Properties of InAlN/GaN Heterostructures Prepared by

Molecular Beam Epitaxy

by

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Duke University

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Jeffrey Glass

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Jie Liu

Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Electrical and Computer Engineering in the Graduate School of Duke University

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ABSTRACT

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Abstract

InAlN thin films and InAlN/GaN heterostructures have been intensively studied over recent years due to their applications in a variety of devices, including high electron mobility transistors (HEMTs). However, the quality of InAlN remains relatively poor with basic material and structural characteristics remain unclear.

Molecular beam epitaxy (MBE) is used to synthesize the materials for this research, as MBE is a widely used tool for semiconductor growth but has rarely been explored for InAlN growth. X-ray photoelectron spectroscopy (XPS) is used to determine the electronic and chemical characteristics of InAlN surfaces. This tool is used for the first time in application to MBE-grown InAlN and heterostructures for the characterization of surface oxides, the bare surface barrier height (BSBH), and valence band offsets (VBOs).

The surface properties of InAlN are studied in relation to surface oxide characteristics and formation. First, the native oxide compositions are studied. Then, methods enabling the effective removal of the native oxides are found. Finally, annealing is explored for the reliable growth of surface thermal oxides.

The bulk properties of InAlN films are studied. The unintentional compositional grading in InAlN during MBE growth is discovered and found to be affected by strain and relaxation. The optical characterization of InAlN using spectroscopy ellipsometry
(SE) is also developed and reveals that a two-phase InAlN model applies to MBE-grown InAlN due to its natural formation of a nanocolumnar microstructure. The insertion of an AlN interlayer is found to mitigate the formation of this microstructure and increases mobility of whole structure by fivefold.

Finally, the synthesis and characterization of InAlN/GaN HEMT device structures are explored. The density and energy distribution of surface states are studied with relationships to surface chemical composition and surface oxide. The determination of the VBOs of InAlN/GaN structures with different In compositions are discussed at last.
Dedication

To my beloved husband

To my lovely dad and mom
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<th>Description</th>
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<tbody>
<tr>
<td>2DEG</td>
<td>Two dimensional electron gas</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>BEP</td>
<td>Beam equivalent pressure</td>
</tr>
<tr>
<td>BOE</td>
<td>Buffered oxide etch</td>
</tr>
<tr>
<td>BSBH</td>
<td>Bare surface barrier height</td>
</tr>
<tr>
<td>CBO</td>
<td>Conduction band offset</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-width at half-maximum</td>
</tr>
<tr>
<td>HEMT</td>
<td>High electron mobility transistor</td>
</tr>
<tr>
<td>HRXRD</td>
<td>High resolution x-ray diffraction</td>
</tr>
<tr>
<td>HVPE</td>
<td>Hydride vapor phase epitaxy</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal-organic chemical vapor deposition</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>RSM</td>
<td>Reciprocal space mapping</td>
</tr>
<tr>
<td>RTA</td>
<td>Rapid thermal annealing</td>
</tr>
<tr>
<td>SE</td>
<td>Spectroscopic ellipsometry</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TOA</td>
<td>Take-off angle</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence band maximum</td>
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Acknowledgements

The process of last five years’ Ph.D. experience is not an easy one. I still remember several times I experienced self-doubt and got lost in the research. However, looking back, a lot of people helped me through these obstacles to reach this point. I am extremely thankful and want to express my deepest appreciations to these people.

Dr. April Brown, my research advisor, without whom I could not have this wonderful opportunity to study in such a wonderful research group. She is always very open-minded and supportive to all my research ideas and inspires me to explore all the possibilities. As a professor in Electrical and Computer Engineering, she owns a wide range of knowledge on physics, chemistry, and biology besides engineering. This always helps me think about my problem in a wider and more fundamental perspective. Moreover, she is always being very caring, warm, and passionate. I am still deeply attracted to her great personality.

Dr. Tong-Ho Kim, our group’s research scientist, who helped me grow a lot of MBE samples, taught me how to use MBE and helped me extensively in research. As a rigorous person, he is very strict with experimental skills for maintaining such an expensive and big machine. I learned a lot from his attitude towards research. His solid background in semiconductors and hands-on experiences helped me solve a lot of mysteries in my study. I still remember a lot of days we stayed in MBE room for
growths, which is normally a tiring and tedious process. However, he can always make it joyful by talking about everything he knew about MBE, semiconductors, his children, life experiences, and jokes. These are the most unforgettable days I have in Duke.

Dr. Maria Losurdo, senior scientist in CNR-NANOTEC, Istituto di Nanotecnologia and Chemistry Department, University of Bari, who taught me XPS fitting and SE modeling. These techniques require a lot of experiences and knowledge, her wide experiences in XPS and SE helped me so much with understanding and modeling my samples. We also collaborated happily and published several works.

Jincheng Li, my husband, who always encourages me when I am in doubt. He is supportive and inspires me to pursue my dreams. I am so happy to have him in my life.

My parents, always supportive to any decision I make.

There are more people I would like to thank, all my current lab mates, Wei Kong, Kristen Collar, and Jincheng Li. The former lab mates who helped me a lot, Congwen Yi, Yang Yang, Pae Wu.

Thank you all.
1. Introduction

In this chapter, a general overview of III-nitride materials development is given to illustrate the historical difficulties of nitride growth and to help motivate the study of ternary nitride InAlN. The two important characteristics which significantly impact material properties, strain and polarization, are then introduced. Strain as a key parameter, which greatly influences III-nitride composition, is later investigated in Chapter 5. Polarization is a crucial property of III-nitrides and significantly impacts InAlN/GaN high electron mobility transistor (HEMT) structure’s surface and band structures. These findings and analysis are discussed in detail in Chapter 7 and 8. Last, an introduction to the HEMT structure is presented to motivate our studies on the electronic properties of the InAlN/GaN heterostructure contained in Chapters 7 and 8.

1.1 III-nitride materials development

The III-nitride semiconducting materials AlN, GaN, InN, and their ternary InAlN, AlGaN, InGaN, and quaternary InAlGaN alloys have attracted great attention during the last two decades. The band gaps of the III-nitrides span the range from 0.65 eV to 6.2 eV [1], making them attractive for optical devices operating from the infrared (IR) to the ultraviolet (UV). Also, their direct band gaps enable efficient photon emission and absorption. Their wide band gaps (compared with 1.1 eV for silicon [2]) are ideal for power devices working at high temperatures and requiring high breakdown voltages.
Their unique properties are valuable for optical devices, such as blue and UV light-emitting diode (LED) [3] and laser diodes [4, 5], high-power, high-speed electrical devices such as Schottky diodes [6], metal oxide semiconductor field effect transistors (MOSFETs) [7], HEMTs [8, 9], and other advanced transistor types. These devices are used in various applications such as computing, automotive, military, aerospace, consumer electronics, medical, and so on. The global GaN semiconductor device market was valued at USD 379.82 million in 2012 and is expected to reach USD 2,203.73 million by 2019 [10] (Figure 1-1).

![Figure 1-1](image.png)

**Figure 1-1:** Global GaN semiconductor device market (USD million) analysis and prediction, showing a steady growth. Values taken from Ref. [10].

Among these, optoelectronics device is still the major market accounting for 96.6% of the whole GaN market [10]. However, the power devices sector is expected to
grow at the fastest rate in the near future due to growing needs of high power devices in the military and in 4G network base stations. Based on the expected growth of electric vehicles and hybrid electric vehicles, the analysis anticipates a compound annual growth rate of the power market of 80% from 2016 to 2020, reaching USD 600 million [11].

In 1938, GaN was first synthesized by Juza and Hahn [12]. Large-area GaN films were deposited on sapphire using chemical vapor deposition (CVD) by Maruska and Tietjen in 1969 [13]. The growth of GaN by metal-organic chemical vapor deposition (MOCVD) followed in 1971 [14]. Though several attempts to fabricate GaN-based devices were made during this time, such as blue GaN LED [15], electroluminescent diodes [16], and solar blind UV detectors [17], the quality of GaN was still unsatisfactory for devices. The first problem lies in its lattice-mismatch with available substrates. Common substrates for nitrides are sapphire, SiC, and bulk GaN. Sapphire is the least expensive but has the largest lattice mismatch (33% difference compared with GaN [18]). SiC has a smaller lattice-mismatch (-3.4% difference compared with GaN [19]) and better thermal properties, but is much more expensive. Bulk GaN is considered the best substrate candidate for nitride growth. However, a technique to grow high-quality bulk GaN for industrial production remains a challenge. Also, due to the extreme high-temperature and high-pressure conditions required for bulk nitride growth, the price of bulk GaN is even higher than that of SiC. Moreover, p-type doping proved to be another problem. The background electron concentration is as large as 1 to 4 x 10^{16} cm^{-3} [20] in
undoped GaN. These unintentional dopants come from impurities such as oxygen. Magnesium is the most commonly used p-type dopant in GaN but it possesses a large ionization energy of approximately 200 meV [21]. At room temperature only around 1% of the incorporated magnesium atoms are ionized.

A breakthrough was made in 1986 which was crucial to enabling the growth of device-quality GaN by Amano et al. using MOCVD [22]. Amano grew a thin layer (~5 μm) of AlN on a sapphire substrate at a low temperature of ~500 °C as a buffer/transition layer followed by a GaN film deposited at higher temperature. The material quality was dramatically improved. After that, a GaN buffer layer was introduced by Nakamura and later became an industry standard [23]. Another milestone was the successful p-type doping of GaN. In 1989, Amano discovered that by treating p-doped GaN with low-energy electron beam irradiation (LEEBI), the activation of the dopant was greatly improved [24]. Three years later, Nakamura introduced a thermal annealing process to activate Mg-doped GaN [25]. This success was based on the fact that due to the formation of Mg-H complexes during growth, MOCVD Mg-doped GaN must be annealed in order to achieve reasonable dopant activation.

After various improvements enabled the growth of the binary nitrides GaN and AlN, the ternary compounds began to attract attention. InGaN is used as the active layer in blue LEDs, which is now a billion-dollar industry [26]. InGaN is also a promising candidate for full-spectrum solar cells [27], as it covers the whole visible light spectral
range. AlGaN has proven to be successful as the barrier layer in AlGaN/GaN HEMTs [28]. InAlN is attracting attention more recently because of its lattice-match to GaN with an indium concentration of ~17-18% [29]. In addition, the InAlN/GaN heterostructure supports a large two dimensional electron gas (2DEG) density of approximately $2.6 \times 10^{13} \text{ cm}^{-2}$ as compared to that of the AlGaN/GaN system at approximately $1.0 \times 10^{13} \text{ cm}^{-2}$ [30].

Figure 1-2 shows the research record counts for different material systems during the last 40 years according to Web of Science statistics [31]. The plot shows that GaN was first studied and experienced a rapid increase during 1990-2000, followed by the studies of AlN, AlGaN, and InGaN. During the last decade or so, the study of these materials is almost saturated. On the other hand, InN and InAlN were less studied at the beginning of nitride history but began to attract more attention starting around 2000. Specifically, InAlN is the least studied material in all these material systems. Thus, in this thesis, the primary focus is InAlN and its related InAlN/GaN HEMT heterostructure. The surface and bulk characteristics of InAlN thin films together with the properties of InAlN/GaN heterostructures are studied in order to improve the understanding and performance of molecular beam epitaxy (MBE) grown InAlN/GaN HEMTs.
Figure 1-2: Record counts of nitride materials in research paper titles as a function of publication year. Raw statistics extracted from Ref. [31].

