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# Structural and elastic properties of InN and InAlN with different surface orientations and doping

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#### Cover:

Reciprocal space maps around the InN (0004) reciprocal lattice point for InN films with different Mg concentrations. Front cover: the reciprocal space map of undoped InN film, which shows *n*-type conductivity. Middle: the reciprocal space map of *p*-type InN:Mg with  $[Mg] = 1 \times 10^{18} \text{ cm}^{-3}$ . Back side: the reciprocal space map of heavily doped InN:Mg with  $[Mg] = 3.9 \times 10^{21} \text{ cm}^{-3}$  and *n*-type conductivity.

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## Abstract

Group–III nitrides, InN, GaN, AlN, and their alloys, have revolutionized solid state lighting and continue to attract substantial research interest due to their unique properties and importance for optoelectronics and electronics. Among the group–III nitrides, InN has the lowest effective electron mass and the highest electron mobility, which makes it suitable for high-frequency and high power devices.  $In_x Al_{1-x}N$  alloys cover the widest wavelength region among any semiconductor systems with band gaps ranging from 0.6 eV (InN) to 6.2 eV (AlN). Thus,  $\ln_x Al_{1-x}N$  is promising for light emitting diodes and laser diodes in a wide spectral range from infrared to deep ultraviolet, as well as for solar cell applications.  $In_x Al_{1-x}N$  thin films are also extensively studied in relation to their application for Bragg reflectors, microcavities, polariton emission and high electron mobility transistors. Despite the intense research, many of the fundamental properties of InN and  $In_x Al_{1-x}N$  remain controversial. For example, the material lattice parameters, stiffness constants, structural anisotropy and defects in nonpolar and semipolar films, effect of impurities and dopants are not established. Furthermore, to fabricate InN based devices, reliable n- and p-type doping should be achieved. At present, control and assessment of p-type conductivity using Mg doping of InN is one of the most outstanding issues in the field.

This thesis focuses on: i) Establishing the structural and elastic properties of  $In_x Al_{1-x}N$  with arbitrary surface orientations (papers I to III); ii) Studying structural and free-charge carrier properties of non/semi-polar and zinc-blende InN (papers IV and V) and iii) Establishing the effects of doping (p and n) on lattice parameters, structural and free-charge carrier properties of InN (Papers VI and VII). The work includes *ab initio* calculations and experimental studies of InN and  $In_x Al_{1-x}N$  materials grown in world-class laboratories in Japan, Europe and the USA.

The first part of the thesis includes general description of the basic material properties. Next, the structural and elastic properties and defects in  $In_xAl_{1-x}N$  and InN are discussed. The experimental techniques and relevant methods used to characterize the materials are described, as well as details on the *ab initio* calculations used in this work are provided. Part II consists of *seven* papers.

In **Paper I** we present the first theoretical analysis on the applicability

of Vegard's linear rule in  $In_x Al_{1-x}N$  alloys in relation to strain related elastic and piezoelectric properties. We derive the elastic stiffness constants and biaxial coefficients, as well as the respective deviations from linearity by using *ab initio* calculations. The stress-strain relationships to extract composition from the lattice parameters are derived in different coordinate systems for  $In_x Al_{1-x}N$  with an arbitrary surface orientation. The error made in the composition extracted from the lattice parameters if the deviations from linearity are not taken into account is discussed for different surface orientations, compositions and degrees of strain. The strain induced piezoelectric polarization is analyzed for  $In_x Al_{1-x}N$  alloys grown psudomorphically on GaN. We establish the importance of the deviation from linearity in the extracted strain values in respect to the piezoelectric polarization.

**Paper II** reports the lattice parameters of  $In_x Al_{1-x}N$  in the whole compositional range using first-principle calculations. Deviations from Vegard's rule are obtained via the bowing parameters, which largely differ from previously reported values. The paper discusses for the first time the implications of the observed deviations from Vegard's rule on the In content extracted from x-ray diffraction.

**Paper III** discusses the lattice parameters and strain evolution in Al-rich  $In_x Al_{1-x}N$  films with composition. Decoupling of compositional effects on the strain determination was accomplished by measuring the In contents in the films both by Rutherford backscattering spectrometry (RBS) and x-ray diffraction (XRD). It is suggested that strain plays an important role for the observed deviation from Vegard's rule in the case of pseudomorphic films. It is found that Vegard's rule in the narrow compositional range around the lattice matching to GaN may be applicable.

**Paper IV** reports the first study of structural anisotropy of non-polar InN and semi-polar InN grown on sapphire and  $\gamma$ -LiAlO<sub>2</sub> substrates. The on-axis rocking curve (RC) widths were found to exhibit anisotropic dependence on the azimuth angle. The finite size of the crystallites and extended defects are suggested to be the dominant factors determining the RC anisotropy in a-plane InN, while surface roughness and curvature could not play a major role. Furthermore, strategy to reduce the anisotropy and magnitude of the tilt and minimize defect densities in a-plane InN films is suggested. The semipolar InN was found to contain two domains nucleating on zinc-blende InN(111)A and InN(111)B faces. These two wurtzite domains develop with different growth rates, which was suggested to be a consequence of their different polarity. We found that a- and m-plane InN films have basal stacking fault densities similar or even lower compared to nonpolar InN grown on free-standing GaN substrates, indicating good prospects of heteroepitaxy on foreign substrates for the growth of InN-based devices.

**Paper V** reports the development of appropriate methods based on X-ray diffraction and Infrared spectroscopic ellipsometry to identify wurtizte and

zinc-blende InN and quantify their phase ratio. Detailed analysis on the formation of the cubic and wurtzite phases is presented and their evolution with film thickness is discussed in detail. The free-charge carrier and phonon properties of the two phases are discussed together with the determination of the surface electron accumulation.

**Paper VI** studies the effect of Mg doping on the structural parameters and free—charge carrier properties of InN. We demonstrate the capability of infrared spectroscopic ellipsometry to identify p—type doping. The paper provides important information on the effect of Mg doping on extended defects and lattice parameters, and also discussed the relationship between doping, defects and carrier mobility.

**Paper VII** presents the first study on the effect of impurities on the lattice parameters of InN using first principle calculations. We considered both the size and the deformation potential effect for  $Mg^0$ ,  $Mg^-$ ,  $Si^+$  and  $O^+$  and  $H_i^+$ . The incorporation of H on interstitial site and substitutional O leads to expansion of the lattice. On the other hand, incorporation of Si or Mg leads to contraction of the lattice. The most pronounced effect is observed for Si. Our results indicate that the experimentally observed increase of the in-plane lattice parameter of Mg doped InN cannot be explained neither by the size nor by the deformation potential effect and suggest that the growth strain is changed in this case. The reported size and deformation potential coefficients can be used to elucidate the origin of strains in InN epitaxial layers and the degree of electrically active impurities.

# Sammanfattning

Grupp III nitrider, såsom InN, GaN, AlN och deras legeringar, har revolutionerat de halvledarbaserade lysdioderna och kommer med största sannolikhet att attrahera ett fortsatt stort forskningsintresse tack vare dess unika egenskaper inom optoelektronik och elektronik. Bland grupp III nitriderna har InN den lägsta effektiva elektronmassan och den högsta elektronmobiliteten, vilket gör In N passande för högfrekvens<br/>– och kraftkomponenter.  $In_x Al_{1-x}N$  legeringar täcker det bredaste vå Våglöngdsspannet bland alla halvledarsystem med bandgap från 0,6 eV (InN) till 6,2 eV (AlN). Alltså är  $In_x Al_{1-x}N$  lovande för lysdioder och laserdioder i ett brett spektralområde, från infrarött till djupt ultraviolett, men också för solcellstillämpningar. Tunna filmer av  $In_x Al_{1-x}N$  har också studerats i stor utsträckning för tillämpningar inom Bragg reflektorer, mikrokaviteter, emission av polaritoner och transistorer med hög elektronmobilitet. Trots denna intensiva forskning förblir många av de fundamentala egenskaperna hos InN och  $In_x Al_{1-x}N$  omdebatterade. Till exempel materialets gitterparametrar, styvhetskonstanter, strukturella anisotropi och defekter i ickepolära och halvpolära filmer samt effekter av föroreningar och dopämnen. Dessutom, för att kunna tillverka InN baserade komponenter krävs en tillförlitlig dopning av p-typ. Kontroll och utvärdering av p-typ konduktivitet genom Mg dopning är för nävarande en av de största frågorna inom ämnet.

Denna avhandling fokuserar på: i) Fastställa strukturella och elastiska egenskaper hos  $In_xAl_{1-x}N$  med godtyckliga ytorienteringar (artikel I till III); ii) studera strukturella och fria laddningsbärares egenskaper hos icke-/halvpolära och sk zinc blende InN (artikel IV och V) och iii) fastställa effekter av dopning (p och n) på gitterparametrar och strukturella och fria laddningsbärares egenskaper hos InN (artikel VI och VII). Arbetet inkluderar *ab initio* beräkningar och experimentella studier av InN och  $In_xAl_{1-x}N$ material, tillverkade på laboratorier i världsklass i Japan, Europa och USA.

Första delen av avhandlingen inkluderar en generell beskrivning av grundläggande materialegenskaper. Därefter diskuteras de strukturella och elastiska egenskaperna samt defekter i InN och  $In_xAl_{1-x}N$ . De experimentella teknikerna och relevanta metoder som använts för att karakterisera materialen är beskrivna, liksom även detaljerna kring *ab initio* beräkningarna som är gjorda i detta arbete. Andra delen av avhandlingen består av sju artiklar.

# Publications included in the PhD thesis

- I. Elastic constants, composition and piezoelectric polarization in  $In_x Al_{1-x}N$ : from *ab initio* calculation to experimental implications for the applicability of Vegard's rule **M.-Y. Xie**, F. Tasnádi, I. A. Abrikosov, L. Hultman and V. Darakchieva *Phys. Rev. B* **86**, 155310 (2012).
- II. Lattice parameters, deviations from Vegard's rule, and E<sub>2</sub> phonons in InAlN
  V. Darakchieva, M.-Y. Xie, F. Tasnádi, I. A. Abrikosov, L. Hultman, B. Monemar, J. Kaminura, and K. Kishino Appl. Phys. Lett. 93, 261908 (2008).
- III. Effects of strain and composition on the lattice parameters and applicability of Vegard's rule in Al-rich Al<sub>1-x</sub>In<sub>x</sub>N films grown on sapphire V. Darakchieva, M. Beckers, M.-Y. Xie, L. Hultman, B. Monemar, J.-F. Carlin, E. Feltin, M. Gonsckorek, and N. Grandjean J. Appl. Phys. 103, 103513 (2008).
- IV. Structural, free-charge carrier and phonon properties of wurtzite and zinc-blende polymorphs in InN epitaxial layers M.-Y. Xie, M. Schubert, J. Lu, A. G. Silva, A. Santos, N. Bundaleski, P. O. Å. Persson, C. L. Hsiao, L. C. Chen, W.J. Schaff, and V. Darakchieva In manuscript
- V. Structural anisotropy of nonpolar and semipolar InN epitaxial layers V. Darakchieva, M.-Y. Xie, N. Franco, F. Giuliani, B. Nunes, E. Alves, C. L. Hsiao, L. C. Chen, T. Yamaguchi, Y. Takagi, K. Kawashima, and Y. Nanishi J. Appl. Phys. 108, 073529 (2010).
- VI. Effect of Mg doping on the structural and free-charge carrier properties of InN M.-Y. Xie, N. Ben Sedrine, L. Hong, S. Shöche, T. Hofmann, M. Schubert, B. Monemar, X. Wang, A. Yoshikawa, K. Wang, Y. Nanishi, and V. Darakchieva In manuscript

VII. Effect of impurities on the lattice parameters of InN M.-Y. Xie, F. Tasnádi, I. A. Abrikosov, L. Hultman and V. Darakchieva In manuscript

#### My contribution to the papers

Paper I. I conceived the idea, I did the calculations in the paper except the *ab initio* calculations, did the data analysis and wrote the first version of the manuscript.

Paper II. I did the XRD measurements and performed the XRD and Raman data analysis. I took part in the discussion of the results.

Paper III. I did the XRD measurements and took part in the discussion of the results.

Paper IV. I did the XRD measurements, TEM analysis and sample preparation. I performed the data analysis and wrote the first version of the manuscript.

Paper V. I did the XRD and AFM measurements and took part in the data analysis.

Paper VI. I did the XRD and AFM measurements, performed the data analysis and wrote the first version of the manuscript.

Paper VII. I conceived the idea, performed the *ab initio* calculation, did the data analysis and took part in writing the paper.

## Publications related to, but not included in the PhD thesis

- I. Unintentional incorporation of H and related structural and free-electron properties of c- and a-plane InN
  V. Darakchieva, K. Lorenz, M.-Y. Xie, E. Alves, W. J. Schaff, T. Yamaguchi, Y. Nanishi, S. Ruffenach, M. Moret and O. Briot *Phys. Status Solidi A* 209, 91 (2012).
- II. Free electron properties and hydrogen in InN grown by MOVPE V. Darakchieva M.-Y. Xie, D. Rogalla, H. W. Becker, K. Lorenz, E. Alves, S. Roffenach, M. Moret and O. Briot *Phys. Status Solidi A* 208, 1179 (2011).
- III. Unintentional incorporation of hydrogen in wurtzite InN with different surface orientations
  V. Darakchieva, K. Lorenz, M.-Y. Xie, E. Alves, C. L. Hsiao, L. C. Chen, L. W. Tu, W. J. Schaff, T. Yamaguchi and Y. Nanishi J. Appl. Phys. 110, 063535 (2011).
- IV. Standard-free composition measurements of Al<sub>x</sub>In<sub>1-x</sub>N by low-loss electron energy loss spectroscopy
  J. Palisaitis, C. L. Hsiao, M. Junaid, M.-Y. Xie, V. Darakchieva, J. F. Carlin, N. Grandjean, J. Birch, L. Hultman and P. O. Å. Persson *Phys. Status Solidi RRL* 5, 50 (2011).
- V. Role of impurities and dislocations for the unintentional n-type conductivity in InN
  V. Darakchieva, N. P. Barradas, M.-Y. Xie, K. Lorenz, E. Alves, M. Schubert, P. O. Å. Persson, F. Giuliani, F. Munnik, C. L. Hsiao, L. W. Tu and W. J. Schaff
  Physica B 404, 4476 (2009).
- VI. Unravelling the free electron behavior in InN
  V. Darakchieva, T. Hofmann, M. Schubert, B. E. Sernelius, F. Giuliani,
  M.-Y. Xie, P. O. Å. Persson, B. Monemar, W. J. Schaff, C. L. Hsiao,
  L. C. Chen, Y. Nanishi *IEEE COMMAD 2008: Optoelectronic and Microelectronic Materials* and Devices p. 90 (2009).
- VII. Strain and compositional analyzes of Al-rich Al<sub>1-x</sub>In<sub>x</sub>N alloys grown by MOVPE: impact on the applicability of Vegards rule V. Darakchieva, M. Beckers, L. Hultman, M. Xie, B. Monemar, J.-F, Carlin, and N. Grandjean *Phys. Status Solidi C* 5, 1859 (2008).

