit tilted growth from $c$-direction due to chemical and dangling incompatibilities besides lattice and thermal mismatches between InN and sapphire substrate; therefore, the nucleation procedure should be improved to avoid tilted growth. The InN thin films grown directly on sapphire (0001) substrates exhibit tensile strain on $c$-lattice constant and compressive force on InN dative bond. However, GaN/sapphire-grown InN films exhibit compressive strain on the $c$-lattice constant and a tensile force on InN dative bond. Short-range crystal anisotropy of sapphire-grown thin films is lower than that of GaN/sapphire-grown thin films. Furthermore, free carrier concentration of InN layers grown on GaN/sapphire templates is twice as high as that of InN layers grown on sapphire substrates, which might be due to crystal anisotropy. Interestingly, carrier mobilities of InN epilayers are almost equal regardless of underlying substrate influence.

The best physical properties of InN material are obtained at the center of thin films. Furthermore, Raman scattering results indicate that dependencies of $E_2$(high) and $A_1$(LO) phonon frequencies on spatial distance along the flow direction are inversely correlated with linewidths of those. Therefore, vibrational bond strength is inversely correlated with InN epilayer quality. Finally, structural and optical results indicate that growth surface might have an uneven temperature distribution. As InN epilayer thickness increases, this influence might increase as well. Therefore, significant changes on the physical properties of InN epilayers above 300 nm thickness might be due to decrease in growth surface temperature by carrier gas sweeping effect.

Vibrational and optical properties of ZGP crystal on (001), (110), and (110) crystalline planes also have been investigated by Raman scattering and infrared (IR) reflection
spectroscopies. The experimental results were compared with the theoretical calculations to understand chalcopyrite distortion effect better. In addition to spectroscopically allowed vibrations of $A_1$, $2B_1$, $2B_2$(LO, TO), and $5E$(TO) modes, forbidden $A_2$ nonpolar mode is also observed due to chalcopyrite distortion ($u$). $B_2$(TO) vibrational mode was observed at 339.8 and 341.2 cm$^{-1}$ on (110) and (110) planes, respectively. Birefringence (i.e., optical anisotropy) of ZGP crystal was calculated from the hydrostatic Raman shift of $B_2$(LO) mode on these planes. The obtained birefringence value of 0.033 is in excellent agreement with reported value of 0.035. However, low-frequency branches of $B_1$ and $B_2$(LO, TO) modes are silent in Raman scattering and IR reflection spectroscopies which might be due to weak polarizability and dipole moments of atomic vibrations. Infrared reflection spectrum exhibit three $E$(LO, TO) mode pairs and a $B_2$(TO) mode. As with Raman scattering, the IR reflection spectrum indicates that mode splitting of pnictide chalcopyrite structure is well established for the low-frequency regions. However, at high-frequency regions, mode splitting of $B_2$ and $E$ modes depends on chalcopyrite distortion parameter, which is likely to be influenced by defect states and growth temperature.

**Open questions and future work**

The growth of InN thin films by HPCVD has provided substantial information to understand optical and structural properties of InN material. However, there is still significant work to be done to eliminate uncertainties in the above discussion. Relevant questions that are still open are origin of high $n_e$, limitation for surface charge accumulation not to influence carrier concentration, decay process of physical properties for thin films thicker than 300 nm, and correlation between structural and optical properties. Therefore, further studies are required to understand these and more about optical and structural properties of InN thin films for commercial mass production and device application of InN material.
APPENDIX: RAMAN TENSORS

A.1. Raman Tensors for $C_{6v}$ Point Group

\[
R[A_1(z)] = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix},
\]  
\[
R[E_1(-x)] = \begin{pmatrix} 0 & 0 & -c \\ 0 & 0 & 0 \\ -c & 0 & 0 \end{pmatrix},
\]
\[
R[E_1(y)] = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & c \\ 0 & c & 0 \end{pmatrix}, \text{ and}
\]
\[
R[E_2] = \begin{pmatrix} d & d & 0 \\ d & -d & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}
\]

A.2. Raman Tensors for $T_d$ Point Group

\[
T_2(x) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a \\ 0 & a & 0 \end{pmatrix},
\]  
\[
T_2(y) = \begin{pmatrix} 0 & 0 & a \\ 0 & 0 & 0 \\ a & 0 & 0 \end{pmatrix}, \text{ and}
\]
\[
T_2(z) = \begin{bmatrix}
0 & d & 0 \\
d & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}.
\] (A.7)

### A.3. Raman Tensors for \(D_{2d}\) Point Group

\[
R(\Gamma_i) = \begin{pmatrix}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & b
\end{pmatrix},
\] (A.8)

\[
R(\Gamma_j) = \begin{pmatrix}
-c & 0 & 0 \\
0 & c & 0 \\
0 & 0 & 0
\end{pmatrix},
\] (A.9)

\[
R(\Gamma_q) = \begin{pmatrix}
0 & d & 0 \\
d & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}, \text{ and}
\]

\[
R(\Gamma_5)_x = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & e \\
0 & e & 0
\end{pmatrix}, \quad R(\Gamma_5)_y = \begin{pmatrix}
0 & 0 & f \\
0 & 0 & 0 \\
f & 0 & 0
\end{pmatrix}.
\] (A.11)