### 1.2 Material properties of III-nitride semiconductors

#### 1.2.1 Strain and stress

The lattice constants of the III-N materials system vary significantly with composition, with the in-plane lattice constants ranging from 3.1106 Å for AlN to 3.538 Å for InN [32] (Figure 1-3). The ternary materials InAlN and InGaN are normally grown on GaN template films on sapphire substrates. Therefore, we must consider the strain and stress accommodation and associated films relaxation in relation to the available substrates for III-N synthesis.
1.2.1.1 Strain

When the lattice constant of an epitaxial film is different from that of the substrate on which it is grown, the film will distort to minimize the overall system energy as shown in Figure 1-4. Strain describes the distortion of the epi-layer materials.
Figure 1-4: (a) Epitaxial layer having different lattice constant with substrate. (b) Epitaxial layer grown on top of substrate showing a lattice distortion described by strain.

To describe strain, we should understand the III-nitrides’ wurtzite crystal structure shown in Figure 1-5 (a) with the in-plane lattice constant \(a\) and out-of-plane lattice constant \(c\) defined [34]. Yellow balls represent III atoms (Ga, In, or Al), while grey balls represent N atoms. The wurtzite crystal structure is a hexagonal crystal.
The primitive translational vectors are shown in Figure 1-5 (b). The vectors ($\overline{a}_1$, $\overline{a}_2$, $\overline{a}_3$) are chosen to represent the unstrained lattice. The distorted vector set ($\overline{a}_1'$, $\overline{a}_2'$, $\overline{a}_3'$) can be expressed in terms of the unstrained vector set as [35]:

$$\overline{a}_1' = (1 + \epsilon_{xx})\overline{a}_1 + \epsilon_{xy} \overline{a}_2 + \epsilon_{xz} \overline{a}_3$$

$$\overline{a}_2' = \epsilon_{yx} \overline{a}_1, + (1 + \epsilon_{yy})\overline{a}_2 + \epsilon_{yz} \overline{a}_3$$

$$\overline{a}_3' = \epsilon_{zx} \overline{a}_1, + \epsilon_{zy} \overline{a}_2 + (1 + \epsilon_{zz})\overline{a}_3$$

(1.1)

where $\epsilon_{ij}$ is defined as the strain tensor (or deformation coefficients) of the system. The strain tensor describes how the unit cell geometry changes due to deformation. In the III-nitrides, the strain tensor has been shown to be symmetric [36]. It includes the normal strain components $\epsilon_{xx}$, $\epsilon_{yy}$, and $\epsilon_{zz}$, and shear strain components $\epsilon_{xy}$, $\epsilon_{xz}$, and $\epsilon_{yz}$.
1.2.1.2 Stress

Stress is used to describe the pressure applied on the crystal by lattice deformation. It is defined by considering a small body which is enclosed by area, $\Delta A$, and measuring the force, $\Delta F$, applied on it with $\Delta A$ approaching 0:

$$\sigma = \lim_{\Delta A \to 0} \frac{\Delta F}{\Delta A} = \frac{dF}{dA}$$ (1.2)

There are three main planes, and for each plane, the stress vector can be decomposed into components in the three directions. In total, there are nine stress vectors as shown in Figure 1-6.

![Figure 1-6: Stress tensor illustration. Image taken from Ref. [37].](image)

$\sigma_{xx}$, $\sigma_{yy}$ and $\sigma_{zz}$ are normal stresses, $\sigma_{xy}$, $\sigma_{yx}$, $\sigma_{xz}$, $\sigma_{zx}$, $\sigma_{yz}$ and $\sigma_{zy}$ are shear stresses. The stress tensor in the III-nitride system is symmetric [36], with
\[
\begin{align*}
\sigma_{xy} &= \sigma_{yx} \\
\sigma_{xz} &= \sigma_{zx} \\
\sigma_{yz} &= \sigma_{zy}
\end{align*}
\]

1.2.1.3 Strain and stress relation

Strain and stress tensors are related through an elastic stiffness tensor \( C_{ijkl} \), a more general form of Hooke’s law. Considering the symmetry of the strain and stress tensors, the relation can be simplified as [35]:

\[
\begin{pmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz} \\
\sigma_{yz} \\
\sigma_{xz} \\
\sigma_{xy}
\end{pmatrix} =
\begin{pmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{pmatrix}
\begin{pmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
\varepsilon_{zz} \\
\varepsilon_{yz} \\
\varepsilon_{xz} \\
\varepsilon_{xy}
\end{pmatrix}
\]

In our study, the growth direction is [0001], defined by a vector pointing from a Ga atom to the nearest N atom. This growth direction can be used to further simplify the relationship. First, shear stresses and shear strains are zero since the angles between the primitive translational vectors are conserved by stress along one of the unit vectors \( \vec{a}_1 \), \( \vec{a}_2 \), or \( \vec{a}_3 \). Secondly, in this direction, the in-plane strain is always isotropic.

Consider the unstrained lattice constant of the epitaxial film is \( a_L,0 \) and \( c_L,0 \), and the lattice constant of the substrate is \( a_S \), \( c_S \). The epitaxial film has a lattice constant \( a_L \) and \( c_L \) after depositing on the substrate. The film is under biaxial strain with
\[ \varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\|} = \frac{a_L - a_{L0}}{a_{L0}} \]

\[ \varepsilon_{zz} = \varepsilon_{\perp} = \frac{c_L - c_{L0}}{c_{L0}} \]  \hspace{1cm} (1.5)

The equation can be simplified as:

\[ \begin{pmatrix} \sigma_{\|} \\ \sigma_{\perp} \end{pmatrix} = \begin{pmatrix} C_{11} + C_{12} & C_{13} \\ 2C_{13} & C_{33} \end{pmatrix} \begin{pmatrix} \varepsilon_{\|} \\ \varepsilon_{\perp} \end{pmatrix} \]  \hspace{1cm} (1.6)

Since the film experiences no stress along the growth direction (\( \sigma_{\perp} = 0 \)), we get:

\[ \frac{\varepsilon_{\perp}}{\varepsilon_{\|}} = -2 \frac{C_{13}}{C_{33}} \]  \hspace{1cm} (1.7)

This equation is widely used in strain and stress calculations for III-nitrides grown in the [0001] direction. The recommended choices of lattice constant, \( a \) and \( c \), and elastic constants, \( C_{11} + C_{12}, C_{31}, C_{33} \) are shown in Table 1-1 according to references [21, 32, 38, 39].

<table>
<thead>
<tr>
<th></th>
<th>( a(\text{Å}) )</th>
<th>( c/a )</th>
<th>( C_{11} + C_{12} ) (GPa)</th>
<th>( C_{31} ) (GPa)</th>
<th>( C_{33} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>3.1106</td>
<td>1.6008</td>
<td>550</td>
<td>100</td>
<td>390</td>
</tr>
<tr>
<td>GaN</td>
<td>3.1892</td>
<td>1.6258</td>
<td>520</td>
<td>110</td>
<td>390</td>
</tr>
<tr>
<td>InN</td>
<td>3.538</td>
<td>1.6119</td>
<td>294</td>
<td>121</td>
<td>182</td>
</tr>
</tbody>
</table>

Table 1-1: Choice of lattice constants and elastic constants for binary nitrides. Lattice constant values taken from Ref. [32]. GaN and AlN elastic constants values taken from Ref. [38]. InN elastic values taken from Ref. [39]. These are in agreement with Ref. [21].
1.2.1.4 Relaxation

Relaxation is another phenomenon related to crystal deformation. As discussed above, when an epi-layer is grown on a lattice-mismatched substrate, it tends to deform to match the substrate (Figure 1-7 (b)). However, when the thickness of an epi-layer goes beyond a certain value (critical thickness), the epi-layer cannot balance the force and tends to go back to its original lattice constant; this process is called relaxation (Figure 1-7 (c)).

![Diagram of Epitaxial Layer and Substrate]

Figure 1-7: (a) Epitaxial layer has a different lattice constant comparing with the substrate. (b) Epitaxial layer grown fully strained, with a matched lattice constant \( a \) to the underlying substrate. (c) Epitaxial layer fully relaxed, with lattice consonant \( a \) same with its original lattice constant.

When relaxation occurs, the epi-layer’s lattice constants do not always go back to the original value. Relaxation, \( R \), is defined as:

\[
R = \frac{a_L - a_S}{a_{L0} - a_S}
\]  

(1.8)

where \( a_S \) stands for the lattice constant of substrate, \( a_L \) is the lattice constant of the relaxed epi-layer, \( a_{L0} \) being the free-standing lattice constant of epi-layer without any stress. In the case of \( a_L = a_{L0} \), \( R = 100\% \), meaning epi-layer relaxed to its original lattice constant.
constant. If \( a_L = a_S \), \( R = 0 \), meaning the epi-layer remained fully strained to the substrate’s lattice. For the general case when \( a_L \) lies between \( a_S \) and \( a_{L0} \), \( R \) is a value between 0 and 1.

1.2.2 Spontaneous and piezoelectric polarization

Polarization is a characteristic of III-nitrides distinguishing them from other III-V materials. The spontaneous polarization, \( P_{sp} \), is relatively large in the III-nitrides. For example, the spontaneous polarization in AlN is 0.081 C/m\(^2\) [40] compared with 0.15 C/m\(^2\) in BaTiO\(_3\) [41], a common ferroelectric material having large spontaneous polarization. The piezoelectric polarization is caused by deformation of the lattice. In AlGaN/GaN based transistors, the piezoelectric polarization is more than five times larger than that of AlGaAs/GaAs structures [42]. The polarization leads to very large internal electric field in nitrides on the order of MV/cm [43]. Throughout this work, we will show how energy band bends due to the electrical field and how this impacts the determination of energy band structures.

The spontaneous polarization (Figure 1-8) of nitrides comes from the unique characteristic that the bond along the c-axis is longer than other bonds, leading to a violation of inversion symmetry. This violation distinguishes the III-nitrides from other cubic semiconductors with four equivalent bonds per atom. This asymmetry creates a slight spatial separation of positive and negative charge centers, generating a dipole for each unit cell. The dipoles in adjacent parallel layers in the bulk will cancel out leaving
only the dipoles at surfaces, forming surface charges. The sheet charge at both surfaces will introduce a spontaneous polarization electric field across the film.

Figure 1-8: Demonstration of spontaneous polarization in nitride materials. Plots from Ref. [36]. (a) Dipole formed due to spatial separation of positive and negative charges. (b) Dipole points downwards. (c) Dipoles neutralize each other in the bulk, leaving negative surface polarization charge and positive bottom polarization charge. (d) Overall spontaneous polarization points downwards.

If the film is strained, the separation of centers of positive and negative charges change, leading to an additional polarization field called piezoelectric polarization, $P_{PZ}$. 
The overall polarization \( P \) in nitrides is the combination of both polarization effects \( P_{SP} \) and \( P_{PZ} \). The relation between piezoelectric polarization and strain is expressed as:

\[
P_{PZ} = \begin{pmatrix}
0 & 0 & 0 & 0 & e_{15} & 0 \\
0 & 0 & 0 & e_{15} & 0 & 0 \\
e_{31} & e_{31} & e_{33} & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
\epsilon_{xx} \\
\epsilon_{yy} \\
\epsilon_{zz} \\
\epsilon_{yz} \\
\epsilon_{xz} \\
\epsilon_{xy}
\end{pmatrix} = \begin{pmatrix}
e_{31}(\epsilon_{xx} + \epsilon_{yy}) + e_{33}\epsilon_{zz} \\
e_{15}\epsilon_{xz} \\
e_{15}\epsilon_{yz}
\end{pmatrix} \tag{1.9}
\]

where \( e_{ij} \) is the piezoelectric tensor. The constants for spontaneous and piezoelectric polarization used in this work are listed in Table 1-2.