### Publications not related to the subject

I. Epitaxial lateral overgrowth of InP on Si from nano-openings: Theoretical and experimental indication for defect filtering throughout the grown layer
 F. Olsson, M. Xie, S. Lourdudoss, I. Prieto and P. A. Postigo

J. Appl. Phys. 104, 093112 (2008).

II. Epitaxial lateral overgrowth of InP in micro line and submicro mesh openings
F. Olsson, M. Xie, F. Gerard, A. r. Alija, I. Prieto, P. A. Postigo and S. Lourdudoss

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## Chapter 1

# Basic properties of InN and InAlN

### **1.1** Short introduction

Why group—III nitride semiconductors, AlN, GaN, InN and their alloys have attracted so much research interest? The main reason is that group—III nitrides have direct band gaps, which cover the energy range from 0.65 eV (InN) [1], to 3.4 eV (GaN) [2], to 6.2 eV (AlN) [3] (see Fig.1.1). In comparison, Si, GaAs and other well developed semiconductors are not suitable for fabricating optoelectronic devices in the violet and blue spectral region, due to their indirect or small band—gaps. Additionally, the high melting points and the high breakdown fields of group—III nitrides make them ideal for high temperature and high power electronic devices [4,5].

Among group—III nitrides, InN has the smallest electron effective mass and the highest electron mobility [1]. Consequently, InN has a great potential for high frequency devices. AlN is considered as a good choice for electronic packaging due to its extremely high band gap energy, high thermal conductivity, high hardness and stability at elevated temperatures and in caustic environments [3]. AlN thin films have been successfully applied for buffer layers to grow high quality GaN on foreign substrates [6]. GaN and its alloys with InN and AlN have been used for fabricating long lifetime bright LEDs and LDs for white, blue and green light emission [7–10]. The blue InGaN LED may be seen as the greatest optoelectronic advance of the past 25 years. In 2010 the first enhancement mode GaN transistors became available and were designed to replace power MOSFETs [11]. An emerging application of InGaN and InAlN is in highly efficient multi—junction solar cells [12].

Despite the significant progress in the filed, there are still many open questions, in particular regarding the least studied members of the III-nitride family, InN and InAlN. For example, the lattice parameters, stiffness constants and band gap energies of InAlN are still debated. The piezoelectric polarization of InAlN with arbitrary surface orientations is not reported. The origin of the unintentional n-type conductivity in InN is still not



Figure 1.1: Band gap energies versus lattice parameters of different compound semiconductors.

elucidated. Reliable assessment of p-type conductivity in InN is a major challenge and the free hole properties have not been established. Very little is known about zinc blende InN due to difficulties to grow pure phase material.

### **1.2** Crystal structure and polarity

Group–III nitrides can crystallize in wurtzite (WZ), zinc-blende (ZB) and rock–salt (RS) structures. Under ambient conditions, wurtzite is the thermodynamically stable structure. ZB InN can be grown on r–plane sapphire [13, 14], cubic GaN [15] and Si(111) [16]. The RS form is possible only under high pressures and can not be realized in the form of epitaxial films.

The WZ structure consists of two interpenetrating hexagonal close-packed (hcp) sublattices offset along the c-axis by 5/8 of the cell height. Each hcp sublattice contains one type of atoms. The space group of WZ III-nitrides is  $P6_3mc$  ( $C_{6v}^4$ ). Each group-III atom is positioned at the centre of a tetrahedron. The four nearest nitrogen neighbouring atoms define the four corners of the tetrahedron. Conversely, each nitrogen atom is coordinated by four group-III atoms in a tetrahedron (see Fig.1.2 a). The WZ structure is usually represented by two lattice parameters a and c (see Fig.1.2). The a lattice parameter is in the basal plane along the [1100] direction. The c lattice parameter is along the [0001] direction and it describes the height of the



Figure 1.2: Schematic representations of the wurtzite (a) and zinc-blende (b) crystal structures of group-III ntrides.



Figure 1.3: Ball and stick models of (0001) or group-III and N or (0001)-polarity surfaces of III—nitrides.

unit cell. Internal parameter u presents the ratio of the anion-cation bond length along the c-axis and the c lattice parameter. In an ideal wurtzite structure the values of the c/a ratio, and the internal parameter, u, are, c/a = 1.633 and u = 3/8 = 0.375, respectively. In all WZ III-nitrides, the experimental c/a ratios are smaller than the ideal value [17], which indicate the inequality of the four anion-cation bonds of the group-III atom. This non-ideality of the crystal structure corresponds to an increase of the effects of polarization in epitaxial layers, which will be discussed in detail in Chapter 3.

The space group of ZB III—nitride is  $F\bar{4}3m$   $(T_d^2)$  and the unit cell is cubic. There are four group—III elements and four nitrogen elements in the unit cell (see Fig.1.2). The unit cells is described by one lattice parameter a. Similar to the WZ structure, each group—III atom of the ZB unit cell is positioned at the centre of tetrahedron and it is coordinated by four nitrogen atoms in the corners, and vice versa.

The main difference between WZ and ZB structures lies in the stacking sequence of the closest packed diatomic planes. In the WZ structure, the group-III and nitrogen atoms are alternating in the biatomic close-packed (0001) planes. Therefore, a stacking sequence of the (0001) plane is formed with an order of 'ABAB...'along the [0001] direction. (0001) plane is



Figure 1.4: Schematic presentation of the wurtzite crystal structure of group-III nitrides. Hatched areas indicate the most often used planes for epitaxial growth: the polar *c*-plane (0001); the nonpolar *a*-plane (11 $\overline{2}0$ ) and *m*-plane (1 $\overline{1}00$ ); and the semipolar *r*-plane (1 $\overline{1}02$ ) and (10 $\overline{1}1$ ).

also called c-plane. In ZB structure, the stacking sequence for the (111) close-packed planes is 'ABCABC...'along [111] direction (see Fig.1.3). This difference in stacking order is due to the different bond angle of the second nearest neighbours. There is a mirror image but no in-plane rotation with the bond angles in the stacking order along the [0001] direction for WZ structure. On the other hand, a 60° in-plane rotation leads to a stacking order of 'ABCABC...' in the zinc blende structure along the [111] direction (see Fig.1.3).

WZ III-nitrides are polar crystals along the [0001] direction. The group-III-polarity, [0001], is the orientation where the single bonds along c-axis is from the group-III atoms toward the N atoms. The N-polarity,  $[000\overline{1}]$ , is the crystal orientation opposite to the group-III-polarity orientation with three bonds away from the group-III atoms toward the N atoms, (see Fig.1.3). The termination of the N or group-III polar surfaces may dependent on growth conditions. For example, the (0001) surface of GaN undergoes transition from N-adatom to G-adatom reconstruction as the growth conditions are changed from N to Ga-rich [18]. However, in InN the polar surfaces are always terminated by In atom reconstructures [18].

Recently, III-nitrides with nonpolar/semipolar surface orientations have attracted considerable attention, due to the possibility to avoid/minimize the built-in electric fields caused by the polarization along the c-axis (further details are given in Chapter 4). (11 $\overline{2}0$ ), a-plane, and (1 $\overline{1}00$ ), m-plane are the two nonpolar planes of WZ III-nitrides, which are perpendicular to the c-plane, (see Fig.1.4). Semipolar planes are the planes that incline an angle with c-plane other than 0° (c-plane) or 90° (nonpolar-planes), for example (10 $\overline{1}1$ ) and (10 $\overline{1}2$ ) (r-plane) planes (see Fig.1.4).



Figure 1.5: Calculated conduction and valence band dispersions using the kp model. The Fermi level position is calculated for  $n = 10^{20}$  cm<sup>-3</sup> (Reprinted figure with permission from J. Wu.*et al.* (2002) *Phys.Rev.B* **66**, 201403. Copyright 2002 by the American Physical Society).

### 1.3 Band structure and electronic properties of InN and InAlN

#### 1.3.1 Origin of the large bandgap in InN

The revision of the band gap energy of InN from 1.9 eV to 0.65 eV is probably the most intriguing change of paradigm in the III—nitride field in the last 10 years [12, 19]. In the early studies on the optical absorption of InN thin films grown by sputtering, it was concluded that the InN bandgap is in the range of 1.7-2.2 eV [20, 21]. However, no near band edge emission in this energy range was ever detected by photoluminesecence experiments. In 2002, the near band edge emission of InN was reported by Davydov et al. and Wu et al. to be at much lower energies, in the range of 0.6-0.8 eV [1,12,19].

It is known that in the case of degenerate semiconductors, optical absorption will not occur for transitions below the Fermi level. Subsequently, the absorption edge is pushed to higher energies. The blue shift of the absorption with respect to the intrinsic bandgap is called the Burstein-Moss shift [22]. Fig.1.5 shows an example of Burstein-Moss effect in InN with free electron concentration of  $10^{20}$  cm<sup>-3</sup> [23]. The conduction band is calculated by using nonparabolic equation [24] and its simplified parabolic form [23] and an intrinsic bandgap energy with  $E_g = 0.64$  eV. It is seen that the Fermi level,  $E_f$ , is displaced deep into the conduction band when the electron concentration is higher than  $10^{19}$  cm<sup>-3</sup>. In such case, the "optical bandgap" of InN could approach 2 eV, when the electron concentration exceeds  $5 \times 10^{20}$  cm<sup>-3</sup> [23].

The "optical" bandgap of InN was measured in thin films grown by sputtering, which are believed to contain large amounts of O [25]. O is a donor in



Figure 1.6: DFT band structure across the Brilloin zone with the determined branch point,  $E_B$  (which is referred in this thesis as the charge neutrality level (CNL)) and surface Fermi level pinning,  $E_{pin}$ , positions (Reprinted figure with permission from P. D. C. King *et al.* (2008) *Phys.Rev.B* **77**, 045316. Copyright 2008 by the American Physical Society).

InN [26] and therefore large free electron concentration in InN could explain the observation of an optical bandgap of 2 eV. In the last years, significant progress in the growth of InN has been made and films with free electron concentration of the order of  $10^{17}$  cm<sup>-3</sup> are achieved [27]. In these samples it was undoubtedly shown by photoluminenscence and absorption measurements that the bandgap of InN is below 0.7 eV [27].

However, even high quality InN films are still unintentional n-type conductive. In order to understand the reason for the high tendency of InN for n-type doping, let us consider the band structure in detail. The charge neutrality level (CNL) is an energy level, at which the surface states change their character from predominantly donor (below) to predominantly acceptor (above) [28]. The CNL is believed to be universal on an absolute energy scale. In contrast to the other III-nitrides where CNL lies within the direct band gap, the CNL in InN is found both experimentally and theoretically at about 1eV above the CBM [28] (see Fig.1.6). With the CNL lying above the CBM, the Fermi level position in InN could be easily increased by both native defects and impurities, such as hydrogen and oxygen. This will contribute to n-type conductivity in InN. According to the amphoteric defect model [29], for a semiconductor with the Fermi level below the CNL, the preferential defects are donors, whereas for the situation of the Fermi level above the CNL, acceptors have lower formation energy. For InN with the CNL above the CBM, the most favourable defects are donor-type native defects, such as nitrogen vacancies. Extrinsic donors also effectively dope InN.



Figure 1.7: (a) Atomic orbital energies of group-III and V elements, (b) conduction and valence band edges of related III-V semiconductors with respect to  $E_{FS}$ ,  $E_{FS}$  is referred in this thesis as CNL (Reprinted figure with permission from P. D. C. King *et al.* (2008) *Phys.Rev.B* **77**, 045316. Copyright 2008 by the American Physical Society).

#### 1.3.2 Chemical trends

The chemical trends may explain why the band structure of InN is so unique among semiconductors. In a simple tight-binding model, the valence band edge energy is given by the bonding state of the anion and cation p-orbitals. Both Ga and In have occupied shallow d-orbitals which can hybridize with N 2p and create a p-d repulsion. The p-d repulsion pushes the valence band maximum (VBM) to higher energies. The In 4d levels in InN are shallower than the Ga 3d levels in GaN (see Fig.1.7 a). In contrast, there is no p-drepulsion pushing the VBM of AlN to higher value, due to the fact that Al does not have occupied d-levels. On the other hand, the conduction band edge results from the anti-bonding state of the cation s-orbitals and N 2s-orbital. The cation s-orbital energy reduces with moving from Al to Ga, but then increases to In (see Fig.1.7). However, the cation-anion bond length increases, and hence the strength of the s-s repulsion, which pushes the CBM to higher energies, decreases, with increasing cation atomic number. Consequently, the CBM energy does not follow the energetic ordering of the cation-s orbital energies; instead, the reduction in s-s repulsion causes a marked reduction in conduction band edge from AlN to InN. Thus, the presence of shallow d-levels in In leads to a relatively high-lying VBM, and the reduction in s-s repulsion with increasing the atomic number leads to low CBM in InN. As a result In has a very narrow band gap with a CBM lying well below the CNL (see Fig.1.7).

#### **1.3.3** Surface electron accumulation

In 2003, Lu *et al.* reported a strong excess sheet charge at the surface of InN films grown by molecular beam epitaxy (MBE) on either AlN or GaN buffers [30]. They derived this strong excess sheet charge by extrapolating the fitted curve of sheet carrier density versus film thickness to zero film thickness [30] (see Fig.1.8). The surface or the interface between InN and its



Figure 1.8: Sheet density as a function of film thickness in InN films grown on GaN or AlN buffer layers (Reprinted figure with permission from H. Lu *etal*, (2003) *Appl.Phys.Lett.* **82**, 1736. Copyright 2003 by the American Institute of Physics).

buffer layer are believed to be the source of the strong excess sheet charge. For InN films on AlN buffer, the residual sheet charge is found to be  $4.33 \times 10^{13}$ cm<sup>-2</sup>, while for InN films on GaN buffer, the residual sheet charge is about  $2.53 \times 10^{13}$  cm<sup>-2</sup>. This result means that carriers are not uniformly distributed in the film. There must be surface or interface charge accumulation. They also found that the average electron mobility in the bulk is higher than for electrons at the surface or interface Soon after these first indications for the presence of electron accumulation at the surface of c-plane InN, its existence was shown unambiguously by high resolution electron energy loss spectroscopy [31].