<table>
<thead>
<tr>
<th>Material</th>
<th>( P_{SP} ) (C m(^{-2}))</th>
<th>( e_{33} ) (C m(^{-2}))</th>
<th>( e_{31} ) (C m(^{-2}))</th>
<th>( e_{15} ) (C m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>-0.0898</td>
<td>1.505</td>
<td>-0.533</td>
<td>-0.351</td>
</tr>
<tr>
<td>GaN</td>
<td>-0.0339</td>
<td>0.667</td>
<td>-0.338</td>
<td>-0.167</td>
</tr>
<tr>
<td>InN</td>
<td>-0.0413</td>
<td>0.815</td>
<td>-0.412</td>
<td>-0.112</td>
</tr>
</tbody>
</table>

### 1.3 High electron mobility transistor structures

#### 1.3.1 III-nitride transistors

Increasing demand for high frequency and high power transistors has accelerated the development of III-nitride-based HEMT which is named ‘the toughest transistor yet’ [46]. Its unique material properties lead to high power and high frequency transistors that can withstand extreme heat when compared with Si, GaAs, SiC, and many other materials typically used for transistors. Its applications include cellular base stations, hybrid electric cars, radar, satellite communication links, and defense. The large
band gaps of III-nitrides (3.42 eV for GaN [1] compared to 1.1 eV for silicon [2]) enables nitride transistors to operate at high temperatures with a large thermal conductivity. Also, it provides a high breakdown voltage (> 3 MV cm\(^{-1}\)) in comparison to GaAs (~0.4 MV/cm) [21].

When AlGaN is grown on top of GaN, the polarization difference leads to the formation of a 2DEG at the GaN surface very close to AlGaN. The 2DEG will not reside in the AlGaN because the large band gap acts as a barrier, thus enabling a high mobility (1500-2200 cm\(^2\)V\(^{-1}\)s\(^{-1}\)) since GaN is undoped and therefore ionized dopant scattering is eliminated. Additionally, the 2DEG usually possesses a high electron density (normally 0.7-1.4 x 10\(^{13}\) cm\(^{-2}\)). The high density combined with the high breakdown voltage lends itself well to the creation of high power and high frequency transistors. The properties of gallium nitride that lead it to outperform other semiconductor materials are listed in Table 1-3 [46] and Figure 1-9 [47].
Table 1-3: GaN based transistors’ properties compared with common materials. Data taken from Ref. [46].

<table>
<thead>
<tr>
<th></th>
<th>Si (AlGaAs/InGaAs)</th>
<th>GaAs (AlGaAs/InGaAs)</th>
<th>InP (InAlAs/InGaAs)</th>
<th>SiC (AlGaN/GaN)</th>
<th>GaN (AlGaN/GaN)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Band gap (eV)</strong></td>
<td>1.1</td>
<td>1.42</td>
<td>1.35</td>
<td>3.26</td>
<td>3.42</td>
</tr>
<tr>
<td><strong>Electron mobility at 300K (cm²/Vs)</strong></td>
<td>1500</td>
<td>8500</td>
<td>5400</td>
<td>700</td>
<td>1000-2000</td>
</tr>
<tr>
<td><strong>Saturated electron velocity (x 10⁷ cm/s)</strong></td>
<td>1.0 (1.0)</td>
<td>1.3 (2.1)</td>
<td>1.0 (2.3)</td>
<td>2.0 (2.0)</td>
<td>1.3 (2.1)</td>
</tr>
<tr>
<td><strong>Critical breakdown field (MV/cm)</strong></td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>Thermal conductivity (W/cmK)</strong></td>
<td>1.5</td>
<td>0.5</td>
<td>0.7</td>
<td>4.5</td>
<td>&gt;1.5</td>
</tr>
</tbody>
</table>

Figure 1-9: Material systems for transistors application showing their power and frequency range. Plot adapted from Ref. [47].
Similar to common silicon MOSFETs, AlGaN/GaN HEMTs have three terminals, source, drain and gate, shown in Figure 1-10.

![Figure 1-10: Depletion-mode InAlN HEMT structure. (a) Without voltage applied on gate, HEMT is on. (b) Negative voltage applied on gate, HEMT is off.](image)

Unlike common enhancement-mode MOSFETs, most AlGaN/GaN HEMTs are operated in depletion-mode. When no voltage is applied to the gate, the 2DEG exists due to the properties of the heterostructure at which it is confined. A negative voltage applied to the gate will restrict the number of electrons available to flow from source to drain. With a high enough voltage, the transistor can be turned off.

1.3.2 InAlN/(AlN)/GaN high electron mobility transistor

1.3.2.1 Introduction

In the following studies, our research will focus on InAlN/(AlN)/GaN heterostructure and HEMTs which in theory provides better electrical and mechanical characteristics than more traditional AlGaN/GaN HEMTs due to the following reasons.
First, at a 17-18% indium composition, InAlN can be grown lattice matched to GaN [29]. On the other hand, AlGaN always has a lattice mismatch with GaN. Lattice matched InAlN is extremely thermally stable even at annealing temperatures well above growth temperature. Moreover, strain relaxation is avoided which would create dislocations within the device leading to a significant drop of electron mobility by ~30% [48].

Second, the spontaneous polarization in InAlN/GaN heterostructure is two times higher than that of AlGaN/GaN as show in Figure 1-11 [36]. As Ambacher et al. pointed out [49], the polarization difference in the AlGaN(InAlN)/GaN heterojunction induces a charge density $\rho_p$ of:

$$\rho_p = - \nabla P = - \nabla (P_{SP} + P_{PZ})$$

(1.10)

in which $P$ is the total polarization difference between AlGaN (InAlN) and GaN, and $\rho_p$ is the polarization charge.
In an AlGaN/GaN heterostructure, the AlGaN is tensilely-strained while the GaN is unstrained, or fully relaxed. Inside the AlGaN, a spontaneous and piezoelectric polarization exist and point downwards ([000\overline{1}]) with the Ga-face GaN direction. The polarization difference is given by:

\[ P(GaN) - P(AlGaN) = P_{SP}(GaN) - (P_{SP}(AlGaN) + P_{PZ}(AlGaN)) \]  \hspace{1cm} (1.11)

This value is normally positive, creating a sheet of positive polarization charge at the interface, thus free electrons will tend to compensate the polarization-induced charge forming the 2DEG.
Since for InAlN/GaN, the structure is lattice-matched or near lattice-matched to the GaN template, no piezoelectric polarization exists. Thus we have the polarization difference:

\[ P(GaN) - P(InAlN) = P_{SP}(GaN) - P_{SP}(InAlN) \]  

(1.12)

As calculated by Kuzmik [8], the polarization values comparing these two structures are shown in Table 1-4, where \( \Delta P_{SP} \) stands for the spontaneous polarization difference, \( \Delta P_{PZ} \) stands for piezoelectric polarization difference, and \( \Delta P \) stands for the sum of these two polarization. The InAlN/GaN heterostructure possesses a larger \( \Delta P \) thus creating more polarization charge at the interface as expressed by equation (1.10). This positive charge attracts more electrons to the interface creating a higher density 2DEG.

**Table 1-4: Spontaneous and piezoelectric polarization difference for InAlN/GaN and AlGaN/GaN heterostructures. Data from Ref. [8].**

<table>
<thead>
<tr>
<th></th>
<th>( \Delta P_{SP} ) ( (ecm^{-2}) )</th>
<th>( \Delta P_{PZ} ) ( (ecm^{-2}) )</th>
<th>( \Delta P ) ( (ecm^{-2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Al_{0.2}Ga_{0.8}N/GaN )</td>
<td>6.5 ( \times 10^{12} )</td>
<td>5.32 ( \times 10^{12} )</td>
<td>1.18 ( \times 10^{13} )</td>
</tr>
<tr>
<td>( In_{0.17}Al_{0.83}N/GaN )</td>
<td>2.73( \times 10^{13} )</td>
<td>0</td>
<td>2.73 ( \times 10^{13} )</td>
</tr>
</tbody>
</table>

Despite all of the advantages of InAlN/GaN HEMTs, these structures are less mature than AlGaN/GaN HEMT structures and the InAlN is relatively low quality.

**1.3.2.2 Asserting AlN interlayer**

Similar to AlGaN/GaN HEMT structures, it is believed that insertion of a thin AlN layer improves structural quality and device electrical behavior for the following
two reasons. First, AlN has a higher band gap than InAlN, providing a better confinement of 2DEG in the channel therefore reducing the impact of alloy scattering, which is high in the InAlN ternary alloy. Second, the AlN interlayer should improve the interface material quality in turn increasing the electron correlation length and decreasing interface roughness. The thickness of the AlN is a critical parameter in this structure. If the AlN is too thin, the 2DEG cannot be separated from InAlN very well. On the other hand, if the AlN is thick enough that it exceeds the critical thickness and gets relaxed, the InAlN grown on top of AlN will be lattice mismatched degrading the InAlN grown on top of it. A study of optimizing the AlN layer thickness shows that a thickness of around 1 to 1.5 nm produces the best electrical characteristics [50].

1.3.2.3 State-of-the-art

InAlN/(AlN)/GaN HEMTs had just started to attract a lot attention at the time this research was initiated. 2DEG density and mobility of HEMTs are the core characteristics determining transistor performance. A summary of these characteristics in various InAlN HEMT structures are shown in Figure 1-12 which contains data for HEMTs grown by MOCVD with an AlN insertion layer [50-57], by MBE with AlN layer [50, 58-62], and without AlN [62]. 2DEG density larger than $3.2 \times 10^{13}$ cm$^{-2}$ [52] has been achieved with MOCVD-grown lattice-matched InAlN. 2DEG mobility has reached 1975 cm$^2$/Vs [62] at 300K with an MBE-grown lattice-matched InAlN/GaN/AlN/GaN structure under N-rich conditions.
A record 370 GHz cut-off frequency was accomplished with a 30-nm-gate-length InAlN/AlN/GaN/SiC HEMT in 2012 by Yue et al. [57]. The performance enhanced was attributed to the reduction of parasitic effects. Current density reached 2.36 A/mm in work reported by Wang et al. using a 8.9 nm lattice-matched InAlN with atomic layer deposition (ALD) grown Al₂O₃ passivation [63]. An output power density of 10.3 W/mm at 10 GHz was demonstrated by Sarazin et al. using MOCVD growth on a SiC substrate. This performance was attributed to optimized low-resistance ohmic contacts and an

Figure 1-12: Mobility and density of 2DEG in InAlN HEMTs from literature with or without AlN insertion layer grown by MOCVD or MBE.
effective Si₃N₄ passivation layer [64]. Enhancement-mode HEMTs structures has been successfully realized [55, 65-69] with InAlN thickness down to 2 nm.

Despite the progress made in device fabrication and performance, an understanding of basic material characteristics, for example, surface states, band offsets, and surface oxidation, is still lacking especially for MBE-grown InAlN. Thus, in this thesis, these problems will be addressed.
2. Experimental techniques

In this chapter, we introduce the experimental techniques used repeatedly throughout this research. X-ray photoelectron spectroscopy (XPS) is utilized in several ways: to examine surface chemistry as a function of depth with angle-resolved XPS, to study chemical properties with depth using XPS and sputtering, and to determine band structure using valence band spectra. Spectroscopic ellipsometry (SE) is used to optically characterize the material to determine structure dielectric function. Hall measurements using a Van der Pauw geometry (VDP Hall) was used to characterize carrier densities and motilities. X-ray diffraction reciprocal space mapping (XRD-RSM) was employed to determine ternary alloy composition taking into account the strain and relaxation within the material.

2.1 X-ray photoelectron spectroscopy

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is a very powerful surface analysis method [70]. The physical principle of XPS is based on the photoelectric effect. X-rays are incident on the sample surface exciting electrons out of the sample. Since only the surface electrons have enough energy to escape, XPS is a surface sensitive tool. The conservation of energy leads to

\[ E_K = h\nu - E_B^p - \phi_{sp} \]  

(2.1)
where $E_K$ is the kinetic energy of emitted electrons, $h\nu$ is the photon energy of x-ray, $E_B^F$ is the binding energy of the electron relative to Fermi level, and $\phi_{sp}$ is the work function of the spectrometer which is a constant.

The electron intensity coming out of the film is quantified in terms of the kinetic energy of the photoelectrons. It is re-plotted as a function of binding energy using equation (2.1). Different binding energies are associated with electrons lying in various atoms and orbitals, affected by their bonding environment, so that chemical information is obtained. All the fittings of XPS spectra in this work are done using CasaXPS software [71].

### 2.1.1 Angle-resolved X-ray photoelectron spectroscopy

Angle-resolved XPS is used to study the properties of the sample surface at various depths. By changing the take-off angle (TOA) $\theta$ of the detector (Figure 2-1), the depth of obtained information $\lambda$ is changed. For $\theta_0 = 90^\circ$, $\lambda_0$ represents the inelastic mean free path of electrons, meaning how far an electron can travel through a solid before losing all its kinetic energy. For a more general angle $\theta_1$, electrons at the same depth $\lambda_0$ cannot pass through the layer to get detected, and the escape length is reduced to

$$\lambda_1 = \lambda_0 \sin(\theta_1) \quad (2.2)$$

In this way, decreasing $\theta$ allows for more surface sensitive information.
Figure 2-1: Schematic diagram of angle-resolved XPS. A change of detector angle $\theta$ leads to the change of escape length $\lambda$, thus affecting the surface sensitivity of measurements.

Table 2-1 shows the escape lengths for different core levels calculated using the NIST inelastic mean free path database 1.2 [72].

**Table 2-1**: Escape lengths for Al 2p electrons in In$_{0.18}$Al$_{0.82}$N and Ga 3d electrons in GaN. Data calculated using Ref. [72].

<table>
<thead>
<tr>
<th>TOA</th>
<th>Al 2p in In$<em>{0.18}$Al$</em>{0.82}$N</th>
<th>Ga 3d in GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°</td>
<td>2.87 nm</td>
<td>2.58 nm</td>
</tr>
<tr>
<td>30°</td>
<td>1.44 nm</td>
<td>1.29 nm</td>
</tr>
</tbody>
</table>

**2.1.2 X-ray photoelectron spectroscopy and sputtering**

XPS in conjunction with Ar sputtering can be used to study chemical environment changes with depth by removing surface material of the sample after each
XPS acquisition. Argon ions are used to sputter off the sample surface layers systematically. After each sputtering step, an XPS spectrum is obtained. This method is relatively straightforward, however, differential sputtering depths due to dissimilar bonding energies in compound materials and surface roughening are common problems.

**2.1.3 X-ray photoelectron spectroscopy valence band maximum**

The valence band maximum (VBM) is determined by extrapolating the linear portion of the leading edge in the XPS valence band spectrum. The energy value is determined with respect to the Fermi level by calculating the intersection with the horizontal offset line as in Figure 2-2 [73].

![Figure 2-2: Valence band spectrum and VBM fitting by XPS. Binding energy of 0 eV showing the Fermi level position.](image-url)
2.2 Spectroscopy ellipsometry

*In situ* SE is utilized herein to characterize the dielectric properties of ternary nitrides. SE measures the change in the light polarization upon its reflection from a sample’s surface. A schematic setup of our ellipsometry system is shown in Figure 2-3.

![Schematic diagram of in-situ SE system installed inside of the MBE.](image)

Our SE system (Horiba Jobin Yvon) is installed inside of the MBE and possesses a photon energy range of 1.5 eV to 6.0 eV. The unpolarized light coming from a Xe lamp is guided by an optical fiber and passes through a polarizer. The light is then incident on the sample surface within the MBE at an incident angle of 70°. The light reflected from the sample surface is collected by the analyzer after it passes through a phase modulator. Polarized light is decomposed into two components, *s* and *p*. *s*-polarized light has its polarization direction perpendicular to the plane of incidence, while *p*-
polarized light has a polarization direction parallel to the plane of incidence.

Ellipsometry measures the complex reflectance ratio $\rho$ defined as [74]:

$$
\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}
$$

(2.3)

where $r_p$ and $r_s$ stand for the complex amplitude of reflected p and s light. $\Psi$ and $\Delta$ represent the amplitude ratio and phase shift. The final measured quantities, $\Psi$ and $\Delta$, are determined as a function of photon energy $E$.

The ratio $\rho$ is then converted into the pseudo-dielectric function $<\varepsilon>$ using the relation:

$$
<\varepsilon> = <\varepsilon_1> + i<\varepsilon_2> = \sin^2\Phi[1 + \tan^2\Phi\left(\frac{1 - \rho}{1 + \rho}\right)^2]
$$

(2.4)

where $\Phi$ is the system’s angle of incidence. The pseudo-dielectric function is the dielectric function of the whole sample including the epi-layer, interlayer, substrate and reflections from their interfaces. In order to obtain real dielectric functions, HORIBA DeltaPsi 2 software [75] is used for modeling the structure in order to extract the dielectric functions of each layer.

**2.3 Van der Pauw Hall measurements**

The VDP Hall method was invented in 1958 [76] and is a widely used technique for obtaining electrical characteristics using the Hall measurement principle. Samples are prepared in the following manner. First, samples are cleaned with a standard solvent cleaning procedure. Four small indium dots are put on the four corners of samples very
close to the edges. The samples are then annealed on a hot plate at 200 °C for 10 minutes so that ohmic contacts are formed. The four dots are numbered 1 to 4 in a counterclockwise order, as shown in Figure 2-4.

![Sample](image)

**Figure 2-4: InAlN sample with four indium dots on the corners showing their numbering.**

The sheet resistance is measured first. We denote \( R_{ab,cd} \) as the resistivity calculated by dividing the injected current into contact \( a \) and taken out of contact \( b \) from the measured voltage between contact \( c \) and \( d \). Currents are first applied vertically in four configurations (for example, apply current to 1 and 2, measure voltage from 3 and 4 to extract \( R_{12,34} \)) and averaged to obtain \( R_{vertical} \). They are then applied horizontally (for example, apply current to 2 and 3, measure voltage from 4 and 1 to extract \( R_{23,41} \)) and averaged to obtain \( R_{horizontal} \). The sheet resistance \( R_s \) is finally calculated using the two resistances as shown in following equations.

\[
R_{vertical} = \frac{R_{12,34} + R_{34,12} + R_{21,43} + R_{43,21}}{4} \quad (2.5)
\]

\[
R_{horizontal} = \frac{R_{23,41} + R_{41,23} + R_{32,14} + R_{14,32}}{4} \quad (2.6)
\]
\[ e^{-\pi R_{\text{vertical}}/R_S} + e^{-\pi R_{\text{horizontal}}/R_S} = 1 \]  

(2.7)

After calculating the sheet resistance, Hall measurements are conducted. When a current flows in a sample (Figure 2-5(a)), the electrons flow in the opposite direction (Figure 2-5(b)). By applying a magnetic field perpendicular to current flow (Figure 2-5(c)), the flowing electrons experience a Lorentz force perpendicular to both the current and magnetic fields, thus creating an accumulation of electrons on one side of the semiconductor. When the electric force created by the accumulated electrons cancels the Lorentz force, the concentration saturates. The saturated electrons form a detectable Hall voltage \( V_H \) (Figure 2-5(d)).
Figure 2-5: Hall measurements with current flow and magnetic field direction denoted. (a) Current flow direction. (b) Electron flow direction. (c) Magnetic field causing electrons accumulating on one side of sample. (d) Resulting Hall voltage direction. Plot taken from Ref. [77].

The measurement of Hall voltage $V_H$ is denoted according to different set ups. For example, $V_{13,P}$ means applying a positive magnetic field as shown in Figure 2-5(c), a current $I_{24}$, and measuring the voltage between contacts 1 and 3. The subscript N means applying a magnetic field with the opposite direction. Note the positive and negative
magnetic fields have the same magnitude. All of the currents applied have the same value. The final $V_H$ is averaged to be:

$$V_H = \frac{V_{13,P} - V_{13,N} + V_{24,P} - V_{24,N} + V_{31,P} - V_{31,N} + V_{42,P} - V_{42,N}}{8}$$  \hspace{1cm} (2.8)$$

It can be theoretically shown that the $V_H$ is:

$$V_H = \frac{IB}{qn_S}$$  \hspace{1cm} (2.9)$$

in which $I$ is the strength of the current, $B$ is the magnitude of magnetic force, $q$ is the electric charge, $n_S$ is the sheet electron density.

The sheet density is then calculated as:

$$n_s = \frac{IB}{qV_H}$$  \hspace{1cm} (2.10)$$

The mobility can be calculated as

$$\mu = \frac{1}{qn_{sR_s}}$$  \hspace{1cm} (2.11)$$

2.4 **X-ray diffraction—reciprocal space mapping**

X-ray diffraction (XRD) is a highly accurate and non-destructive method used widely in semiconductor structural characterization yielding film composition, strain, relaxation, layer thicknesses, superlattice period, defects, tilt, twist, and many other properties. Among a variety of different XRD techniques, the $\omega - 2\theta$ scan and reciprocal space mapping (RSM) are the two methods most used to determine III-nitride epitaxial layer properties. In $\omega - 2\theta$ scan, $\omega$ stands for the angle between x-ray and film surface,
while $2\theta$ is defined as the angle between the incident x-ray beam and detector. During measurement, the detector angle $2\theta$ is moved at twice the rate as the sample rotation about $\omega$. Although this method is powerful, it only gives the information about the out-of-plane lattice constant $c$ between crystal layers. If the film is partially relaxed, it becomes challenging to get compositional information from just the lattice constant $c$. RSM can help solve this problem.

Before covering the RSM, reciprocal space should be understood. Any vector in reciprocal space can be represented with three primitive vectors $b_1$, $b_2$, and $b_3$ defined in the following as a function of primitive vectors in real space $a_1$, $a_2$, and $a_3$.

$$b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}$$

$$b_2 = 2\pi \frac{a_3 \times a_1}{a_1 \cdot (a_2 \times a_3)}$$

$$b_3 = 2\pi \frac{a_1 \times a_2}{a_1 \cdot (a_2 \times a_3)}$$

(2.12)

Each vector (point) in reciprocal space $d_{hkl}^*$ is related to a vector in real space $d_{hkl}$ with the relation $d_{hkl}^* = 1/d_{hkl}$. $d_{hkl}$ is the vector drawn from the origin of the unit cell to intersect the first crystallographic plane in the $hkl$ plane family at $90^\circ$. Thus, in the reciprocal space, each point stands for a series of parallel planes in the real space.