The surface electron accumulation of InN affects the basic electrical characterization of InN films. The bulk electron concentrations of an InN film could not be revealed by using single-field Hall effect measurement. Instead, the average electrical properties of the entire InN film are obtained, including the electronic properties through the surface, bulk and interface regions. For p-type InN, the p-type region beneath the surface electron-rich region is difficult to characterize. Because of the surface electron accumulation, almost all metal/InN contacts exhibit Ohmic behavior. The surface electron accumulation has implications for achieving and assessing p-type doping in InN and its potential device applications.

The observed electron accumulation at the surface of n-type InN is due to the presence of positively charged donor-type surface state. Due to CNL of InN laying below CBM, as explained in section 1.3.2, the surface CBM is laying at a much lower position below the CNL at the surface and thus the surface states have a strong tendency to be donors. The calculation of WZ InN band structure reveals that the  $\Gamma$ -point CBM of the surface is much lower than the overall conduction band [28]. A band bending of 0.56 eV is reported for a InN film with surface state density of  $2.5 \times 10^{13}$ cm<sup>-2</sup> [31]. In such case, the surface Fermi level is found to be pinned close



Figure 1.9: Surface and bulk density of states for InN with (a) polar surface orientation (b) nonpolar surface orientation (Reprinted figure with permission from C. G. Van de Walle and D. Segev, (2007) *J.Appl.Phys.* **101**, 081704. Copyright 2007 by the American Institute of Physics).

to but below the CNL [31]. It is also found that the band bending decreases as bulk free electron concentration increases [28]. Recent calculations of the density of state (DOS) of InN explained the origin of the surface states and band bending [32]. Fig.1.9 shows the density of state for the stable surface structures found for moderate In/N ratios on the In polar c-plane and nonpolar m-plane of InN. It is seen that two sets of states occur for the polar (0001) and nonpolar (1100) InN surfaces. For the polar (0001) surface both the In-In occupied states and the In dangling bond related states occur above the CBM. This is a direct consequence from the InN band structure and its large electron affinity. The presence of the occupied surface states above the CBM provides an immediate explianation for the electron accumulation at the surface of the InN. Because the number of surface states is much larger than the number of available bulk states in the near-surface accumulation layer, the surface Fermi-level position is approximately determined by the position of the upper portion of the occupied surface states.

For the m-plane surface at moderate In/N ratio (see Fig.1.9 b), the occupied N-dangling bond surface states are close to the VBM. Similar results are also obtained for the a-plane surface. Therefore the theory predicts that at moderate In/N ratio, electron accumulation should not be present at the non-polar surfaces. However the presence of electron accumulation at the nonpolar and semipolar surfaces of InN has been inferred from



Figure 1.10: Band gap energies of  $In_x Al_{1-x}N$  as a function of In content (x) estimated by using absorption Ref. [36] and ellipsometry Ref. [37] as well as the respective parabolic fits to the data.

X-ray photoemission spectroscopy (XPS), generalized infrared spectroscopic ellipsometry (GIRSE) and Raman scattering spectroscopy [33–35]. This can be attributed to growth under In-rich conditions, for which the nonpolar surfaces are predicted to show surface electron accumulation [32]. The surface electron accumulation is even found at the surface of ZB InN [34].

### 1.3.4 Band gap energies and electron accumulation in InAlN

The band gap energies of InAlN as function of In composition are still not conclusively established due to difficulties to grow high quality InAlN in the entire compositional range. Typically the bandgap energy of an alloy,  $A_x B_{1-x}C$ , is described as linear interpolation between the bandgap energies of the binaries and small deviation from from the linearity:  $E_g(A_x B_{1-x}C) = xE_g(AC) + (1-x)E_g(BC) - \delta(1-x)x$ , where  $\delta$  is refereed as bowing parameter. Recent works based on absorption and spectroscopic ellipsometry measurements show that the band gap bowing is  $4.7\pm0.4$  eV [36] and  $5.36\pm0.36$  eV [37], respectively (see Fig. 1.10)

High resolution X-ray photoemission spectroscopy (XPS) was used to investigate the presence of electron accumulation in InAlN [38]. Fig. 1.11 shows the surface and bulk Fermi levels for undoped InAlN films with different compositions relative to the CNL and band edges. For InN, the surface Fermi level lies significantly above the bulk Fermi level (see Fig. 1.11), which results in strong surface electron accumulation. Similar to InN, significant surface electron accumulation in  $In_xAl_{1-x}N$  with In content larger than 0.6. The bulk Fermi level and surface Fermi level are virtually coincident for  $In_{0.59}Al_{0.41}N$ , which indicates that there is almost no electron accumulation.



Figure 1.11: Surface and bulk Fermi level for undoped InAlN relative to the CNL and band edges (Reprinted figure with permission from P. D. C. King *etal*, (2008) *Appl.Phys.Lett.* **92**, 172105. Copyright 2008 by the American Institute of Physics).

The samples become insulating with further increase of Al. As a consequence, the bulk Fermi level could not be detected by single—field Hall effect measurements (see Fig.1.11). This is due to the fact that both the CNL and Fermi level move closer toward the middle of the direct bandgap as the Al concentration increases.

### 1.4 Growth

Among the III-nitrides, InN is the most difficult to be grown. The cation-to-anion bond energy of InN is 1.93 eV, which is much weaker than the corresponding energy of AlN (2.88 eV) and GaN (2.2 eV) [39]. As a consequence, in comparison to GaN and AlN, InN has much lower dissociation temperature. In addition, the equilibrium vapor pressure of N<sub>2</sub> over InN is extremely high. Therefore, for a long time, researchers experienced difficulties in obtaining high-quality InN, which impeded the investigation of its fundamental properties. The fabrication of high quality InN films is also hindered by the lack of native substrates. The lattice and thermal mismatches with the most commonly used commercial substrates, such as SiC, sapphire, Si and GaN, exceed 10%. In recent years a significant improvement in the growth of InN has been achieved [40–43]. The best InN up to date is grown by MBE and has room temperature electron mobility and bulk electron concentration of 3570 cm<sup>2</sup>/Vs and  $1.5 \times 10^{17}$  cm<sup>-3</sup>, respectively [43].

In MBE growth, a nitrogen flux activated by different means (microwave resonance or radio-frequency plasmas) and atomic In form InN at the substrate, which is kept at elevated temperature. The growth is controlled by kinetics of the surface processes: adsorption, migration and dissociation, incorporation of atoms into the crystal lattice and thermal desorption. Controling of the V/III ratio was found to be by far the most important issue in order to obtain high-quality MBE InN [44]. It is known that



Figure 1.12: Growth structure diagrams, In flux vs. substrate temperature, for typical plasma-assisted MBE growth of (a) In-face InN (Reprinted figure with permission from C. S. Gallinat *etal*, (2007) *J.Appl.Phys.* **102**, 063907. Copyright 2007 by the American Institute of Physics) and (b) N-face InN (Reprinted figure with permission from G. Koblumüller *etal*, (2007) *J.Appl.Phys.* **101**, 083516. Copyright 2007 by the American Institute of Physics).

growth at cation-rich conditions could enhance migration of the cations [45]. High-quality GaN can be grown under slightly Ga-rich conditions. However, it is difficult for In to be evaporated from the surface if the In vapor pressure is higher than the equivalent nitrogen pressure [45]. Consequently, In droplets will form. Throughout the growth process, nitrogen pressure should be held slightly higher than the thermo-equilibrium pressure [45]. Growth temperature also plays an important role for the growth of high quality In N. Due to the low dissociation temperature and high equilibrium  $N_2$  vapor pressure over InN, the growth should be performed at low temperatures about or below  $500^{\circ}$ C [46]. On the other hand a low growth temperature can not guarantee high migration of In [46] and the growth proceeds via the formation of three-dimensional islands [47, 48]. Besides, high defect densities and high unintentional impurity concentrations are also reported for InN films grown at low temperatures [49, 50]. The thermal stability of InN varies with polarity, different growth temperatures and III/V ratios are required to grow good quality InN with N and In polarities [45].

Fig.1.12 shows growth structure diagrams for typical plasma-assisted MBE process of (a) In-face [51] and (b) N-face InN [52]. Under different growth conditions (growth temperature and In/N ratio at constant N flux 7.3 nm/min), two kinds of growth surfaces are observed for In-polar InN: In droplet on top of adlayer structure and no adlayer terminated surface (dry) (see Fig. 1.12 a). For N-polar InN, there are three different growth regions (see Fig. 1.12 b): In droplets on top of adlayer, dry and In adlayer. In order to achieve good quality InN, the growth should proceed at the

border between In droplet + adlayer and dry growth regions for In-polar InN (see Fig. 1.12 a). On the other hand, for N-polar InN the growth should proceed in the In-adlayer region (see Fig. 1.12 b). In comparison with N-polar, In-polar InN requires lower growth temperature due to increased thermal decomposition. At slightly In-rich conditions, In-polar InN shows a significant reduction in growth rate at 470°C and over 500°C there is no growth. Consequently the growth window is very narrow. For N-polar InN, the growth rate reduces significantly when the growth temperature is below 570°C and over 635°C there is no growth. Besides, the selection of substrate, the use of buffer layers and nitridation of the substrate also have effects on the polarity and quality of InN [45].

In metal organic vapor phase epitaxy (MOVPE), a chemical reaction, which involves pyrolysis of trimethyl-In and ammonia  $(NH_3)$  on a heated substrate is used to grow InN. In this case the growth process is controlled by diffusion in the crystallizing phase surrounding the substrate. The metalorganics have relatively high vapor pressures, which allows their transport to the substrate using a carrier gas  $(N_2 \text{ or } N_2 + H_2)$ . MOVPE is well established growth technique in industry, however MOVPE growth of InN is challenging. The growth requires low temperature to decrease the decomposition of InN, but high temperature is needed to crack NH<sub>3</sub>. To solve this issue laser assisted activation of ammonia molecules or nitrogen plasma have been used. The electrical properties of state-of-the-art MOVPE InN are not as good as those of MBE InN films [43, 53]. This is partly attributed to the low dissociation rate of ammonia at the typical InN growth temperatures [54]. Moreover, avoiding hydrogen contamination from ammonia  $(NH_3)$  and trimethylindium  $([CH_4]_3In)$  is still a big challenge for MOVPE InN. The lowest free electron concentration and the highest room temperature electron mobility for MOVPE InN, up to date, are  $1 \times 10^{18}$  cm<sup>-3</sup> and 1180 cm<sup>2</sup>/Vs, respectively [55, 56].

Due to high miscibility gap between InN and AlN binaries, early theoretical calculations predicted high mixing instability and strong spinodal decomposition of InAlN materials [57]. Phase separation and a columnar microstructure in InAlN induced by lateral composition modulation was reported for MBE InAlN films [58–61]. On the other hand InAlN grown by MOVPE exhibits excellent composition uniformity for layers thinner than 100 nm [62–64]. In order to reduce the difference in the growth temperatures between the two binaries, N—polar growth of InAN is pursued [45]. Recently, good quality InAlN have been achieved also by MBE [60,65].

# Chapter 2

# Defects and doping in InN

InN, as a semiconductor with a very narrow bandgap, is sensitive to the presence of defects and impurities. InN can be doped readily by native defects and impurities and shows n-type conductivity. Defects and impurities in InN can greatly affect free carrier properties and consequently have strong effects on the efficiency of recombination, transport and luminescence. Achieving and characterizing p-type doping and control of n-type conductivity have now become major challenges in the field of InN and related materials.

As described in section 1.3.1, InN has a strong propensity for n-type doping due to its unique band structure. Impurities, such as interstitial hydrogen, substitutional hydrogen on N-site, oxygen on N-site and silicon on In-site as well as native point defects, such as nitrogen vacancies are thought to be responsible for the unintentional n-type conductivity. Those unintentionally present donors in InN may compensate intentionally introduced p-type dopants, such as Mg.

### 2.1 Point defects

#### 2.1.1 Donors

Hydrogen is a common impurity in semiconductors. In most semiconductors, hydrogen is found as an interstitial impurity: it behave as a donor in p-type semiconductors and in n-type semiconductors it acts as an acceptor. Hydrogen in those semiconductors improve significantly the electronic properties, since hydrogen passivates intrinsic defects and other impurities. However, in InN, interstitial hydrogen,  $H_i^+$ , is a donor [66].  $H_i^+$  in InN can break N-In chemical bond by strongly bonding to nitrogen.  $H_i^+$  is also found to be a fast diffuser, which can be mobile at relatively modest temperature [66]. Hydrogen can also occupy a nitrogen site and form a substitutional hydrogen in the 2+ charge state,  $H_N^{2+}$  [66]. As a donor, hydrogen can be easily incorporated into InN as grown by the common methods, MBE and MOVPE. *ab initio* calculation reveals that the formation energy of  $H_i^+$  and  $H_N^{2+}$  in InN is smaller than the formation energies of native point defects (see Fig.2.2 a) [66,67]. The



Figure 2.1: Bulk electron concentration,  $N_b$  vs bulk H concentration,  $H_b$  (Reprinted figure with permission from V. Darakchieva *etal*, (2010) *Appl.Phys.Lett.* **96**, 081907. Copyright 2010 by the American Institute of Physics).

experimental results also point out that hydrogen is ubiquitous phenomenon in InN grown by MBE [68, 69] and MOVPE [55]. Ref. [55, 68, 69] indicate that hydrogen plays a major role for the unintentional n-type doping in InN (see Fig.2.1). Similar to electrons in InN, H is also found to be accumulated at the surface [69]. A significant decrease of H concentration is found for InN samples after annealing in nitrogen atmosphere [55, 70]. The decrease of H concentration was associated with a significant increase of electron mobility and the decrease of bulk electron concentration [55, 70, 71]. Accumulation of H is also observed at m-plane and a-plane InN surfaces [70,72].

Other than H, oxygen and silicon are two common donors in InN. In InN, O occupies the N site,  $O_N^+$  and Si is expected to occupy the cation site,  $Si_{In}^+$ . Theoretical calculations indicate that the formation energies of  $O_N^+$  and  $Si_{In}^+$  are also much smaller than the formation energies of native point defects (see Fig.2.2 b) [67]. This indicate that InN is easily contaminated by extrinsic dopants.