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Figure 2-6: RSM range, showing an $\omega$ scan as an arc scanning, $\omega$-2$\theta$ scan showing straight line through original point. Plots from Ref. [78].

RSM is performed by collecting the $\omega - 2\theta$ scans with an offset of $\omega$ for each scan represented in reciprocal space. Figure 2-6 shows different scan regions in reciprocal space denoted by $Q_x$ and $Q_y$ as the x and y axes. $\omega$ scan is an arc centered on the origin, $\omega - 2\theta$ scan is a straight line pointing away from the origin. Since RSM is basically $\omega - 2\theta$ scan with sweeping $\omega$, the final effect is sweeping a two-dimensional mapping around a chosen point in reciprocal space, related to a series of planes in real space.

The RSM is chosen to be over the normal $\omega - 2\theta$ scan due to effects such as strain shifts points in reciprocal space, a straight line cannot cover both the peaks of substrate and epi-layer as shown in Figure 2-7.
Figure 2-7: (a) Without strain, \( \omega-2\theta \) scan stands for the straight line can measure both the substrate and epi-layer. (b) With strain, lattice shifts, \( \omega-2\theta \) scan fails to measure both the substrate and epi-layer. Plots taken from Ref. [79].

A typical asymmetric (10\textoverline{1}5) RSM of InGaN grown on GaN is shown in Figure 2-8.

Figure 2-8: Typical RSM showing GaN substrate and InGaN epitaxial layer peaks.
Two peaks are shown in the plot, with the upper peak is for the GaN substrate while the bottom peak is for the InGaN epi-layer. For any material, the in-plane lattice constant $a$ and out-of-plane lattice constant $c$ are related to the peak’s x and y position in RSM $Q_x, Q_y$ plotted with the following relation:

$$
a = \frac{\text{constant}_1}{Q_x}$$

$$
c = \frac{\text{constant}_2}{Q_y} \quad (2.13)$$

The constants are not necessary for the calculation since the properties of the substrate are normally known and can be used as a reference. We denote $a_L, a_S$ to be the in-plane lattice constants of the epi-layer and substrate, $c_L, c_S$ to be the out-of-plane lattice constants of epi-layer and substrate respectively. $Q_{Sx}, Q_{Sy}$ represent the measured x and y position of substrate peak in RSM. $Q_{Lx}, Q_{Ly}$ represent the measured x and y position of epi-layer peak in RSM. With respect to equation (2.13), it is deduced that

$$
\frac{c_L}{c_S} = \frac{Q_{Sy}}{Q_{Ly}}
$$

$$
\frac{a_L}{a_S} = \frac{Q_{Sx}}{Q_{Sy}} \quad (2.14)
$$

With these equations, as long as the substrate’s $a_S$ and $c_S$ is known, the epi-layer’s lattice constants $a_L$ and $c_L$ can be calculated. Also, the lattice mismatch between substrate and layer can be calculated as:

$$
M_b = \frac{a_L - a_S}{a_S} = \frac{Q_{Lx} - Q_{Sx}}{Q_{Lx}}
$$
\[ M_\perp = \frac{c_L - c_S}{c_S} = \frac{Q_{Ly} - Q_{Sy}}{Q_{Ly}} \] (2.15)

It is interesting to note that if the substrate and epi-layer peak lie in the same vertical line as the line shown in Figure 2-8, meaning \( Q_{Lx} \) is equal to \( Q_{Sx} \), \( M_\parallel \) is equal to 0. It can be concluded that there is no in-plane lattice mismatch between the epi-layer and substrate, meaning the epi-layer is fully strained to the substrate with no relaxation.

Another interesting line denoted in Figure 2-8 is the tilted line connecting the substrate peak and the origin of RSM plot. Any peak that lies on this line should have the same \( Q_y/Q_x \) ratio since it get crossed the origin. Considering equation (2.13), it is clear that \( a/c \) should be a constant in this situation. As all the wurtzite crystals, including InN, AlN, GaN, and their compound material, all have the same \( a/c \) ratio when they are fully relaxed, it means if the epi-layer peak lies on this tilted line, the epi-layer is fully relaxed. The epi-layer still keeps its original lattice constant regardless of the effect from substrate.

If the epi-layer peak lies between the tilted line and vertical line as the case shown in Figure 2-8, it means the epi-layer is partially relaxed.

Since strain can be expressed as

\[ \varepsilon_{xx} = \varepsilon_{yy} = \frac{a_L - a_{L0}(x)}{a_{L0}(x)} \] (2.16)

\[ \varepsilon_{zz} = \frac{c_L - c_{L0}(x)}{c_{L0}(x)} \] (2.17)
\[
\frac{\epsilon_{zz}}{\epsilon_{xx}} = \frac{\epsilon_{zz}}{\epsilon_{yy}} = -\frac{C_{13}(x)}{C_{33}(x)}
\]

(2.18)

where \(a_{L0}\) and \(c_{L0}\) are the unstrained (totally relaxed) in-plane and out-of-plane lattice constants, \(C_{13}(x)\) and \(C_{33}(x)\) are the elastic constants of epi-layer. These are functions of composition \(x\), for example indium composition \(x\) in In\(_{x}\)Ga\(_{1-x}\)N. From these equations, it can be deduced that

\[
\frac{c_L - c_{L0}(x)}{c_{L0}(x)} \frac{a_{L0}(x)}{a_L - a_{L0}(x)} + 2 \frac{C_{13}(x)}{C_{33}(x)} = 0
\]

(2.19)

The above equation is used to calculate composition \(x\) in the epi-layer, in addition, \(a_{L0}, c_{L0}\), and strain \(\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}\) can also be determined.

Finally, the relaxation is calculated as

\[
R(x) = \frac{a_L - a_S}{a_{L0} - a_S}
\]

(2.20)

3. MBE growth of III-nitride materials

In this chapter, we discuss optimization of the epitaxial growth of III-nitride materials including the essential layers of the InAlN/AlN/GaN HEMT structures such as the GaN buffer, the AlN interlayer, and the InAlN epi-layer. The GaN buffer layer is crucial for HEMT device performance since it provides the channel for 2DEG transport. A smooth GaN buffer with low background doping level is required. The AlN interlayer is important for the improvement of the 2DEG mobility, and its thickness is a critical parameter which requires careful control. Finally, optimized growth conditions are
explored for the InAlN epi-layer. SE, VDP, atomic force microscopy (AFM), and XRD are used for the characterization of these films.

### 3.1 Basics of molecular beam epitaxy

MBE is a widely used tool for semiconductor material growth both in academic laboratories and industry. It is an ultra-high-vacuum (UHV) technique utilizing physical deposition from individual effusion cells installed for each element.

Popular tools for III-nitrides growth includes MBE and MOCVD etc. A detailed comparison of these growth methods is shown in Table 3-1 [80].

<table>
<thead>
<tr>
<th></th>
<th>MBE</th>
<th>MOCVD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source</strong></td>
<td>Metal, gas</td>
<td>MO, NH₃</td>
</tr>
<tr>
<td><strong>Source safety</strong></td>
<td>Safe</td>
<td>Higher safety risk</td>
</tr>
<tr>
<td><strong>Deposition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>temperature for</td>
<td></td>
<td></td>
</tr>
<tr>
<td>InAlN (°C)</td>
<td>400-600</td>
<td>600-1100</td>
</tr>
<tr>
<td><strong>Pressure (torr)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Growth rate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(µm/hour)</td>
<td>0.5-1</td>
<td>2-4</td>
</tr>
<tr>
<td><strong>Interface control</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Very good: atomic</td>
<td>Medium: layers</td>
</tr>
<tr>
<td></td>
<td>layers</td>
<td>below 3-4 nm</td>
</tr>
<tr>
<td><strong>Parasitic reactions</strong></td>
<td>None (reaction only on substrate)</td>
<td>High</td>
</tr>
</tbody>
</table>

As shown in Table 3-1, MBE is very good at controlling layer thicknesses and maintains a highly defined interface with resolution down to an atomic layer. But its growth rate is much lower compared with MOCVD and HVPE. Typical growth rate for
GaN is 2-4 µm/h using MOCVD, and 0.5–1.0 µm/h using MBE [81]. Currently, MBE is primarily used at the research level and used for the development of complex structures.

A schematic diagram of a MBE system is shown in Figure 3-1.

![Schematic diagram of a typical MBE system](image)

**Figure 3-1:** Schematic diagram of a typical MBE system. Plot adapted from Ref. [82].

The system is comprised of three chambers. Substrates are first loaded into the introduction chamber (10^8 torr), then transferred to a buffer chamber (10^9 torr) where samples are degassed, and finally to the growth chamber (10^{-11} torr). The cells are heated to a specific temperature in order to achieve the desired flux from the cell and incident on the sample. Flux values are calibrated before growth using a beam flux monitor to
ensure repeatability of film growth. When a cell’s shutter is open, heated atoms will evaporate out of the crucible and will be incident on a heated substrate for epitaxial growth.

The flux is continuous and drives the system into supersaturation. Adsorbed adatoms can migrate or diffuse and may experience one or more of several surfaces as shown in Figure 3-2. Adatoms bond to form islands in the nucleation process. The adatom concentration may fluctuate and this gradient drives them to hop or diffuse to existing islands in the coarsening process. Adatoms may be incorporated into an existing island or at a step edge, both processes lead to growth of the film. Adatoms may also desorb from the surface or exchange with second layer atoms. All these kinetic processes affect the MBE growth and the final properties of the film.

Figure 3-2: Schematic illustration of major processes occurring during growth from the vapor. Plot adapted from Ref. [83].
3.2 GaN buffer optimization

Commercially available GaN template layers grown on sapphire usually do not meet the requirements for further nitride epi-layer growth due to its rough surface, high dislocation density, and high residual doping level. Thus, a GaN buffer layer with higher quality is usually deposited on GaN templates as the first step of MBE growth. The goal is to produce a smooth GaN layer with minimum residual electron density so that parallel conduction can be minimized providing higher mobility in HEMT structure.

For MBE grown GaN, the III, V fluxes and growth temperature are control parameters determining GaN surface characteristics and residual doping [84-89]. MBE GaN’s growth diagram is shown in Figure 3-3 with the y axis denoting Ga and N flux difference, and the x axis denoting sample growth temperature.
Figure 3-3: Growth diagram of GaN in MBE with y axis showing flux difference between Ga and N, x axis showing MBE growth temperature. Plot adapted from Ref. [84].

This diagram is divided into three sections. The section below the stoichiometry line (the horizontal line when Ga and N flux difference is zero) with N-rich conditions yields GaN with rough surfaces containing a high density of pits. The section above the stoichiometry line is Ga-rich growth and is divided into two parts. The right side is the intermediate region in which smooth surface can be obtained with Ga forming a metal accumulation wetting layer which helps to smooth the surface. The left section being the Ga-droplet region, in which excess Ga results in droplet formation on surface. Studies show that the best quality of GaN buffer can be obtained right on the line separating the Ga-droplet and intermediate region without Ga droplet formation[84]. Further study shows that GaN grown with around two monolayer (ML) of Ga adlayer coverage will
follow step-flow growth mode instead of layer-by-layer growth mode thus can achieve
the best surface[90].