In N has six possible native point defects: vacancies,  $V_N$  and  $V_{In}$ ; interstitial,  $N_i$  and  $In_i$ ; and antisites,  $N_{In}$  and  $In_N$ . Theoretical calculations predicted that  $V_N$ ,  $In_i$  and  $In_N$  have relatively low formation energies and due to the high formation energy, the contributions from  $N_i$ ,  $N_{In}$  and  $V_{In}$  to the free carrier concentration are neglectable [67]. In p-type InN, when the Fermi level approaches 0.1 eV the charge state of  $V_N$  changes from + to 3+, implying that in p-type InN  $V_N$  will efficiently compensate the free holes. Experimental re-



Figure 2.2: Calculated formation energies as a function of Fermi level for (a)  $H_i^+$  and  $H_N^{2+}$  (Reprinted figure with permission from A. Janotti and C. G. Van de Walle. (2008) *Appl.Phys.Lett.* **92**, 032104. Copyright 2008 by the American Institute of Physics); (b)O\_N^+, Si\_{In}^+ and  $Mg_{In}^-$  (Reprinted figure with permission from X. M. Duan and C. Stampfl, (2009) *Phys.Rev.B* **79**, 035207. Copyright 2009 by the American Physical Society).  $V_N^+$  is shown as comparison.

sults [68, 69, 73] indicate that impurities rather than native defects associated with dislocations are responsible for the unintentional n-type conductivity. However more work needs be done to clarify this issue.

#### 2.1.2 Acceptors

In InN, substitutional Mg, substitutional C and  $V_{In}$  act as acceptors. Mg occupies In site with the lowest formation energy of 1.84 eV in n-type In-polar InN (see Fig.2.2 b) [26]. The calculated ionization energy of Mg<sub>In</sub> is 0.12 eV (p-type), which is in good agreement with the experimental value of 0.1 eV [26]. C<sub>N</sub>, has the smallest formation energy of 3.17 eV under In-rich conditions and 4.33 eV under N-rich conditions [26]. The formation energy of C<sub>N</sub> acceptor is higher than the formation energy of Mg<sub>In</sub>. This is similar to the behavior of Mg and C in GaN [74]. The high formation energy of V<sub>In</sub> leads to low V<sub>In</sub> concentrations, wich was experimentally observed for <sup>4</sup>He<sup>+</sup> irradiated InN films [75].

#### 2.1.3 p-type doped InN

Due to the unique band structure of InN, p-type doping is difficult to be either achieved or demonstrated. The presence of a inversion layer at the surface blocks the assessment of p-type region beneath the surface electron accumulation layer. One could not obtain the properties of the bulk InN film by using single-field Hall effect measurements. However, alternative methods, including electrolyte capacitance-voltage measurement [76], thermopower [77], InN-layer thickness-dependent Hall effect-measurements [78], variable magnetic field Hall effect measurement [79] and IR spectroscopic ellipsometry [80] have been successfully applied to characterize the buried p-type layer. Much effort have been directed towards achieving p-typeconductivity on InN [81,82]. The only successful p-type conductivity in InN was achieved by Mg-doping with Mg concentrations, [Mg], ranging from  $1 \times 10^{18}$  cm<sup>-3</sup> to  $3 \times 10^{19}$  cm<sup>-3</sup> [81,82]. The *p*-type window of Mg doped InN is explained by the necessity to overcome the high density of unintentional introduced donors, such as H, O and native defects on the lower end and the increasing defect concentration on the upper end. In Ga-polar GaN it has been reported that polarity inversion takes place once [Mg] exceeds certain threshold, which hinders further incorporation of Mg [83–85]. Similar polarity inversion was also found recently for Mg doped In-polar InN [86]. The authors examined the polarities of a series of Mg doped InN samples with different doping concentrations from  $10^{16}$  to  $10^{21}$  cm<sup>-3</sup> in order to estimate the critical [Mg] value for the polarity inversion. Different chemical etching behaviors of In- and N-polar InN were used to identify the film polarities. In-polarity was identified for samples with [Mg] below  $5.6 \times 10^{18}$  cm<sup>-3</sup> and N-polarity for samples with [Mg] over  $1.6 \times 10^{19}$  cm<sup>-3</sup>. Therefore the authors concluded that the critical [Mg] value for the nucleation of inversion domains (IDs) from In polarity to N polarity in InN is about  $1 \times 10^{19}$  cm<sup>-3</sup>. These results were also confirmed by TEM cross section images showing that high density V-shaped IDs nucleate in Mg-doped In-polarity InN sample at [Mg] of about  $1 \times 10^{19}$  cm<sup>-3</sup> [86].

### 2.2 Extended defects

#### 2.2.1 Threading dislocations

For III—nitride heteroepitaxial layers, dislocations can be divided into two groups: misfit dislocations and threading dislocations. Misfit dislocations are caused by the differences in the lattice parameters between epitaxial layer and substrate. This type of dislocations are confined to the interface between the epitaxial layer and substrate. Threading dislocations (TD) originate at the interface with the substrate and propagate through the layer reaching the sample surface. There are three types of threading dislocations in c—plane WZ InN: edge type dislocations (a–type) with Burger's vector  $b_a=1/3\langle 11\bar{2}0\rangle$ , screw type (c–type) with  $b_c=[0001]$  and mixed type (a+c–type) with  $b_{a+c}=1/3\langle 11\bar{2}3\rangle$ . Because screw—related type dislocations tend to bend and annihilate, edge—type dislocations are dominant in InN with a typical density of  $10^{10}$  cm<sup>-2</sup>. The effect of dislocations on the free electron concentration in InN is debated. Models, derived on the basis of single field Hall effect measurements favor  $V_N^+$  associated with dislocations as the major origin of free electrons in InN [87,88]. In these works, the decrease in free electron con-

Dislocation type	b	Bounds
Frank-Shockley partial	$1/6\langle 2\bar{2}03\rangle$	I <sub>1</sub>
Shockley partial	$1/3\langle 1\overline{1}00\rangle$	$I_2$
Frank partial	$1/2\langle 0001\rangle$	E
Pure(a-)type	$1/3\langle 11\bar{2}0\rangle$	none
$\operatorname{Pure}(a+c-)$ type	$1/3\langle 11\bar{2}3\rangle$	none
$\operatorname{Pure}(c-)$ type	$1/6\langle 2\bar{2}03\rangle$	none
Stair-rod	$1/6\langle 10\overline{1}0\rangle$	BSFs/PSFs
-	$1/6\langle 3\bar{2}\bar{1}0\rangle$	-

Table 2.1: Summary of useful data on dislocations found in nonpolar and semipolar III-nitride films.  $\boldsymbol{b}$  is the dislocation Burgers vector (after Ref. [91]).

centration with film thickness (measured for films with different thicknesses) is correlated with the decrease in density of dislocations (measured along the thickness of a single film [88] or with an anticipated experimental decrease of dislocation density [87]). However, no direct correlation between electron concentration and density of dislocations is reported. On the contrary, several works have shown that no such correlation can be found [68, 69, 89]. Recent density functional theory (DFT) modified pseudopotential calculations show that all cores (4-, 5/7- and 8- atom cores) modify the band structure of InN, in particular the low coordinated atoms in the 8-atom core dislocation [90]. A shallow fully occupied state near the VBM and an empty state in the conduction band are induced by the semiconducting 8-atom core dislocations. The authors also pointed out that the stoichiometric 4- and 5/7-cores can enhance the n-type conductivity in InN, since due to the In-In interactions, the Fermi level is pinned above the CBM even in the absence of an external dopant. This may explain the debate of the effect of dislocations on the free carrier concentration from experimental works. Different types of cores in In *n* can act or not as donors. It is possible that depending on the growth conditions different types of dislocation cores are formed and thus different dependencies of the free-electron concentration on the dislocation density are observed in experiments. More work is required to clarify this issue. On the other hand, consensus has been reached that dislocations have strong effect on the mobility of free electrons. It was reported by several research groups that the increase in edge type dislocations leads to decrease in free electron mobility [73].

Additionally, defect densities in heteroepitaxial non-polar and semipolar films are much higher than in c-plane films and conventional defect-reduction techniques are less successful. Whereas c-plane III-nitride films usually contain pure edge, mixed or screw threading dislocations, nonpolar and semipolar films contain additional defects, as summarized in table 2.1

#### 2.2.2 Stacking faults

Stacking faults (SF) represent one or two layer interruption in the stacking sequence. There are five types (three intrinsic faults, the extrinsic and the prismatic) of stacking faults that can be found in WZ III-nitrides layers. The stacking order of WZ III-nitrides is 'ABABAB...' along the [0001] direction (see section 1.2). Intrinsic faults  $I_1$  and  $I_2$  have stacking order of '...ABABCBCBC...' and '...ABABCACAC...', respectively, are the result from joining two different stacking sequences.  $I_1$  and  $I_2$  are bounded by the Frank-Shockley partials of  $b=1/6\langle 2\bar{2}03\rangle$  and  $b=1/3\langle 1\bar{1}00\rangle$ , respectively. I<sub>3</sub> with stacking order of '...ABABCBABA...' originates in an isolated stacking error. Extrinsic faults (E) is formed by the insertion of an atomic plane with a stacking sequence of '...ABABCABAB...' and is bounded by Frank partials of b=1/2(0001). Heteroepitaxial nonpolar GaN typically contains high densities of basal-plane stacking faults, about  $10^5 \text{cm}^{-1}$  [92]. The corresponding value for a-plane InN is in the range from  $8 \times 10^5$  cm<sup>-1</sup> to  $1.5 \times 10^6$  cm<sup>-1</sup> [93] and for m-plane InN is about  $2 \times 10^5$  cm<sup>-1</sup> [94]. The stacking variation along [0001]/[111] direction suggests the possibility of polytypic superlattice or heterocrystalline structures. Due to the differences in the CBM and VBM between WZ InN and ZB InN, rectangular quantum wells are formed at the interface between WZ InN and ZB InN with the natural band discontinuities of  $\Delta E_c = 0.099 \text{ eV}$  and  $\Delta E_v = 0.069 \text{ eV}$  [95]. It is reported that cubic inclusions in hexagonal matrices confine free carriers and act as recombination centers, which can reduce the strength of the optical transitions [95].

## 2.3 Structural anisotropy in nonpolar and semipolar InN films

Group-III nitrides with nonpolar surfaces are intensively investigated over the last several years due to the possibility to avoid the strong internal electric fields in the active regions of optoelectronic devices and to improve their efficiency [96]. Despite the progress in growth optimization, there is still much room for improvement [97]. All the material properties of nonpolar nitride films appear more complicated and impose more challenges on the measurements and analyses. The extended defect densities in nonpolar III nitride films are significantly higher compared to c-plane grown material. In particular, stacking faults are of the order of  $10^5 \text{ cm}^{-2} - 10^6 \text{ cm}^{-2}$ . In addition, the strain in a-plane GaN was shown to have anisotropic character [98]. Further the full with at half maximum (FWHM) of the on-axis rocking curve of nonpolar GaN was also found to be anisotropic [6]. Namely, the  $(11\overline{2}0)$  $\omega$  rocking curves (RC) is found to be strongly dependent on the azimuth angle with respect to the scattering plane having either "M" - or "W"-shape dependence on the azimuth angle. This anisotropic behavior of the RC FWHM in nonpolar GaN was attributed to the combined or sole effect of anisotropic distribution of dislocations [6,99], tilt [99] wafer bending [100],


Figure 2.3: FWHM of the on-axis RC for a-plane InN film - (11 $\overline{2}0$ ) and m-plane InN - (1 $\overline{1}00$ ) as function of the azimuth angle between the plane of incidence and the projection of the InN [0001] axis ( $\phi$ =0 corresponds to direction parallel to the projection of the InN [0001]. After Ref. [109].

and stacking faults [92, 101]. Surface roughness was also shown to affect the RC broadening [92] and therefore may further contribute to the observed anisotropy [102]. While the structural anisotropy of nonpolar GaN films have been extensively studied [6, 96, 98–101, 103, 104] the information on the structural characteristics of nonpolar InN is very scarce [105, 106] and detailed studies were first reported only for films grown on GaN substrates [107, 108]. However, the nonpolar GaN substrates are not only extremely expensive but also have a limited supply. The heteroepitaxy on foreign substrates is still the practical way to get large scale InN and related alloys and device heterostructures at low cost. Recently, we have reported the first experimental study on the structural anisotropy of a-, m- and semipolar (1011) plane InN grown on r-plane sapphire and (100)  $\gamma$ -LiAlO<sub>2</sub>. We found that the RC FWHM of a-plane InN grown on r-plane (1102) sapphire exhibits "M" shape with minima parallel to [0001] direction and maxima parallel to  $[1\overline{1}00]$  direction (see Fig.2.3) [109]. The structural analysis (see for details 4.1) indicated that the geometrical size of the crystallites and Frank-Shoklev-type partial dislocations are responsible for the observed anisotropy. On the other hand, it was concluded that surface roughness and film curvature do not play a role in this case [109]. It was also shown that the degree of the structural anisotropy and its magnitude can be minimized by combing higher nitridation temperature and higher growth temperature [109]. m-plane InN grown on (100)  $\gamma$ -LiAlO<sub>2</sub> was found to exhibit "W" shape RC anisotropy with maxima for the [0001] direction and minima for the perpendicular direction (see Fig.2.3) [109].

In this case it was concluded that lateral coherence length is the dominant factor causing the RC anisotropy, while the tilt plays a minor role [109].

Additionally, different types of substrate also affect nonpolar InN quality. Important finding was that the basal plane stacking faults densities in the nonpolar-InN films grown on r-plane sapphire or  $\gamma$ -LiAlO<sub>2</sub> are lower than the respective densities in films grown on GaN free-standing substrates [94,109]. In semipolar (1011) InN the on-axis rocking curve was found to have "W" shape behavior [109]. However, in contrast to nonpolar InN, the semipolar film grows as two (1011) domains, rotated with respect to each other by 90° [109]. The two domains are suggested to nucleated on ZB InN (111)A and (111)B faces with In(0001)-polarity or N(0001)polarity, respectively [109].

## Chapter 3

# Strain, elastic properties and piezoelectric polarization in InN and InAlN

#### 3.1 Strain and stress

Due to the lack of native substrates, group—III nitrides are typically grown on foreing substrates resulting in built—in strain in the films. Strain has a profound effect on materials fundamental properties as it may change the crystal symmetry and the electronic band structure. For instance, the optical, polarization and vibrational properties of heteroepitaxial thin films and heterostrucures are affected by the unintentional strain present in such systems. Often, strain is intentionally introduced in semiconductor thin films in order to modify the device performance, e.g., in laser diodes and light—emitting diodes or to create new functionalities, e.g., generation of two dimensional electron gas (2DEG) in high electron mobility transistors (HEMTs) and large in—plane optial polarization anisotropy for data storage devices, sensors, and biophotonics.

In linear elasticity theory the relation between the stress  $\sigma$  and strain  $\epsilon$  tensors in films with wurtzite crystal structure is given by:

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2(C_{11} - C_{12}) \end{pmatrix} \cdot \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ 2\epsilon_{yz} \\ 2\epsilon_{xy} \end{pmatrix},$$

$$(3.1)$$

where  $C_{ij}$  are the elastic stiffness constants and the x-,y-, and z-axes are chosen along the [11 $\overline{2}0$ ], [1 $\overline{1}00$ ] and [0001] directions, respectively. The strains along the main crystallographic directions can be experimentally determined

by:

$$\epsilon_{xx} = \frac{a - a_0}{a_0}, \ \epsilon_{yy} = \frac{m - m_0}{m_0}, \ \epsilon_{zz} = \frac{c - c_0}{c_0},$$
 (3.2)

where  $a_0$  and  $c_0$  are the strain-free lattice parameters, a and c are the measured lattice parameters, and  $m_0 = \sqrt{3}a_0$ .

Sapphire and SiC are among the most often used substrates to grow group-III nitrides, and typically growth is realized on the basal (0001) c-plane of the substrates (see Fig.1.4). In all these instances the nitride films grow along the [0001] direction. The six-fold symmetry of the basal planes of the WZ (nitrides, SiC) and rhombohedral (sapphire) crystal structures dictates their isotropy in the basal plane and hence the thermal expansion coefficients, piezoelectric and elastic properties should be the same for any direction within the c-plane. As a consequence the films grown on c-plane substrates experience isotropic biaxial in-plane strain. Recently, there has been a strong research interest in growing III-nitrides with nonpolar and semipolar orientations (with the c-plane inclined with respect to sample surface) in order to avoid or minimize the effects of the polarization fields in device heterostructures and enable efficient green and white light emitting diodes [110]. To enable nonpolar and semipolar growth substrate surfaces different from the conventional c-plane are typically employed (see Fig.1.4). Whenever growth is realized on non-c-plane oriented sapphire and SiC surfaces the nitride films will be under anisotropic biaxial strain (independently of the film orientation) as a consequence of the anisotropy of the growth surfaces. For instance, a-plane III-nitrides films grown on r-plane sapphire are expected to experience anisotropic strain in the basal plane because of the difference in thermal expansion coefficients between substrate and film, and the different lattice mismatches along the two main in-plane directions [98].

Biaxial stress is described by vanishing stress along the growth direction of epitaxial films. This is because their surfaces are free to expand or contract. In other words,  $\sigma_{zz} = 0$ ,  $\sigma_{xx} = 0$ , and  $\sigma_{yy} = 0$  for films with c-, a-, and m-plane surface orientations, respectively. It follows then from Eq. 3.1 that the strain along the growth direction can be expressed by the two in-plane strain components. For c-plane films, it has the following form:

$$\epsilon_{zz} = -\frac{C_{13}}{C_{33}}(\epsilon_{xx} + \epsilon_{yy}). \tag{3.3}$$

Since in this case the in-plane strain is isotropic  $\epsilon_{xx} = \epsilon_{yy}$ , the out-of-plane strain can be expressed as

$$\epsilon_{zz} = -R^B_{c-plane}\epsilon_{xx},\tag{3.4}$$

with  $R^B_{c-plane} = 2 \frac{C_{13}}{C_{33}}$  being the biaxial relaxation coefficient.

For nonpolar a- and m-plane III-nitride films, the strain in the basal plane is no longer isotropic  $\epsilon_{xx} \neq \epsilon_{yy}$  and the out-of plane strains are related

to the in-plane components via:

$$\epsilon_{xx} = -R^B_{nonpolar} \begin{pmatrix} \epsilon_{yy} \\ \epsilon_{zz} \end{pmatrix}$$
(3.5)

and

$$\epsilon_{yy} = -R^B_{nonpolar} \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{zz} \end{pmatrix}, \qquad (3.6)$$

for the a- and m-plane, respectively, with a biaxial coefficient, which has a vector form due to the anisotropy of the in-plane strain:

$$R_{a-plane}^{B} = R_{m-plane}^{B} = R_{nonpolar}^{B} = \begin{pmatrix} C_{12}/C_{11} \\ C_{13}/C_{11} \end{pmatrix}.$$
 (3.7)

In the case of arbitrary surface orientation, inclined by an angle  $\theta$  the strain-stress relationships is given by [111]:

$$A_z \epsilon_{zz} = A_x \epsilon_{xx} + A_y \epsilon_{yy}, \tag{3.8}$$

where

$$A_x = C_{12} - C_{13} - (C_{12} + C_{13})\cos 2\theta,$$
  

$$A_y = C_{11} - C_{13} - (C_{11} + C_{13})\cos 2\theta,$$
  

$$A_z = C_{33} - C_{13} + (C_{13} + C_{33})\cos 2\theta$$

are the biaxial relaxation coefficients.

In addition to biaxial stress, uniaxial or hydrostatic stress may be also present in III nitride films. For example, hydrostatic strain is introduced by impurities in III-nitrides,  $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} \neq 0$  [112, 113]. Uniaxial stress is described by vanishing stress in the basal plane and the force along the growth direction of epitaxial films. For c-plane epitaxial films, under uniaxial stress along the growth direction  $\sigma_{xx} = \sigma_{yy} = 0$  and  $\sigma_{zz} \neq 0$ . Then from Eq. 3.1, the relationship between strains is  $\epsilon_{xx} = -\nu\epsilon_{zz}$ , where  $\nu$  is the Poisson ratio,

$$\nu = \frac{C_{13}}{C_{11} + C_{12}} \tag{3.9}$$

In the case of hydrostatic stress, all stress components are nonzero, namely  $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} \neq 0.$ 

#### 3.2 Lattice parameters

The WZ structure is described by two lattice parameters a and c (see Fig.1.2 in section 1.2). The experimental and calculated strain free lattice parameters  $a_0$  and  $c_0$  of InN and AlN are listed in table 3.1. The calculated lattice parameters of InN and AlN, by using generalized gradient approximation (GGA)

Table 3.1: Strain free lattice parameters  $a_0$  and  $ac_0$  of InN and AlN, and the respective deviations from Vegard's rule.

-	a [Å]		c [Å]				
InN	$3.53774^{a}$	$3.589^{c}$	$5.7037^{a}$	$5.793^{c}$			
AlN	$3.113^{b}$	$3.131^{c}$	$4.9816^{b}$	$5.012^{c}$			
δ	$0.0412 \pm 0$	$0.0039^{c}$	$-0.060 \pm$	$0.0039^{c}$			
<sup>a</sup> experimental Ref. [118]							
<sup><math>b</math></sup> experimental Ref. [119]							
$^{c}ab$ initio Ref. [114]							

for the exchange-correlation potential, are larger than the experimental values. The GGA overestimation of the lattice parameters is 0.6% (1.5%) for AlN (InN), which lies in the typical (0%-3%) range. In early studies, linear variation (Vegard's rule) from one binary to the other in lattice parameters a and c was used to describe the strain free lattice parameters of  $\ln_x Al_{1-x}N$ , namely  $\xi(x) = x\xi^{InN} + (1-x)\xi^{AlN}, \xi = a, c$ . The linear variation of lattice parameters was also assumed in the estimation of In composition, x. However, small deviations (see table 3.1) from Vegard's rule in lattice parameters a and c obtained from ab initio calculation have been recently reported [114]. It was also shown that by using the deviation values, a more accurate In composition can be achieved from X-ray diffraction measured lattice parameters of  $\ln_x Al_{1-x}N$  [114]. Indications that the lattice parameters of InAlN may deviate from Vegard's rule are also obtained experimentally [115–117]

In an epitaxial film, the in-plane relaxation, R, is defined as  $R=100(a_s - a)/(a_s - a_0)\%$ , where  $a_s$  is the in-plane lattice parameter of the substrate. For pseudomorphic growth, R=0 or  $a=a_s$  and for R=100% the layer is totally relaxed as its lattice parameter is equal to the strain-free value  $a=a_0$ . On the other hand, size effect caused by impurities or native defects as well as deformation-potential effect related to free-carrier concentrations can also affect the lattice parameters. However, comparing the changes caused by different factors, impurities play a minor role in the variation of the lattice parameters. For example, according to our ab initio calculations,  $Mg_{In}^-$  in InN has a size effect of  $-1.12 \times 10^{-24}$  cm<sup>3</sup> [120]. A Mg concentration of  $10^{21}$  cm<sup>-3</sup> would change the lattice parameters with 0.001 Å. In other words very large concentrations are needed to produce effect on the lattice parameters detectable by X-ray diffraction measurements.

#### 3.3 Stiffness constants

Studying the effect of strain on the fundamental material properties requires the knowledge of elastic constants, which describe the response to an applied

-	<i>ab</i> initio calculation				experiment
-	GGA		LDA		-
$C_{11}$	$197^{a}$	-	$229^{c}$	$233.8^{d}$	$225(7)^{e}$
$C_{12}$	$93^a$	-	$116^{c}$	$110.0^{d}$	$109(8)^{e}$
$C_{13}$	$76^a$	$70^{b}$	$97^{c}$	$91^{d}$	$108(8)^{e}$
$C_{33}$	$201^a$	$205^{b}$	$238^{c}$	$238.3^{d}$	$265(3)^{e}$
$C_{44}$	$48^a$	-	$50^c$	$55.4^{d}$	$55(3)^{e}$

Table 3.2: Stiffness constants of InN in GPa.

 $^{a}$ Ref. [111]

 $^{b}$ Ref. [124]

<sup>c</sup>Ref. [121]

 $^{d}$ Ref. [122]

 $^{e}$ Ref. [125]

macroscopic stress (see Eq. 3.1). Similar to the lattice parameters, the stiffness constants,  $C_{ii}$ , of  $In_x Al_{1-x}N$  were assumed to vary linearly with composition. In early study the experimental and calculated stiffness constants of InN and AlN are listed in table 3.2 and 3.3, respectively. Recent *ab* initio calculations show that the  $C_{ii}$  of InAlN do not vary linearly with composition [111, 121]. The calculated stiffness constants of InAlN and the respective deviations from Vegard's rule in  $C_{ij}$  are listed in table 3.4. Our GGA stiffness constants based on 128-atom-supercell [111] are lower than the LDA results [121, 122] (see table 3.4). In general, LDA is overbinding, which results in higher elastic constants. One the other hand, 128-atom-supercell provides not only a more realistic description of a random alloy, but also ensures a more accurate prediction of the elastic constants [123] compared to the calculations based on 32-atom-supercell [121] or unit cell [122]. It has been shown that the elastic constants of nitride alloys obtained from supercell calculations can depend on both the size and the atomic configuration of the cell [123]. The dependence becomes weaker with increased supercell size and accordingly, larger supercells ensure more solid results and a better convergence.

Our analysis on the effect of the deviations on alloy composition shows that a more accurate composition could be achieved by using the deviations from Vegard's rule in the stiffness constants and in lattice parameters [111]. If  $[1\overline{100}]$  and [0001] are used to extract alloy composition the deviations from Vegard's rule need to be accounted for [111].

#### 3.4 Piezoelectric polarization

Wurtzite is the structure with the highest symmetry compatible with the existence of spontaneous polarization and the piezoelectric tensor has three independent nonvanishing components. Therefore, polarization in III nitride

-	<i>ab</i> initio calculation				experiment
-	GC	GGA LDA		DA	-
$C_{11}$	$376^{a}$	-	$397^{c}$	$410.0^{d}$	396 <sup>e</sup>
$C_{12}$	$126^{a}$	-	$145^{c}$	$142.4^{d}$	$137^{e}$
$C_{13}$	$98^a$	$94^{b}$	$115^{c}$	$110.1^{d}$	$108^{e}$
$C_{33}$	$356^a$	$377^{b}$	$371^{c}$	$385.0^{d}$	$373^{e}$
$C_{44}$	$116^a$	-	$115^c$	$122.9^{d}$	116 <sup>e</sup>

Table 3.3: Stiffness constants of AlN in GPa.

<sup>a</sup>Ref. [111] <sup>b</sup>Ref. [124] <sup>c</sup>Ref. [121]

 $^{d}$ Ref. [122]

 $^{e}$ Ref. [126]

Table 3.4: Calculated stiffness constants of InAlN alloys for different In composition and respective deviations from Vegard's rule.

-	C <sub>11</sub>	$C_{12}$	$C_{13}$	$C_{33}$	$C_{44}$
$GGA^a$	98.6	22.7	-4.4	6.3	47.3
$LDA^{b}$	80	8.7	-3	25	35

<sup>a</sup>Ref. [111] <sup>b</sup>Ref. [121]

materials will have both a spontaneous and a piezoelectric component. Fig.3.1 shows the bonds between In and N atoms and the polarization vector,  $P_0$ . The electron cloud is closer to the N atoms and the direction of  $P_0$  is parallel to the electric field from the cation to N. In the ideal tetrahedron, both in-plane and vertical components of the polarization are zero, since the four bonds are equal. However, the nonideality of the internal parameter u in WZ III–nitides results in nonzero vertical components of polarization in the tetrahedron. As a result, due to the lack of inversion symmetry, the III–nitides crystal exhibit a large macroscopic polarization along the [0001] crystal direction. The degree of non–ideality of the the c/a ratio or u governs the strength of the spontaneous polarization is zero, due to its equal cation–anion bonds.

The spontaneous polarization is given by

$$\vec{P}_{sp} = \frac{p_{sp}}{\varepsilon_0 \varepsilon} \vec{z} \tag{3.10}$$



Figure 3.1: Ball-and-stck configuration of wurtzite InN with polarization  $P_0$ and net polarization  $\Delta P_0$ .

Table 3.5: Spontaneous polarization coefficients and piezoelectric polarization coefficients in C m<sup>-2</sup> for InN and AlN as well as the corresponding deviations from Vegard's rule.

-	$p_{sp}$	$e_{31}$	$e_{33}$	$e_{15}$
InN	$-0.042^{a}$	$-0.49^{b}$	$0.73^{b}$	$-0.40^{b}$
AlN	$-0.090^{a}$	$-0.58^{b}$	$1.55^{b}$	$-0.48^{b}$
deviations	$0.071^{c}$	-	-	-

<sup>a</sup>Ref. [128] <sup>b</sup>Ref. [129] <sup>c</sup>Ref. [127]

where  $p_{sp}$  is the spontaneous polarization coefficient,  $\varepsilon_0$  is the electrostatic dielectric constant,  $\varepsilon$  is the dielectric constant of the material and  $\vec{z}$  is the unit vector along the [0001] direction. As the surface orientation change from c-plane to nonpolar plane, the spontaneous polarization decreases from  $p_{sp}/(\varepsilon_0\varepsilon)$  to 0. The value of  $p_{sp}$  of InN and AlN are listed in Table 3.5. A nonlinear variation of  $p_{sp}$  with In composition is reported from theoretical calculations [127]. The nonlinear variation of  $p_{sp}$  of InAlN is attributed to a microscopic hydrostatic stress in the alloy caused by the lattice mismatch between InN and AlN as well as bond alternation, which arise from the atomic size mismatch [127].