To find the best growth condition for our MBE system, we first studied the
influence of temperature on material quality with the Ga flux set right on the separating
line between the Ga droplet and intermediate section for each temperature. The N-
plasma was set to be consistent with 350 W/1.0 sccm for all samples. 300 nm GaN films
with growth temperatures varying from 710 °C to 770 °C were studied. AFM results
show smooth surfaces for all samples. VDP Hall measurements were performed with
the results shown in Figure 3-4.

![Graph showing electron concentration and conductivity of GaN buffers by VDP Hall measurements grown under different growth temperatures.](image)

Figure 3-4: Electron concentration and conductivity of GaN buffers by VDP Hall measurements grown under different growth temperatures.
The VDP results indicate that GaN grown at 750 °C has the lowest electron conductivity so that parallel conduction is minimized. At this growth temperature, the residual electron concentration in GaN buffer is around 0.1% of the 2DEG concentration. Thus, most of the conduction is through the 2DEG providing the foundation for good device performance. The low electron concentration also ensures large breakdown voltage for HEMT devices.

Next, to experimentally find the right Ga flux, we target the largest Ga and N flux difference without Ga droplet formation. A series of fluxes were used with the N-plasma condition set as constant while changing Ga flux magnitude at a growth temperature of 750 °C. The characteristics of two representative samples Bu1 and Bu2 grown at conditions on the different sides of separating line are showed in Table 3-2. In this table, the Ga flux is monitored by the measurement of effusion cell beam equivalent pressures (BEP).

<table>
<thead>
<tr>
<th></th>
<th>Ga BEP ($x 10^{-8}$)</th>
<th>AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu1</td>
<td>34.3619</td>
<td>Ga droplet</td>
</tr>
<tr>
<td>Bu2</td>
<td>33.4475</td>
<td>No droplet</td>
</tr>
</tbody>
</table>
Figure 3-5: 2 x 2 \( \mu \text{m}^2 \) AFM of GaN buffer samples showing surface sensitive to Ga flux. (a) Bu1 with higher Ga flux shows Ga droplets on surface. (b) Bu2 with lower Ga flux shows smooth surface without Ga droplet formation.

Although Bu1 was grown with a Ga BEP (flux) only slightly larger than Bu2, the AFM results (Figure 3-5) demonstrates that Ga droplets are formed while sample Bu2 does not possess droplets, showing the flux control is crucial for GaN growth. Thus, we use the growth condition of Bu2 to guide our future HEMT structure’s GaN buffer growth.

### 3.3 Thin AlN layer optimization

The growth of an ultrathin AlN layer on top of the GaN buffer was studied for the growth of the insertion layer in the InAlN/AlN/GaN HEMT structure. The main target is to achieve an AlN thickness around 1 nm for the purpose of achieving the best possible 2DEG mobility in the HEMT structure (Figure 3-6) according to Butte et al. [50].
Figure 3-6: 2DEG mobility measured in room temperature as a function of AlN interlayer thickness for InAlN/GaN HEMT structure. The dashed line is a guide to the eye. Plot from Ref. [50].

The growth temperature of 750 °C was used as this is the growth temperature of GaN buffer. Thus, AlN can be grown right after the GaN buffer without waiting for temperature change, to best maintain the quality of GaN buffer. AFM result (Figure 3-7 (b)) shows a flat AlN surface with root mean square (RMS) of 0.748 nm. To characterize the thickness of the AlN, in situ SE was utilized as it is a non-destructive method sensitive to thickness characterization. A thickness of 0.98 nm was modeled from SE fitting (Figure 3-7 (a)) demonstrating well-controlled growth thickness. Details of modeling of nitrides using SE simulation can be found in Chapter 6.
3.4 InAlN growth by molecular beam epitaxy

Among all the ternary nitrides, InAlN is the most challenging to synthesize and, as a consequence, has been less studied. The large bonding energy difference between Al-N and In-N drives phase separation within the InAlN. Also, InN and AlN have very different optimal growth temperatures. At approximately 585 °C, In desorption begins to rapidly increase [91, 92], while Al lacks adequate surface diffusion.

We investigated the growth conditions of nearly lattice-matched InAlN on GaN templates at growth temperatures ranging from 400 to 540 °C under III>N, III=N, or III<N flux conditions to generate the growth diagram shown in Figure 3-8.
The different regimes of InAlN growth are a function of both the growth temperature and the growth rate which is determined by the In and Al fluxes. When the growth rate is high, which we have when III>V, excess indium will be present on the InAlN surface and will coalesce into In droplets. The line indicates the III=V stoichiometric condition, while the area under the line describes nitrogen-rich conditions. This diagram is similar to work by Fernandez-Garrido et al. [93].

Notice that in this diagram, the stoichiometric line does not merely depend on the III and V fluxes but also on the growth temperature. At low temperature, this line is almost flat since In desorption is insignificant. When the temperature is increased to around $450 \, ^\circ\text{C}$, InN starts to decompose providing excess In that partially reincorporates...
into the crystal until effective stoichiometry at the growth front is reached. The excess In provides In at lower In flux, thus the line is lowered at higher temperatures. At temperatures higher than 585 °C, which is not shown in this diagram, In starts to desorb.

Under the conditions where III<V at 400 to 540 °C, we successfully synthesized smooth InAlN films with AFM RMS roughness ~ 0.28 nm incorporating indium composition x ranging from 0.1 to 0.3 with narrow full-width at half-maximum (FWHM) in XRD less than 400 arc-sec which is comparable to MOCVD-grown InAlN. In subsequent works, three sets of InAlN samples grown under typical growth temperatures 400 °C, 450 °C, and 540 °C (dashed line on Figure 3-8) with various thicknesses were extensively studied under conditions shown in Table 3-3. These samples were all grown under N-rich condition so that indium droplets could not form and smooth surfaces can be achieved. Studies of various characteristics of these samples are demonstrated in Chapters 4, 6, 7, and 8.
Table 3-3: Growth condition for A, B, C set of InAlN samples.

<table>
<thead>
<tr>
<th>Sample series</th>
<th>Growth Temp ($^\circ$C)</th>
<th>BEP ratio Al/In</th>
<th>III/V</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>400</td>
<td>1.27</td>
<td>0.60</td>
<td>0.169</td>
</tr>
<tr>
<td>B</td>
<td>450</td>
<td>1.23</td>
<td>0.62</td>
<td>0.182</td>
</tr>
<tr>
<td>C</td>
<td>540</td>
<td>1.01</td>
<td>0.33</td>
<td>0.098</td>
</tr>
</tbody>
</table>

XRD (0002) $\omega$-20 scans and (10\overline{1}5) RSM scans were used to determine their indium incorporation. Figure 3-9 shows the results of (10\overline{1}5) asymmetric RSM.
Figure 3-9: (10\overline{1}5) asymmetric RSM of (a) A set with In composition 16.90%. (b) B set with In composition 18.20%. (c) C set with In composition 9.8%.

It can be observed that all three films have InAlN layer peak aligned to the GaN peak along the x axis, showing InAlN films are all lattice-matched to GaN substrate. Series A and B are regarded as strain free with incorporation 16.9% and 18.20%. The growth temperature for series C is higher, approaching the critical point where In-N
bonds dissociate, and thus there was a lower incorporation of indium, and the film is strained on top of GaN.

### 3.5 Conclusions

We successfully grew smooth GaN buffer layers with RMS = 0.457 nm without Ga droplets under Ga-rich conditions at T₆ = 750 °C. Using these conditions, we achieve a low residual donor concentration of ~6 x 10¹¹ cm⁻², which is much lower than the 2DEG concentration (~0.1%) so that it will not inhibit the device performance. A thin AlN layer with RMS = 0.748 nm is achieved with T₆ = 750 °C. Furthermore, InAlN with RMS ~0.28 nm is successfully grown with XRD FWHM less than 400 arc-sec.
4. InAlN surface cleaning and oxidation

4.1 Introduction

Oxide studies on nitride surfaces are of great importance as they profoundly change the properties of nitrides in the following ways. First, studies show that oxides change the GaN surface due to atomic rearrangement forming electrical states [94-98]. As a result the electrical behavior of nitride materials and devices is modified. Garcia et al. [99] observed an increase in the band bending with oxide formation. Jeon et al. [100] found that the Schottky barrier height of GaN-metal interfaces increased with oxide formation. Higawaki [101] found that oxide formation at the AlGaN surface pinned the Fermi level. Second, oxide formation impacts GaN optical properties through the alteration of the dielectric function: decreasing its real part and increasing imaginary part [102]. Last but not least, oxide removal is a key process required for semiconductor device fabrication [103, 104]. Extensive research in silicon and GaAs shows that oxides can influence epitaxy, defect concentrations and type, metal contact quality etc. For InAlN, oxidation is shown to decrease the 2DEG density and mobility in InAlN/GaN HEMT structures, as well as the gate leakage current [105-107].

4.2 InAlN: native oxide and surface cleaning

Surface cleaning process to remove the native oxide and hydroxides remains a challenge for the nitrides. In situ and ex situ cleaning methods have been explored in order to remove oxides from nitride surfaces to initiate epitaxial growth or fabricate
devices. Argon sputtering has been employed for cleaning [108], however it was found that the surface becomes rough after sputtering and cannot be recovered after annealing. Furthermore, chemical treatments, such as exposure to HF and HCl were found to be relatively effective at removing oxides, however chemical residues such as F and Cl were hard to eliminate [109]. Annealing in NH$_3$ was found to be effective but requires temperatures as high as 1100 °C for the thermal desorption of oxygen [109]. Herein, we carried out experiments and analysis to determine the properties of native oxides on InAlN. In addition, we explored means of removing the oxides.

4.2.1 Experimental

InAlN samples were grown by MBE and exposed to the ambient lab environment for approximately two years. A HF etch and buffered oxide etch (BOE) (10:1) carried out for 10 minutes were explored due to their successes in removing the native oxides of binary nitrides [110]. InAlN samples were first cleaned with trichloroethylene for 5 minutes, acetone for 5 minutes, and methanol for 5 minutes. The samples were then rinsed with deionized water (DI water) for 2 minutes and dried with N$_2$ gas. After this standard solvent cleaning procedure, the samples were etched in HF or BOE. The etched samples were then rinsed with DI water again to remove any residual acid and then dried with N$_2$ gas. After this cleaning procedure, the samples were quickly loaded into the XPS system.
XPS was used to characterize the surface chemistry before and after etch. XPS survey scans (1200 to -5 eV) were conducted with a pass energy of 160 eV and region scans of Al 2p, O 1s, C 1s, In 3d, and N 1s core levels with a pass energy of 20 eV. The instrument was calibrated to an Au 4f\textsubscript{7/2} binding energy of 84.0 eV. Each sample’s spectrum was then calibrated to the C 1s peak at 285.0 eV for possible charging during measurements.

### 4.2.2 Results

From the survey scan the atomic percentage of each element can be deduced. The oxygen atoms percentage at each surface are shown in Table 4-1. After etching, the percentage of oxygen is greatly reduced. The BOE etch is found to be slightly more effective than the HF etch with ~7% more of the oxide removed.