When strain is applied, the corresponding change of u results in an extra polarization, termed piezoelectric polarization. The piezoelectric polarization,



Figure 3.2: Schematic of WZ crystal structure with an arbitrary surface orientation.

 $P_{pz}$ , for WZ III-nitride is defined as

$$\begin{pmatrix} P_{pz}^{x} \\ P_{pz}^{y} \\ P_{pz}^{z} \\ P_{pz}^{z} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ \epsilon_{yz} \\ \epsilon_{xz} \\ \epsilon_{xy} \end{pmatrix}$$
(3.11)

where  $e_{ij}$  and  $\epsilon_{ij}$  are piezoelectric polarization coefficient and strains, respectively. The piezoelectric polarization coefficients of InN and AlN are listed in Table 3.5. The piezoelectric polarization for c-plane III-nitride film is

$$P_{pz} = 2e_{31}\epsilon_{xx} + e_{33}\epsilon_{zz}$$
  
=  $2\epsilon_{xx}(e_{31} + e_{33}\frac{C_{13}}{C_{33}})$  (3.12)

This is in normal coordinate system. The piezoelectric polarization along the growth direction, z', for WZ III–nitride with arbitrary surface orientation is

$$P_{pz}^{z'} = \sin\theta e_{15}\epsilon_{yz} + \cos\theta e_{31}(\epsilon_{xx} + \epsilon_{yy}) + \cos\theta e_{33}\epsilon_{zz}$$
(3.13)

where  $\theta$  is the angle of inclination between the surface plane and the *c*-axis (see Fig.3.2).

Very recently, we have reported that apart from the nonpolar surfaces (a-plane or m-plane), InAlN with  $(10\overline{1}2)$  and  $(11\overline{2}3)$  surface orientations exhibit vanishingly small piezoelectric polarization for all compositions [111]. Bernardini *et al* pointed that the Vegard's rule fails to reproduce the piezoelectric polarization of InAlN although the piezoelectric coefficients were linearly dependent on composition [127]. Nonlinear piezoelectric constants of the pure binary compounds on the strain state [127].

## Chapter 4

# Characterization and theoretical calculation techniques

#### 4.1 X-ray diffraction

As a versatile and non-destructive analytical method, X-ray diffraction (XRD) has been widely employed in characterization of structure, texture and composition of different samples – from epitaxial films to powder and liquids. X-rays are electromagnetic waves with wavelength in the range from 0.01 nm to 10 nm or energy in the range from 0.125 keV to 125 keV. X-ray photons can be scattered by electrons in the material elastically or inelastically. Elastic scattering occurs when photons collide with inner tightly bound electrons, which is the most important effect for X-ray diffraction. In the process of elastic or coherent scattering, there is no energy transfer, thus, the X-ray photon energy remains constant. When X-rays impinge on periodic structures with geometrical variations on the length scale of their wavelength, such as crystal lattice, constructive interference could be observed, which gives information about the reciprocal lattice of the structures. The reciprocal space is the Fourier transform of the electron density distribution. Since the source electrons are localized at the atomic core, the obtained pattern is directly related to the lattice structure of the sample.

The scattering vector is the difference between the incident wave vector,  $\vec{k_i}$ , and the scattered wave vector,  $\vec{k_s}$ , with  $\vec{q} = \vec{k_s} - \vec{k_i}$ . Constructive interference occurs when the scattering vector,  $\vec{q}$ , is equal to a vector of the reciprocal lattice,  $\vec{q} = \vec{G}$ , namely  $\vec{G} = \vec{k_s} - \vec{k_i}$ . Fig.4.1 demonstrates the relationship between  $\vec{G}$ ,  $\vec{k_s}$  and  $\vec{k_i}$ . A sphere centered at the beginning of the incoming wave vector  $\vec{k_i}$ , with a radius of the length of wave vectors,  $1/\lambda$ , in reciprocal space is termed Ewald's sphere. The sphere represents all possible diffraction vectors having the same magnitude and origin from  $\vec{k_i}$ . In Fig.4.1, the reciprocal lattice points intersected with Ewald sphere give possible ends of  $\vec{k_s}$  when  $\vec{G} = \vec{k_s} - \vec{k_i}$  is satisfied. Since the orientation of the reciprocal and the real lattice are fixed,  $\vec{k_i}$  and  $\vec{k_s}$  can be defined by the incident angle,  $\omega$ , and the scattering angle,  $2\theta$  (see Fig.4.1). The two angles,  $\omega$  and  $2\theta$ , are defined by the relative position of the X-ray source, the sample and the detector. Knowing



Figure 4.1: X-ray diffraction visualized by the Ewald construction.

these values, the lattice spacings,  $d_{hkl}$ , of the diffracting family of lattice planes (hkl) can therefore be obtained:

$$|\vec{q}| = \frac{1}{d_{hkl}} = \frac{2\sin\theta}{\lambda} \tag{4.1}$$

 $\vec{q}$  can be an integral multiple of the shortest possible reciprocal lattice vector  $\vec{q} = n\vec{q_0}$ , thus, the lattice spacing d can be obtained from Bragg's equation:

$$|n\vec{q_0}| = \frac{n}{d} = \frac{2\sin\theta}{\lambda} \tag{4.2}$$

Bragg's equation describeds the dependence of the scattering angle  $2\theta$  on the lattice spacing d along the particular direction.

#### 4.1.1 Measurement modes and experimental procedures

The XRD experiments reported in the thesis have been performed by different types of diffractometers in low-resolution (LR) and high-resolution (HR) modes. These include the X'pert MRD from Philips, Empyrean from PAN-alytical and D8 discovery form Bruker. In the first case a parabolic graded mirror and a two-bounce hybrid monochromator were set at the primary side and a channel cut analyzer is used on the secondary side, which offers a resolution of about 0.004°. The schematic view of this type of diffractometers is shown in Fig.4.2.

The X-rays are generated by bombarding Cu target with a focused electron beam. Four main components with  $K_{\beta}$ ,  $K_{\alpha 1}$ ,  $K_{\alpha 2}$  and continuous spectrum are emitted from the target. After the monochromator, the  $K_{\beta}$ component of the generated X-rays is completely suppressed, the remaining beam is monochromatic composed mainly of  $K_{\alpha 1}$  ( $\lambda = 1.54059$  Å) the  $K_{\alpha 2}$ 



Figure 4.2: Schematic of a high–resolution diffractometer. The different scan angles are indicated.

radiation being suppressed to less than 0.1 %. The divergence slit commonly used after the monochromator was the  $1/8^{\circ}$  fixed slit which produced a beam of 12 ×0.3 mm<sup>2</sup> vertically divergent and horizontally parallel beam. Comparing with other optics, such as the Ge four-crystal (220) monochromator, the multilayer mirror and the two-bounce hybrid monochromator set-up offers much higher intensity while the resolution is maintained relatively high. In LR mode, similar set-up is used on the primary side but on the secondary side a position sensitive detector and no monochromator are used. This allows the collection of all signals diffracted from the sample.

Fig.4.2 also shows the possible scan axes. The five typical scans that can be used are  $\omega$ -scan,  $2\theta$ -scan,  $2\theta - \omega$  scan,  $\phi$ -scan and  $\chi$ -scan. The angle  $2\theta$  refers to the angle between the incident and diffraction beams, while  $\phi$  is the azimuth angle, which describes the rotation of the sample around the axis normal to the samples surface.  $\chi$  is the tilt angle, which describes the tilt of the sample with respect to the surface and  $\omega$  is the angle of incidence.  $2\theta - \omega$ scan is often used for determining the lattice parameters of a sample. During the measurement, the sample is rotated by  $\omega$  and the detector is rotated by  $2\theta$ with an angular ratio of 1:2. As a result, the scan change the magnitude of the scattering vector, but the direction of the scattering vector remains the same (see Fig.4.3). For  $2\theta - \omega$  scans, the resulting diffractions have the x-axis in units of  $2\theta$ . The symmetric  $2\theta - \omega$  scan with the x-axis in units of  $\theta$  is also called  $\theta - 2\theta$  scan, as the offset of the incident angle is zero, namely  $\omega = \theta$ . The reciprocal space points obtained from symmetric  $2\theta - \omega$  scan are in the vertical line of reciprocal space (see Fig.4.3).  $\omega$  scan is also called rocking curve since the sample is rocked around the  $\omega$  axis. During the  $\omega$  scan measurement, the  $2\theta$  axis and often the magnitude of the scattering vector,  $\vec{q}$ , are fixed while the direction of  $\vec{q}$  is changed (see Fig. 4.3).

#### 4.1.2 Data analysis

#### Lattice parameters and composition

For wurtzite structure, the lattice space,  $d_{hkl}$ , of a plane with Miller indexes



Figure 4.3: Schematic representation of the reciprocal lattice points and different scans.

 $\{hkl\}$  can be expressed as

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + k^2 + hk}{a^2}\right) + \frac{1}{c^2}$$
(4.3)

where a and c are the lattice parameters [130]. In a typical procedure of lattice parameter determination for c-plane nitrides,  $d_{00l}$  and  $d_{h0l}/d_{0kl}$  should be measured. The *c*-lattice parameter can be directly determined form  $d_{00l}$ . The *a*-lattice parameter can be deduced from either  $d_{h0l}$  or  $d_{0kl}$  and the measured c-lattice parameter. The  $d_{00l}$  is determined from  $2\theta - \omega$  diffractograms detected for the Bragg's symmetrical set-up. In order to improve the accuracy of the lattice parameters determination, we typically measured the symmetric peaks at six different azimuth angles, rotated by 60° with respect to each other. Then we obtained an average value of the c-lattice parameter. The a-lattice parameter is determined in an analogous way. We measured the asymmetric (105) reflection at six different azimuth angles. Then we calculated the value of the a lattice parameter with Eq.4.1 using the average c lattice parameter and  $d_{105}$ . Since the magnitude of the scattering vector along  $q_x$  and  $q_z$  is directly related to the lattice parameters a and c, respectively (see Fig.4.2), the lattice parameters can also be deduced from the asymmetric reciprocal space maps [131]

$$c = l \frac{2\pi}{q_z} \tag{4.4}$$

and

$$a = \frac{2\pi}{q_x} \sqrt{\frac{4}{3}(h^2 + k^2 + hk)}$$
(4.5)

The measured lattice parameters of ternary alloys can be used to estimate the alloy composition. Usually, validity of Vegard's rule is assumed, i.e., the *relaxed* lattice parameters of the ternary are assumed to follow linear relationship (Vegard's rule) with the relaxed lattice parameters of the respective binaries. However, often the lattice parameters of III nitride alloys deviate from Vegard's rule. Recently, we have shown by *ab initio* calculations that the  $\ln_x Al_{1-x}N$  lattice parameters slightly deviate from Vegard's rule [114]. Although small, these deviations are important to account for in order to determine the alloy composition correctly. Since the lattice parameters of alloy epitaxial films are functions of both the alloy composition and strain in the films, these two contributions must be separated. This is realized by taking into account the fact that epitaxial films are under biaxial strain. In the case of *c*-plane InAlN films for example, the composition is determined from:

$$\frac{c_{In_xAl_{1-x}N} - c_0(x)}{c_0(x)} = -\frac{2C_{13}(x)}{C_{33}(x)} \times \frac{a_{In_xAl_{1-x}N} - a_0(x)}{a_0(x)},$$
(4.6)

where  $c_{In_xAl_{1-x}N}$  and  $a_{In_xAl_{1-x}N}$  are the measured alloy lattice parameters,  $c_0$  and  $a_0$  are the relaxed parameters and  $C_{ij}$  are the alloy stiffness constants.

For a-plane InAlN the composition can be determined from:

$$\frac{a_{In_xAl_{1-x}N} - a_0(x)}{a_0(x)} = -\frac{2C_{12}(x)}{C_{11}(x)} \times \frac{m_{In_xAl_{1-x}N} - m_0(x)}{m_0(x)} -\frac{2C_{13}(x)}{C_{11}(x)} \times \frac{c_{In_xAl_{1-x}N} - c_0(x)}{c_0(x)}.$$
(4.7)

and for arbitrary surface oriented InAlN films Eq.3.8 can be used. For further details see Ref. [111].

#### Phase ratio

The integral intensity of a Bragg reflection is given by:

$$I_h = SCFm_h T_h L_p |F_h|^2 A_{\theta 2\theta}(t) \frac{V}{V_{uc}^2}, \qquad (4.8)$$

where SCF is a scaling factor related to the specific instrument settings (scan velocity, slit width etc.),  $m_h$  is the multiplicity of a Bragg reflection,  $T_h$  is the texture factor of  $h^{th}$  reflection,  $L_p$  is the Lorentz-polarization factor,  $F_h$  is the structure factor,  $A_{\theta 2\theta}(t)$  is the absorption factor, V is the irradiated crystal volume and  $V_u$  is the unit cell volume.  $m_h$  and  $T_h$  are 1 for single crystals.

The Lorentz-polarization factor,  $L_p$  is expressed as

$$L_p = (1 + \cos^2 2\theta) / \sin^2 \theta \tag{4.9}$$

and the absorption factor,  $A_{\theta 2\theta}(t)$ , is given by

$$A_{\theta 2\theta} = 1 - \exp(\frac{-2\mu t}{\sin \theta}), \qquad (4.10)$$

where t is the film thickness,  $\mu = \rho \mu_m$  is the linear attenuation coefficient,  $\rho$ 

is the density,  $\mu_m$  is the absorption coefficient and  $\theta$  is the diffraction angle.