<table>
<thead>
<tr>
<th>Oxygen percentage</th>
<th>Native oxide</th>
<th>HF etch</th>
<th>BOE etch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18.3%</td>
<td>6.51%</td>
<td>5.68%</td>
</tr>
</tbody>
</table>

Figure 4-1 shows the O 1s core level peaks and their fits before and after the two etches. Fitting was done with peaks assigned to In-O-In at 530.0 eV, Al-O-Al at 531.0 eV, In-O-H at 531.6 eV, and Al-O-H at 532.4 eV, following Akazawa et al. [111]. It is observed that before etching, oxides have Al-O-H as the dominant oxide component; the HF and BOE etches remove all or most of the In-O-In and Al-O-Al oxide components,
and attack a large amount of the Al-O-H component, leaving a small amount of Al-O-Al on the surface. The BOE is slightly more effective in reducing the Al-O-Al. Thus, throughout this work, the BOE etching recipe is used for cleaning prior to further treatments.

Figure 4-1: O 1s peak fitting for InAlN before and after two etching methods.
As stated earlier, the Al-related oxides are dominant in comparison to the In-related oxides. This is expected since the concentration of In is less than that of the Al at the surface. The In surface composition can be calculated using the intensities of the In 3d and Al 2p core levels. For this sample, the indium composition is found to be 21%. In addition, the Al oxides are more stable. The Ellingham diagram is a useful tool for showing compound stabilities as a function of temperature. The Ellingham diagram of the Al and In-related oxides is shown in Figure 4-2 [112]. The diagram shows the reaction-specific Gibbs free energy (ΔG) (y-axis) which is a measure of the thermodynamic driving force for the reaction. The Gibbs free energy can be calculated as:

\[ \Delta G = \Delta H - T \Delta S \]  \hspace{1cm} (4.1)

where \( \Delta H \) is the change in enthalpy, \( T \) is absolute temperature, and \( \Delta S \) is the change in entropy. The enthalpy change, \( \Delta H \), stands for the actual energy that is liberated when the reaction occurs. The entropy change, \( \Delta S \), is a measure of the change in the possibilities for disorder in the products compared to the reactants. Since \( \Delta H \) and \( \Delta S \) are usually constant with temperature unless a phase change occurs, a plot of \( \Delta G \) as a function of \( T \) can be drawn as a series of straight lines.

In Figure 4-2, smaller \( \Delta G \) means that the reaction is more likely to occur because the products are more stable. From the diagram we can see that Al\(_2\)O\(_3\) is the more stable oxide compared with In\(_2\)O\(_3\) over the entire temperature range.
However, the above diagram does not consider the hydroxides. The stability of aluminum oxides and aluminum hydroxides has been studied by Digne et al. [113], showing that at room temperature, the more hydrated oxide, Al(OH)$_3$, has a lower surface energy compared with AlOOH and Al$_2$O$_3$ thus being the most stable form of the oxide at room temperature.
Figure 4.3: Surface energy of Al oxides and hydroxides as a function of temperature. Larger $\theta$ value means more hydrated. It shows Al hydroxides are more stable in lower temperature, while Al oxides become more stable with increasing temperature. Figure from Ref. [113].

With an increase in temperature to ~65°C, conversion from Al(OH)$_3$ to AlOOH occurs [114]. Above ~477°C, Al$_2$O$_3$ becomes the most stable form [113]. These results are consistent with our XPS data and analyses showing that the InAlN native oxide possesses aluminum hydroxides as its dominant component at room temperature.

### 4.3 Thermal oxidation of InAlN

Oxidation methods produce high-quality oxides are needed in order to reduce the current collapse phenomena [115] in nitride HEMTs, as well as for applications in gate dielectrics in metal-oxide-semiconductor HEMT (MOS-HEMT) structures to reduce current leakage. Common oxidation methods include annealing [101], ALD [116, 117],
MOCVD deposition [118], MBE deposition [119], photoelectronchemical oxidation [120], and hydrogen peroxide oxidation [121, 122]. These oxidation methods include oxidizing the nitrides directly or depositing other materials such as SiN, MgO, ZrO, SiO₂, HfO₂, and Al₂O₃ etc. on top of the nitride thin film.

Several thermal oxidation studies have been carried out on the binary nitrides AlN [110, 123-125], GaN [96, 97, 110, 126, 127], InN [128-132]. For the ternary nitrides, a lot of studies have been carried out on AlGaN/GaN HEMTs [100, 101, 120, 133-140], but only a few on InGaN [141]. Successful thermal oxidation of InAlN was first studied by Alomari et al. [105, 142, 143] followed by several other groups [106, 107, 144, 145]. These studies use MOCVD-grown InAlN with indium compositions from 13% to 21%. The oxidation took place when the samples were annealed in pure O₂ atmosphere at 600-800 °C for 1-8 minutes. The oxides were found to have thicknesses of ~0.5-3 nm and were crystal [105]. The oxidation mechanism was found to be diffusion-limited. Oxides are discovered to deteriorate the device performance by decreasing the 2DEG density and mobility as well as creating a high density of trap states that cause gate lag.

### 4.3.1 Experimental

Sample B3 with indium incorporation of 18.2% and a thickness of 15 nm is discussed in the following as a representative sample used for the annealing studies. Its growth conditions are listed in detail in Chapter 3.
After growth, the sample was etched in BOE for 10 minutes and dried with N₂ gas to remove the native oxide. A rapid thermal annealing (RTA) was performed to thermally oxidize the films. A longer annealing time was found to result in oxygen diffusion to the InAlN/GaN interface subsequently degrading the 2DEG mobility [106, 107]. Thus, RTA is used here in order to minimize the sample time when ramping up the temperature. This is the first study using RTA for the thermal oxidation of InAlN.

Three different annealing recipes are studied as shown in Table 4-2.

<table>
<thead>
<tr>
<th>Annealing recipe No.</th>
<th>Ambient</th>
<th>Time duration (minutes)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N₂</td>
<td>1</td>
<td>800</td>
</tr>
<tr>
<td>2</td>
<td>air</td>
<td>1</td>
<td>800</td>
</tr>
<tr>
<td>3</td>
<td>air</td>
<td>5</td>
<td>800</td>
</tr>
</tbody>
</table>

The ramping speeds for heating and cooling for all three recipes were kept same. An annealing temperature of 800 °C was chosen since a very low oxide growth rate was observed for annealing below 750 °C [137] for GaN and the oxidation rate significantly increases at higher temperature 875–900 °C. As the oxidation rate for AlN is even lower than that of GaN [138], we expect the annealing temperature for InAlN should be higher than 800 °C. 800 °C is also a typical temperature used in thermal oxidation of InAlN [105-107, 143-145].
After the RTA, the samples were quickly put into XPS vacuum system for further analysis. Previous studies focus on the effect of the oxide on InAlN HEMT device performance, while detailed chemical composition and bonding conditions are lacking. Thus, these properties are studied here.

4.3.2 Results

The estimated oxide layer thicknesses for InAlN before and after each annealing recipe is shown in Figure 4-4. The oxide layer thickness can be estimated using a method for calculating the oxide layer thickness on top of a metal developed by Strohmeier [146] and Carlson et al. [147] following the equation below:

\[ d = \lambda_{ox} \sin \theta \ln \left( \frac{N_m \lambda_m}{N_{ox} \lambda_{ox}} \frac{I_{ox}}{I_m} + 1 \right) \]  

(4.2)

where \( \lambda_{ox} \) and \( \lambda_m \) are the electron inelastic mean free paths for Al 2p photoelectrons generated by Al x-rays in the oxide and metal, \( \theta \) is the photoelectron TOA, \( N_{ox} \) and \( N_m \) are the volume densities of the Al atoms in the oxide and metal layer, \( I_{ox} \) and \( I_m \) are the area intensities of oxide and metal peak components in the around Al 2p region scan. In our study, the inelastic mean free path of Al 2p in InAlN \( \lambda_m \) with a value of 2.9 nm is calculated using the NIST electron effective-attenuation-length database [72] following the theoretical equation developed by S. Tanuma et al. [148]. The volume density of Al in InAlN and oxides will vary with the oxide type—oxide (\( Al_2O_3 \)) or hydroxides (\( Al_2O_3 \cdot xH_2O \)), with different amounts of water bound to
the surface. Comparing to the ratio of 1.5 used for aluminum oxides on aluminum [146], we used a ratio of 1.1 here by considering mass density of AlN to be 3.23 g/cm³, InN 6.81 g/cm³, and Al₂O₃ 3.97 g/cm³ [21]. Note that this method is not a truly accurate measurement of oxide thickness since several parameters are approximations, but gives a rough idea of how much oxide is on top of InAlN.

Figure 4-4: Oxide thickness on sample B3 shown for each treatment condition.

Clearly, the oxygen thicknesses on sample increase with longer annealing time or higher oxygen percentage in the annealing ambient. Interestingly, even after annealing in N₂ ambient, the small amount of oxygen in the chamber increases the amount of oxygen on the sample surface.

XPS O 1s peaks are fit for the BOE etch, and the three annealing conditions so that the oxidation components can be compared (Figure 4-5). The fitting procedure is the
same as our previous O 1s fitting. In-O-In and In-O-H components are too small to be fit in the O 1s peaks, and thus will be analyzed using the In 3d core level spectrum. Al-O-Al and Al-O-H are the dominant components in the O 1s core level spectra.

Figure 4-5: XPS O 1s peaks fitting of sample B3 under different annealing conditions.
Apart from the observation that the Al oxides are dominant, the chemical composition of Al oxides significantly change with different annealing procedures as seen in Figure 4-5. The Al-O-H peak remains relatively stable across different conditions. The Al-O-Al peak increases dramatically with annealing.

The Al 2p spectra are fit with two peaks: Al-N bonding at a lower binding energy and Al-O bonding at higher binding energy with a peak separation of 0.8 eV and a FWHM difference of 0.2 eV. The Al-O bonding is a convolution of both Al-O-Al and Al-O-H components since they are difficult to distinguish due to their similar binding energies [146]. The Al-O peak increases significantly after annealing, confirming the formation of Al₂O₃ on the surfaces.
Figure 4-6: Sample B3 Al 2p peaks fitting (a) Before annealing. (b) After 1 min N$_2$ annealing. (c) After 1 min air annealing. (d) After 5 min air annealing.

The Al oxide composition percentages are determined by calculating by the Al-O / (Al-O + Al-N) ratio and are plotted in Figure 4-7, showing that oxide amounts are increasing on the surface.
Figure 4-7: Al-O percentage in Al 2p peaks calculating by Al-O / (Al-O + Al-N) intensities.

The In 3d 5/2 core level peaks are fit with two peaks assigned to In-N bonding and In-O bonding as shown in Figure 4-8. A peak separation of 1 eV is used for the fit similar to that used for InN/oxide [149].
It is interesting to observe that with annealing in N$_2$, nitrogen seems to replace some amount of oxygen, causing In-O component percentage to decrease, while annealing in air results in growth of the indium-related oxides.

### 4.5 Conclusions

The surface properties of InAlN and surface oxides are studied using XPS. Native oxides are comprised primarily of Al(OH)$_3$, together with AlOOH, In(OH)$_3$, Al$_2$O$_3$ and In$_2$O$_3$. HF and BOE effectively remove most of the native oxide with the
exception of a small amount of Al(OH)$_3$. Finally, RTA is used to demonstrate for the first time the reproducible growth of oxides on InAlN surfaces. Annealing environments of N$_2$ and air are both studied. These thermal oxides are found to be primarily comprised of Al$_2$O$_3$. These chemical composition studies are the basis for our study (Chapter 7) on the impact of the surface oxide on InAlN/GaN surface states and barrier heights.
5. The relationship between strain and composition in InAlN

5.1 Introduction

In this chapter [150], the change in composition of InAlN in the growth direction [0001] is studied and related to the film strain that develops during growth. Bulk InGaN is also studied for comparison. The accommodation of strain during epitaxy is of crucial importance in determining key material parameters including composition and microstructure. The technologically-important InAlN compounds can be grown on GaN using MBE at compositions that are strain-free (In~17%-18% in InAlN [151]), or with compressive or tensile-strain. InGaN can only be grown compressively-strained to GaN. Herein, we focus on the relationship between compositional uniformity as determined by the In incorporation in relation to the Al and Ga (Group III) elements as a function of depth under varying strain conditions, specifically with full strain accommodation or partial relaxation during growth.