Let us consider a situation when the film consists of two polymorph domains,  $\alpha$  and  $\beta$ , each with a single crystal orientation h and k, respectively. The volume fraction of different polymorph domains can be obtained from the ratio of the integral intensities (see Eq.4.8) of the  $h^{th}$  reflection of polymorph  $\alpha$  and the  $k^{th}$  reflection of polymorph  $\beta$ 

$$\frac{V^{\alpha}}{V^{\beta}} = \frac{I^{\alpha}_{h}L^{\beta}_{p}|F^{\beta}_{k}|^{2}A^{\beta}_{\theta 2\theta}(t)(V^{\alpha}_{uc})^{2}}{I^{\beta}_{h}L^{\alpha}_{p}|F^{\alpha}_{h}|^{2}A^{\alpha}_{\theta 2\theta}(t)(V^{\beta}_{uc})^{2}}$$
(4.11)

and

$$\sum_{i} V^{i} = 100\% \tag{4.12}$$

#### Texture

The texture or the preferred orientation of a crystal can be estimated from pole figure measurements. Pole figures are described by the intensity function,  $I(\phi,\chi)$  in polar coordinate with radius of  $\chi$  and circular distance of  $\phi$ . In the thesis, pole figures are mainly used to identify the epitaxial relationships and the presence of different polytypes. The two axes  $\chi$  and  $\phi$  are restricted to  $0 \le \phi \le 360^{\circ}$  and  $0 \le \chi \le 90^{\circ}$ . The epitaxial relationship can be revealed by the orientation of epilayer and the substrate. Samples containing two (or more) polymorphs, such as ZB InN films with WZ InN inclusions, different phases can be identified via the appearance of Bragg's reflection from certain plane in  $2\theta - \omega$ . However, a simple  $2\theta - \omega$  scan along one azimuth direction could not reveal all the information. Therefore, pole figures should be performed to analyze the presence of different polymorphs in an epitaxial film [113, 132].

#### Mosaic structure

Due to the lack of native substrate, InN is usually grown on GaN-buffered sapphire or Si substrates. The lattice and thermal expansion coefficient mismatch between the film and the substrate results in strain in the epilavers. When a critical thickness is reached, dislocations starts to form at the interface between the film and the substrate in order to release the strain. Heteroepitaxial films with high densities of dislocations are often described by the mosaic block model schematically illustrated in Fig.4.4. Within this model, the layer is assumed to be composed of many crystallites, called mosaic blocks. The mosaic blocks are not perfectly aligned with each other. The out-of-plane rotation perpendicular to the surface normal is the mosaic tilt while the in-plane rotation around the surface normal is the mosaic twist (see Fig.4.4) [133] The density of dislocations with a Burger's vector component along [0001], i.e., screw and mixed type of dislocations in c-plane oriented III-nitride films is related to the tilt. The density of edge type dislocations are related to the twist.

Since mosaic blocks are misoriented with each other, X-rays can only be coherently scattered in a single mosaic block. As a result, the dimensions



Figure 4.4: Illustration of the mosaic block model. The individual islands are twisted and tilted, therefore edge, mixed and screw type threading dislocations form in the layer.  $d_{lat}$  and  $d_{vert}$  are denoted the lateral and vertical coherence lengths, respectively.

of a single block are called vertical and lateral coherence lengths, where the terms vertical and lateral are referred to directions perpendicular and parallel to the surface, respectively (see Fig.4.4). To obtain the four characteristic parameters of a mosaic layer structure: tilt, twist, vertical and lateral coherence lengths, the influence of the mosaicity on the reciprocal lattice points, i.e. the distribution of the scattered intensity in reciprocal space, has to be investigated. An infinite crystal lattice with a perfect three—dimensional periodicity corresponds to  $\delta$ —like reciprocal space points. In contrast, for real heteroepitaxial layers, reciprocal lattice points are rather broad and with an elliptical shape. Fig.4.5 illustrate the broadening in the reciprocal space points due to lateral coherence length, vertical coherence length, twist and tilt.

A misorientation tilt of the mosaic blocks is associated with a reciprocal lattice point broadening perpendicular to the reciprocal lattice vector of the corresponding reflection. In this case, the broadening increases with the length of the reciprocal lattice vector (see Fig.4.5 (d)) [133]. In contrast, a finite lateral coherence length leads to a reciprocal space point broadening in the  $(q_x, q_y)$  plane, which is independent of the reflection order (see Fig.4.5 (a)). Hence the symmetric diffraction peaks, which correspond to reciprocal space points on the  $q_z$  axis are used, to derive the tilt and the lateral coherence length. A useful method to separate the contributions of tilt and lateral coherence length is the Williamson-Hall plot, a plot of the FWHM of the rocking curve as a function of the reflection order  $(\sin \theta)/\lambda$ . Using reciprocal lattice unit, FWHM is expressed by the term  $(\beta \omega \sin \theta)/\lambda$ , where  $\beta \omega$  is

the FWHM in angular units, and  $\theta$  and  $\lambda$  are the scattering angle and the wavelength of the X-rays [134]. The tilt is then obtained from the slope of the plot and the lateral coherence length is derived from the inverse of the value of intersection with y axis.

The broadening of the reciprocal lattice points due to the twist lies in the (qx, qy) plane (see Fig.4.5 (b)). Therefore, the derivation of the twist requires a so-called in-plane measurement. The measurement requires that an X-ray beam impinges the sample surface at an incident angle close to the critical angle, which is difficult to be achieved. Instead, we followed the method suggested by Shrikant *et al* [135]. This included measurement of the FWHM of th (002), (103), (102), (101) and (302) diffraction peaks with the inclination angles of 0°, 31.86°, 42.99°, 61.79° and 70.32°, respectively. The following model is fit to the FWHM as a function of the inclination angle in order to obtain the twist [135]:

$$W(result) = \{ [W_{eff}^{twist}[\Gamma_0]]^n + [W_{eff}^{tilt}[\Gamma_0]]^n \}^{\frac{1}{n}}$$

$$W_{eff}^{twist}[\Gamma_0] = W_0^{twist}[\Gamma_0] \exp(-m\frac{W_{eff}^{tilt}[\Gamma_0]}{W_0^{tilt}[\Gamma_0]})$$

$$W_{eff}^{tilt}[\Gamma_0] = W_0^{tilt}[\Gamma_0] \exp(-m\frac{W_{eff}^{twist}[\Gamma_0]}{W_0^{twist}[\Gamma_0]})$$

$$W_0^{twist}[\Gamma_0] = \cos^{-1}[\cos^2(\Gamma_0)\cos(W_y) + \sin^2(\Gamma_0)]$$

$$W_{eff}^{tilt}[\Gamma_0] = \cos^{-1}[\sin^2(\Gamma_0)\cos(W_z) + \cos^2(\Gamma_0)]$$

where  $\Gamma_0$  is the angle of inclination,  $W_y$  and  $W_z$  are the FWHM of the distribution perpendicular and parallel to the surface, n is a constant between 1 and 2, m is a parameter between -1 and 1, and  $W_0^{tilt}[0]$  and  $W_0^{twist}[90]$  are the tilt and twist angle, respectively.

A limited vertical coherence length is related to a reciprocal lattice point broadening along the  $q_z$  direction (see Fig.4.5(c)). The vertical coherence length is commonly related to the thickness of the layer for single crystalline layer. From the inverse of the value of y intersection, the vertical coherence length can be estimated. In addition, the heterogeneous strain along c axis can be obtained directly from the slope of Hall–Williamsion plot [134].

Dislocations lead to distortion of the crystal lattice. The dislocation is often described by Burger's vector, which represents the magnitude and direction of the lattice distortion of dislocation in a crystal lattice. Different types of dislocation have impact on different families of planes. Fig.4.6 shows the effect of screw, mixed and edge types of dislocations on FWHMs of different crystal planes. Screw type dislocations that have Burger's vector along < 0001 > distort the periodicity of the lattice along out-of-plane < 0001 > direction. Edge type dislocations introduce in-plane distortion to the lattice along  $1/3 < 11\overline{2}0$  >. The density of screw type dislocations can be obtained from the tilt



Figure 4.5: Broadening of the reciprocal lattice points due to (a) lateral coherence length, (b) twist, (c) vertical coherence length and (d) tilt. (a) and (b) show top-views and (c) and (d) show side-views. Gray ellipses show reciprocal lattice points and white structures show schematically real-space structures.



Figure 4.6: Influences of pure-screw, mixed and pure-edge type dislocations on RC widths of different families of lattice planes.

using the equation [134]:

$$N_{scw} = \frac{tilt^2}{4.35c^2}$$

Similarly the density of edge dislocation can be derived from the twist by using the equation:

$$N_{ed} = \frac{twist^2}{4.35a^2}$$

### 4.2 Transmission electron microscopy and focussed ion beam

#### Transmission electron microscopy

Transmission electron microscopy (TEM) is a powerful technique and has been used to investigate the microstructure of materials. In TEM, a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. Like X-ray diffraction, in crystalline samples the superposition of all individual electron waves scattered by the atoms leads to interference effects. Accordingly, an image and electron diffraction patterns are formed behind the specimen in back focal plane and image plane of objective lens, respectively. Using an aperture in this image plane, the reflections can be selected and a lattice image can be generated. The bright-field image can be obtained when the direct beam is used. While diffracted beams is selected for observing dark-field. The images are sensitive to non-isotropic distortions of the lattice. Since dislocations can cause a local distortion of the crystal lattice, TEM images are usually used to investigate the density of dislocations. The lattice planes are bent around the dislocation, resembling a variation of the diffraction conditions across the specimen. To observe the dislocation, the specimen should be tilted so that the bent planes around the dislocation fulfill the Bragg condition. Since the contrast in the image is caused by this selected family of lattice planes and the diffracting planes are not precisely at the position of the dislocation, the contrast in the image is slightly changed with respect to the real position. The projection of diffraction pattern and the image can be switched by changing the projection of the object plane or image plane. Fig.4.7 shows the formation of diffraction pattern and image. The electron diffraction also fulfill Bragg's rule as well as the Ewald sphere, and the technique is usually used to study material structure. The wavelength of electrons accelerated in TEM is much smaller than the wavelength of X-rays. Therefore the scattering angles in electron diffraction are much smaller than the corresponding angles for X-rays, which means that the radius of the Ewald sphere is much larger in electron diffraction than in Xray diffraction. As a result, electron diffraction will reveals the structure of material by two dimensional distribution of reciprocal lattice points. Different structures or polytypes can be identified by the distribution of the reciprocal lattice points. Another benefit of electron diffraction is that the area of interest can be simply selected by the selected area aperture and selected area electron diffraction (SAED) could be obtained. The high-resolution TEM reveals the crystallographic structure of a sample at atomic scale. In the high-resolution mode, the images and diffraction patterns can be transferred to each other by fast Fourier transform. The process is usually applied to identify the stacking faults or the mixture of different phases. Additionally, the inelastic scattering of the electrons from the specimen can generate X-rays, which can be used to analyze the chemical phases of the material. On the other hand, the change of the direction of the elastically scattered electrons depend on the mass of the nuclei. As a consequence, the mass-dependent contrast in the obtained image can be used to distinguish different alloys or materials.

#### Focussed ion beam

Samples for high—resolution TEM measurement should be thinner than 100 nm. The electron beam can not be transmitted through a sample thicker than 100 nm. Therefore, the sample should be thinned to electron transparency before the TEM measurement. Ion milling, crushing and focussed ion beam are commonly used methods for TEM sample preparation. The samples for TEM measurement in the thesis are prepared by focussed ion beam (FIB). The benefit of the technique is the area and directions can be carefully selected when the sample is prepared by FIB. In addition, in FIB preparation only a tiny part of the sample is cut while the rest is preserved. The certain orientation of the sample should be identified by XRD texture measurement before preparing with FIB. During the sample preparation, progressively ion beam currents from 2 nA to 50 pA with typically 30 kV are used to mill away materials from the desired area which is protected by a 1  $\mu$ m thick Pt strip. The thickness of the final specimen could typically reach <100 nm. The disadvantage of the technique is that it may damage the sample surface.



Figure 4.7: The formation of image and diffraction pattern in TEM.

#### 4.3 Atomic Force microscopy

Atomic force microscopy (AFM) is a variation of scanning probe microscopy (SPM), with resolution on the nanometer scale. The main application of AFM is to measure surface topography. The most attracting feature of AFM is that it can work in ambient air environment, while most of the electron microscopes work in vacuum. The AFM uses the vibration of a cantilever with a sharp tip at its end. The tip scans over the surface in the near field, which means there is a very close distance between the tip and the surface. Thus only the top layer of tightly bound atoms can be detected. To obtain excellent resolution, sharp tip with radius of a few nanometer and very steep side wall is used. When the tip approaches the surface, Van der Waals forces between the tip and the sample lead to a deflection of the cantilever. The deflection is measured using a laser point reflected from the cantilever.

There are three modes of AFM that are mainly used: contact mode, noncontact mode and tapping mode. In these modes, to maintain constant force between tip and sample surface, the tip-sample spacing is adjusted. The distances that the tip travels at each point form the topographic image of the sample surface. The invention of tapping mode is a milestone for AFM. The technique allows high resolution topographic images of sample surface that are easily damaged. Tapping mode overcomes the problems of the contact and noncontact modes by alternately placing the tip in contact with the surface and then lifting the tip off the surface to move to next point with a high frequency. During the measurement, the cantilever oscillation amplitude is maintained constant by a feedback loop. The digital feedback loop then adjusts the tipsample spacing to maintain a constant force between the sample and tip. The oscillation amplitude of tapping mode is large enough to prevent the adhesion between the tip and the sample.

#### 4.4 Infrared spectroscopic ellipsometry

Ellipsometry, in general, determines the complex ratio  $\rho$  of linearly independent electric field components of polarized electromagnetic plane waves. More specific, it measures the *change* of the polarization state of an electromagnetic plane wave upon interaction with a sample. Explicitly, ellipsometry determines the ratio:

$$\rho = \left(\frac{B_p}{B_s}\right) / \left(\frac{A_p}{A_s}\right),\tag{4.13}$$

where amplitudes A stand for incident and B for exciting waves. Traditionally, this ratio is measured in reflection or transmission for light polarized parallel (p), and perpendicular (s) to the plane of incidence [136]. The plane of incidence with the respective notations is defined in Fig. 4.8. The result of an ellipsometry measurement is usually presented by real-valued parameters  $\Psi$ and  $\Delta$ , where  $\tan \Psi$  is defined as the absolute value of the complex ratio, and  $\Delta$  denotes the relative phase change of the p and s components of the electric field vector [136].

#### 4.4.1 Standard ellipsometry

In the standard ellipsometry situation  $\Psi$  and  $\Delta$  do not depend on the polarization state of the incident plane waves, which are then defined as follows

$$\rho = \frac{r_p}{r_s} = \tan \Psi \exp\left(i\Delta\right). \tag{4.14}$$

Here  $r_p$  and  $r_s$  denote the *p*- and *s*-polarized complex reflection coefficients. This situation is realized when c-plane III-nitride films are grown on isotropic surfaces, such as (0001) sapphire and SiC, or Si.

#### 4.4.2 Generalized Ellipsometry

For optically anisotropic materials it is necessary to apply the generalized ellipsometry approach because coupling between the p (parallel to the plane of incidence) and s (perpendicular to the plane of incidence) polarized incident electromagnetic plane wave components occurs upon reflection off the sample surface. In the thesis, the optical axes of the corundum-structure sapphire and WZ structure InN sample constituents are optically anisotropic with uniaxial



Figure 4.8: Definition of the plane of incidence (p plane) and the incidence angle  $\Phi_a$  through the wave vectors of the incident and emerging (reflection set up) plane waves.  $A_p$ ,  $A_s$ ,  $B_p$ , and  $B_s$ , denote the complex amplitudes of the p and s modes before and after reflection, respectively. P and A are the azimuth angles of the linear polarizer used, e.g., in the standard arrangement of rotating-analyzer (polarizer) ellipsometer. P, or A are equal to zero if their preference directions are parallel to the p plane. (Both P and A rotate clockwise with respect to the light propagation.)

optical properties [33, 98, 131, 137]. In the generalized ellipsometry formalism, the interaction of electromagnetic plane waves with layered samples is described within the Jones or Müller matrix formalism. The Müller matrix renders the optical sample properties at a given angle of incidence and sample azimuth, and data measured must be analyzed through a best-match model calculation procedure. The sample azimuth is defined by a certain in-plane rotation with respect to the laboratory coordinate system's z axis, set by the sample surface (x - y plane) and the plane of incidence (x - z plane), with the z axis being parallel to the sample normal, and the coordinate origin at the sample surface. The sample azimuth angle is here defined as the angle between the projection of the sapphire c-axis onto the sample surface and the x-axis, which is the intersection of the plane of incidence with the sample surface. In the generalized ellipsometry situation the Stokes vector formalism, where real-valued matrix elements connect the Stokes parameters of the electromagnetic plane waves before and after sample interaction, is an appropriate choice for casting the ellipsometric measurement parameters. The Stokes vector components are defined by  $S_0 = I_p + I_s$ ,  $S_1 = I_p - I_s$ ,  $S_2 = I_{45} - I_{-45}$ ,  $S_3 = I_{\sigma+} - I_{\sigma-}$ , where  $I_p$ ,  $I_s, I_{45}, I_{-45}, I_{\sigma+}$ , and  $I_{\sigma-}$  denote the intensities for the p-, s-, +45°, -45°, right-, and left-handed circularly polarized light components, respectively [138]. The Müller matrix is defined by arranging incident and exiting Stokes vector into matrix form

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix}_{\text{output}} = \begin{pmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{12} & M_{22} & M_{23} & M_{24} \\ M_{13} & M_{32} & M_{33} & M_{34} \\ M_{14} & M_{42} & M_{43} & M_{44} \end{pmatrix} \begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix}_{\text{input}} .$$
(4.15)

This situation is realized when III-nitrides are grown on anisotropic surfaces such as non-c-plane oriented sapphire and SiC. Examples in this sense are nonpolar and semipolar nitride films grown on r-plane sapphire.

# 4.4.3 Ellipsometry model dielectric function and data analysis

Spectroscopic ellipsometry is an indirect method and requires a detailed model analysis in order to extract relevant physical parameters. Thus, a stratified layer model analysis using parameterized model dielectric function approaches is employed to analyze the ellipsometry data set. The ellipsometry data are analyzed using a stratified layer model including the sapphire substrate and the InN layer. The light propagation within the entire sample stack is calculated by applying a  $4\times4$  matrix algorithm for multilayer systems assuming plane parallel interfaces. In order to reduce parameter correlation data measured from the same sample obtained at multiple angles of incidence and multiple sample azimuth angles are analyzed simultaneously. A regression analysis (Levenberg-Marquardt algorithm) is performed, where the model parameters are varied until calculated and experimental data match as close as possible (best-match model). This is done by minimizing the mean square error ( $\chi^2$ ) function which is weighed to estimated experimental errors ( $\sigma$ ) determined by the instrument for each data point.

For necessary and convenient reduction of unknown parameters, analytical descriptions of the dielectric function components of each sample constituent (substrate, InN layer) are needed. In the thesis, samples grown on sapphire substrates have been investigated. So, typically in our analysis, the substrate material is considered ideally as single-crystalline and one tensor is sufficient to render the optical properties. The infrared optical properties and tensor description of sapphire follows that reported previously [139], and which were taken with no further changes.

At IR wavelengths there are two main contributions to the model dielectric function of the III-nitride materials: from polar phonons and from free-charge carriers. For wurtzite InN (or any other WZ III-nitride), which is an uniaxial material, the dielectric function tensor is diagonal, and its main values differ for polarizabilities parallel (||) and perpendicular ( $\perp$ ) to the lattice c-axis. For c-plane this tensor reads

$$\varepsilon_{\mathrm{WZ},(0001)} = diag\left(\varepsilon_{\perp}, \varepsilon_{\perp}, \varepsilon_{\parallel}\right), \qquad (4.16)$$

The wavelength dependence of the dielectric function in the spectral vicinity of a polar lattice resonance is commonly described by a harmonic Lorentzian oscillator, which may be represented in fractional decomposition form [140]:

$$\varepsilon = \varepsilon_{\infty} \frac{\omega_{\rm LOj}^2 - \omega^2 - i\omega\gamma_j}{\omega_{\rm TOj}^2 - \omega^2 - i\omega\gamma_j}.$$
(4.17)

The index "j" stands for the dielectric function parameters for polariz-

ability functions parallel (||) or perpendicular  $(\perp)$  to the lattice c-axis.

For zinc-blende InN (or any other ZB III–nitride), which is isotropic material, the dielectric function tensor is diagonal, and its main value is equal to the isotropic dielectric function,  $\varepsilon_{\text{ZB}}$ 

$$\varepsilon_{\rm ZB} = diag\left(\varepsilon_{\rm is}, \varepsilon_{\rm is}, \varepsilon_{\rm is}\right),$$
(4.18)

where *diag* indicates the diagonal matrix.

The wavelength dependence of the dielectric function due to polar vibrations is described by the same harmonic Lorentzian oscillator approach:

$$\varepsilon_{\rm is} = \varepsilon_{\infty} \frac{\omega_{\rm LO}^2 - \omega^2 - {\rm i}\omega\gamma}{\omega_{\rm TO}^2 - \omega^2 - {\rm i}\omega\gamma},\tag{4.19}$$

where  $\omega_{\rm TO}$ ,  $\omega_{\rm LO}$  and  $\gamma$  are transverse optical (TO), longitudinal optical (LO) frequencies, and broadening parameter, respectively, and  $\varepsilon_{\infty}$  is the high-frequency dielectric constant.

In addition to the contribution from polar phonons, the contribution from free-charge carriers to the InN model dielectric function need to be accounted for. The classical Drude equation holds sufficiently for description of the contribution to  $\varepsilon_{\rm Dr}$  due to free charge carriers [141, 142]

$$\varepsilon_{\rm FC} = -\frac{{\rm e}^2 N_{\rm s}}{\tilde{\varepsilon}_0 m_{\rm eff} \omega (\omega + {\rm i}\gamma_{\rm p})}.$$
(4.20)

where  $N_{\rm s}$ ,  $m_{\rm eff}$ , and  $\gamma_{\rm p}$  are the free-charge-carrier volume density, effective mass, and plasma broadening parameters, respectively ( $\tilde{\varepsilon}_0$  is the vacuum permittivity, and e is the amount of the electrical unit charge). The plasmon broadening parameter is related to the optical mobility parameter

$$\gamma_{\rm p} = \frac{e}{m_{\rm eff}\mu}.\tag{4.21}$$

For simplicity, the anisotropy of the WZ InN effective mass tensor is assumed small in this thesis. This assumption is based on the observation that the ellipsometry data analyzed and discussed did not provide sufficient sensitivity to differentiate between different effective mass parameters for polarization parallel and perpendicular to the InN c-axis. The resulting free charge carrier contribution is then rendered by an isotropic tensor

$$\varepsilon_{\rm Dr} = diag \left( \varepsilon_{\rm FC}, \varepsilon_{\rm FC}, \varepsilon_{\rm FC} \right),$$

$$(4.22)$$

In epitaxial films containing both the WZ and the ZB InN polymorph a concept for mixed-phase, multiple-domain, group-III nitride thin films needs to be implemented. We followed a linear averaging scheme, which was previously used to calculate the effective dielectric tensor properties of mixed-phase cubic and hexagonal boron nitride thin films at long wavelengths [143]. In this concept, each domain is represented by its individual tensor as it would occur if the entire layer would be homogeneously filled by that domain. Then, all tensors of all occurring domains are added by weighing factors representing their volume fraction. In this linear homogenization approach, the effective dielectric tensor is obtained as the sum of individual contributions and the common contribution caused by free charge carriers,  $\varepsilon_{\rm Dr}$ .

$$\varepsilon = \sum_{i} f_i \varepsilon_i + \varepsilon_{\rm Dr}, \qquad (4.23)$$

where the summation goes over the individual polymorph domains, *i*.

The volume fraction parameters must obey

$$1 = \sum_{i} f_i. \tag{4.24}$$

In principle the dielectric function and and thickness of all sample layers can be determined from an ellipsometry experiment by adjusting calculated data to measured data using the discussed parameterized model dielectric function. The standard model for analyzing SE data consists of a sequence of parallel layers with abrupt interfaces and specially homogeneous dielectric functions, bound between the semi-infinite substrate and the ambient. Then, a regression analysis, here using Levenberg-Marquardt fitting algorithm, is performed, where model parameters are varied until calculated and experimental data match as closely as possible. The minimization is realized by using the maximum likelihood approach [142, 144]. Fitting a parameterized model dielectric functions to experimental data, simultaneously for all spectral data points, provides a direct connection between measured data and physical parameters of interest.

#### 4.5 *ab*-initio calculations

Theoretical investigation of solids requires the solution of a many-body problem with macroscopic, Avogadro's number of interacting electrons. This complex, unsolvable problem can be reduced to a solvable one-electron problem, where each electron is moving in an effective potential caused by the other electrons. Density functional theory (DFT) is an exact method to make this reduction [145]. In DFT one uses the ground state electron density instead of the many-body wave function to express expectation value of physical quantities. In real applications, however, DFT requires approximations. The exchange and correlation between the electrons can not be mapped exactly to a single electron problem. The local density approximation (LDA) and the generalised gradient approximations [145]. Since LDA overbinds crystals GGA is applied in predicting crystal structures in good agreement with experiments [146]. Accordingly, GGA obtained elastic stiffness constants are expected close while the LDA derived values reasonably higher than experiments. It is proven that generally both LDA and GGA underestimates the band gap of semiconductors  $\left[146\right].$ 

### Chapter 5

# Summary of the results and contributions to the field

The thesis is focused on exploring some of the unknown properties and unsolved issues in the field of InN and  $In_xAl_{1-x}N$  materials. Spacial attention is paid to the elastic, structural and free-charge carrier properties and their interrelation.

#### $In_xAl_{1-x}N$

 $In_x Al_{1-x}N$  has found many applications from distributed Bragg reflectors to active layers in high-mobility field effect transistors. However, accurate determination of composition in  $In_x Al_{1-x}N$  remains an issue and many of its properties are still debated. We have reported for the first time a detailed study on the lattice parameters and stiffness constants of  $In_x Al_{1-x}N$  and discuss in detail their deviations from Vegard's rule, and effects on the determination of alloy composition (paper I, II and III). In paper I we also reported for the first time the piezoelectric polarization behavior for  $In_x Al_{1-x}N$  with arbitrary surface orientations, which is pseudomorphycally grown on GaN, and discussed the implications of the deviations from Vegard's rule in the lattice parameters and stiffness constants. The detailed discussions in **paper I** provide guidance to experimentalists on the appropriate approaches to estimate composition and piezoelectric polarization for  $In_x Al_{1-x}N$  with different compositions, surface orientations and degrees of strain. The derived stress-strain relationships for  $In_x Al_{1-x}N$  film with an arbitrary surface orientation are applicable to wurtzite group-III nitride and II-oxide epitaxial ternary alloys and can be used to extract composition in such films in different coordinate systems depending on the specific measurement and sample conditions.

#### Structural anisotropy in nonpolar, semipolar and mixedphase InN epitaxial films

There is strong research interest in growing III-nitride materials with nonpolar or semipolar surface orientations due to the possibility to avoid the detrimental effects of the polarization fields in polar device heterostructures. While nonpolar and semipolar GaN and  $\ln_x \operatorname{Ga}_{1-x} N$  have been extensively studied,

the information on InN was very scarce. We have reported the first study on the structural anisotropy of a-, m-, and  $(10\overline{1}1)$  plane oriented InN films grown on sapphire and  $\gamma$ -LiAlO<sub>2</sub> (**paper V**). We have discussed and concluded on the major sources of anisotropy in nonpolar and semipolar InN films and suggested strategy to reduce the anisotropy and minimize defect densities in a-plane InN films. We have found that a- and m- plane InN films have basal stacking fault densities similar or even lower compared to nonpolar InN grown on free-standing GaN substrates, indicating good prospects of heteroepitaxy on foreign substrates for the growth of InN-based devices. We have reported the first combined detailed study of structural and infrared optical properties of zinc-blende InN containing wurtzite InN inclusions (paper **IV**). Mixed-phase III-nitride films are commonly found due to the metastability of the zinc-blende structure, but researchers have largely overlooked this problem in InN. In **paper IV** we have developed appropriate methods based on X-ray diffraction and infrared spectroscopic ellipsometry to identify wurtizte and zinc-blende InN and quantify their phase ratio. We further provided important new information on the phonon, free-charge carrier and surface electron accumulation properties of zinc-blende and semipolar wurtzite InN.

# Effect of impurities and dopants on the structural and free-charge carrier properties of InN

All InN is unintentionally n-type doped and it exhibits the peculiar electron accumulation at its surface. Consequently, achieving and assessing p-type conductivity in InN are major challenges in the filed. We have presented evidence that contactless infrared spectroscopic ellipsometry can be successfully applied to prove p-type conductivity and study the properties of free holes in InN doped with Mg (**paper VI**). For the first time we present a detailed combined study on the effect of Mg doping on the lattice parameters, structural characteristics and free-charge carrier properties of InN epitaxial films (**paper VI**). Our findings are important step forward in controlling p-type conductivity in InN. We also have determined for the first time the effects of the most common impurities and dopants, H, O, Si and Mg, on the lattice parameters of InN by using *ab initio* calculations (**paper VII**). The reported size and deformation potential coefficients can be used to elucidate the origin of strains in InN epitaxial layers and the degree of electrically active impurities (**paper VII**).

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