The compositional pulling effect is central to this discussion and was first observed in the GaInP/GaAs [152, 153] and AlInAs/InP [154] material systems in which strain was found to perturb the composition so that the lattice mismatch between the epitaxial layer and substrate is minimized. A compositional variation with depth of III-nitride materials was first observed in InGaN grown by MOCVD and has been referred to as a pulling effect implying a similar mechanism to the cases above [155]. A
decreasing indium concentration from the surface of the InGaN to the InGaN/GaN interface was observed with the In composition varying by 6% for a film 75±5 nm thick. In addition, it was found that the higher indium content surface was more relaxed with a tetragonal distortion of -2.17% compared with the bulk having a tetragonal distortion of -2.63%. The authors conclude that strain hinders the incorporation of indium atoms in the InGaN lattice, and is the driving force for the compositional pulling effect observed in InGaN films. Several other groups also observe this pulling effect both in epitaxial InGaN [156] and InGaN/GaN quantum wells [157]. Growth temperature (T_g) and growth rate were both found to modify the indium concentration as a function of depth [158, 159].

For InAlN, compositional changes with depth have been previously observed and discussed in context of the same phenomenon in InGaN but have not been categorized as a pulling effect. Compositionally-graded InAlN films with compressive strain or at the lattice-matched composition have been studied [160-163]. To the best of our understanding, there was no report on the characteristics of compositionally-graded InAlN films with tensile strain prior to our publication on the work reported in this chapter. Also, the relationship between strain accommodation and the incorporation of Group III atoms is still the subject of active discussion and no clear common mechanism has been established for both InGaN and InAlN.
5.2 Experimental

InAlN and InGaN films were grown using a Veeco GEN II RF-plasma-assisted MBE. InGaN films S1 and S2 of ~250 nm thickness were grown on commercial MOCVD GaN templates on sapphire. Growth was initiated with a 50 nm GaN buffer on the template at $T_g = 680 \degree$C under Ga-rich conditions. InGaN films were grown at $T_g = 600 \sim 640 \degree$C. InAlN films S3 and S4 of ~177 nm thickness were grown on commercial hydride vapor phase epitaxy (HVPE) GaN template on sapphire as a substrate. The same GaN buffer was used and InAlN was grown at $T_g = 400 \sim 480 \degree$C with a III/V ratio ~ 1. All films were grown with nitrogen plasma conditions of 350W/1.0sccm.

XPS was carried out using a Kratos Axis UltraTM instrument with a monochromatic Al Kα source of kinetic energy 1486.6 eV. Depth-profiling XPS was achieved using argon ion sputtering of the sample surface between measurements. After each sputtering step, an XPS spectrum was obtained. Survey scans (1200 to -5 eV) were conducted with a pass energy of 160 eV and region scans of Al 2p, O 1s, C 1s, In 3d, Ga 2p, Ga 3d, and N 1s core levels were done with a pass energy of 20 eV. An ion pump current of 1x10^-4A and a stationary ion beam with energy of 2 keV were chosen to minimize damage to the sample surface. The sputter rate of the XPS is determined by three variables: the current flow of electrons, the ion beam energy and the sputter size. Different values of these parameters were used. The optimization of the sputtering process includes: 1) ensuring that the sputter spot overlaps with the x-ray spot position.
2) using a smaller beam energy to minimize physical damage to the sample surface. 3) ensuring that the analyzed area is at least 10 times smaller than the crater size so that edge effects are not present, and finally 4) keeping the current flow constant during sputtering. An analysis spot size of 15 μm was used, as it was approximately 10 times smaller than the sputter crater size. AFM (Bruker Digital Instruments Dimension 3100) is used to characterize the surface morphology.

5.3 Results

Figure 5-1 shows the Ga 2p spectrum acquired during sputtering of a 250 nm-thick InGaN film. The peak located around 1116 eV has an intensity that varies with depth indicating variation in the abundance and chemical environment of the film constituents. The sputter rate was determined using the profilometer after sputtering. The indium composition, x, in In$_x$Ga$_{1-x}$N was calculated using the following equation:

$$x = \frac{\text{Peak intensity (In 3d)}}{\text{RSF (In 3d)}} \cdot \frac{\text{Peak intensity (In 3d)}}{\text{RSF (In 3d)}} + \frac{\text{Peak intensity (Ga 2p)}}{\text{RSF (Ga 2p)}}$$

(5.1)

where the peak intensity is that of the XPS core level peaks, and RSF is the relative sensitivity factor associated with a particular core level provided by CasaXPS software version 2.3.15 [71]. The same calculation is applied to In$_x$Al$_{1-x}$N with Ga substituted by Al.
In order to confirm the reliability of our approach, the compositional profile of a commercial $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ film was obtained. Our results show that the $\text{Al}/(\text{Al+Ga})$ ratio is constant with film depth, however, we determined that the film contained 25% Al instead of its nominal value of 20%. Calculations have shown that the bond energies of AlN, GaN and InN are 11.52 eV/atom, 8.92 eV/atom and 7.72 eV/atom respectively [164]. The weaker Ga-N bond in comparison to the Al-N bond leads to the preferential sputtering of Ga. Therefore, although the absolute value of composition should be corrected due to differences in sputtering rates, the compositional trends in our study are taken as reliable.
High resolution x-ray diffraction (HRXRD) was conducted using a Philips X’Pert PRO HR XRD System with a Cu Ka1 (1.5405 Å) x-ray source and Ge (220) hybrid monochromator to determine the strain of the films. Both rocking curve ω-2θ scans around the (0002) plane and RSM scans conducted around the (10\(\overline{1}5\)) plane using a triple-axis detector was obtained.

Figure 5-2 (a) shows the profiles of the In/(In+Ga) ratio determined using XPS for the InGaN film S1 grown at 600 °C. This InGaN sample is found to have three regions showing clear differences in the In incorporation behavior: a 20 nm indium-rich surface, a region with homogeneous In composition of 75 nm thickness, and a region linearly decreasing in In of 155 nm thickness at the substrate interface. Figure 5-2(b) shows the (10\(\overline{1}5\)) RSM of the S1 film from which we determine that the film is 78% relaxed. The vertical line delineates a pseudomorphically grown epi-layer and the tilted line a fully relaxed epi-layer. Figure 5-2(c) shows the (0002) ω-2θ scan and simulation assuming a constant relaxation and homogeneous composition. The simulation results can be found in Table 5-1, Simulation 1. It can be seen that the InGaN peak located on the left side of GaN peak has a shoulder on the left side. The RSM peak associated with the InGaN is broad, indicating inhomogeneous relaxation throughout the film. By considering relaxation as determined at the edge of the InGaN RSM peak as indicated by the arrow in Figure 5-2(b), a three-layer structure with relaxations of 90%, 80% and 70% can be determined. The new simulation of the ω-2θ scan based on this relaxation profile is
shown in Figure 5-2(d) shows significantly improved agreement with the experimental data. The results are shown in Table 5-1, Simulation 2. Both the XPS data and the XRD-derived composition and thickness profile confirm compositional grading in the film with increasing In composition towards the more relaxed surface. Also, the thicknesses of the three layers obtained with these independent techniques are comparable. Figure 5-2(e) and (f) show the AFM image of the morphology of S1 before and after sputtering, the RMS roughness is 1.96 nm before and 0.465 nm after sputtering for a 2x2 μm² area. This indicates that the surface is smoother after sputtering and the commonly observed roughening of surface with sputtering is not a problem in our study. This is likely a result of the fact that the ion beam energy of 2 keV is small compared with the normally used 5 keV beam energy.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness (nm)</th>
<th>x</th>
<th>Relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>109.26</td>
<td>0.26</td>
<td>78%</td>
</tr>
<tr>
<td>2</td>
<td>56.47</td>
<td>0.25</td>
<td>80%</td>
</tr>
<tr>
<td>3</td>
<td>165.14</td>
<td>0.22</td>
<td>70%</td>
</tr>
</tbody>
</table>

Table 5-1: XRD ω-2θ simulation results of sample S1.
Figure 5-2: (a) XPS In composition profile of sample S1. (b) Asymmetric (1015) RSM of S1. (c)(d) HRXRD triple axis (0002) ω-2θ scan and simulation with one layer structure and with three-layer structure containing different degrees of relaxation. The three-layer structure provides a better simulation match to the experimental data. (e)(f) AFM morphology of S1 before and after sputtering showing that the surface becomes smoother after sputtering.

These same techniques and analysis were used to characterize InGaN film S2, grown at 640 °C. The results are shown in Figure 5-3. The XPS-determined composition profile in Figure 5-3(a) shows that with the exception of a very thin ~ 10 nm surface layer, the In composition is homogeneous with depth. The RSM in Figure 5-3(b) shows that the InGaN peak is directly above the GaN substrate, indicating that S2 is fully strained. Finally, the ω-2θ scan as shown in the inset of Figure 5-3(a) can be simulated.
with a good fit using a single, fully-strained layer with 214.13 nm thickness and 12% indium with a thin 25.72 nm surface containing 15% indium rich layer.

Two InAlN films grown at different temperatures have also been studied. Figure 5-4(a)(b) shows the results for the InAlN film S3 grown at 400 °C. A homogeneous composition with no relaxation is observed. The film possesses 0.65% tensile strain. The ω-2θ scan is well simulated with a 177.73 nm single layer InAlN containing 12% of indium. Figure 5-4(c)(d) shows the results of the InAlN film S4 grown at 480 °C. The indium composition is found to increase from the sample surface to the bulk as shown in Figure 5-4(c). The RSM InAlN peak in Figure 5-4(d) is asymmetric indicating that some of the film is completely strained and some is partially relaxed. The ω-2θ scan (the inset

**Figure 5-3:** (a) Indium composition profile of S2. The inset shows HRXRD triple axis (0002) ω-2θ scan and simulation of S2. (b) Asymmetric (10\overline{1}5) RSM of S2.
of Figure 5-4(c)) is well simulated by a two-layer structure with a 20% partially relaxed surface containing 12% In and a fully strained layer at the substrate with 13% In. A graded composition may yield a better simulation. The XPS and XRD data are in agreement. Both InAlN films are found to have cracks, which can be observed using optical microscopy. These cracks result from the large tensile strain when the In composition is less than 17%.
Figure 5-4: (a)(c) Indium composition profile of S3 and S4. The inset shows HRXRD triple axis (0002) $\omega$-2$\theta$ scan and simulation of S3 and S4. (b)(d) Asymmetric (1015) RSM of S3 and S4.

These results indicate that both for InGaN and InAlN, fully strained samples have homogeneous composition with depth, while relaxed samples show a depth-
dependent indium composition. The XPS results are consistent with XRD simulations when a multi-layer relaxation and graded composition is assumed. However, InGaN and InAlN show different trends in terms of indium composition resulting from non-unity indium incorporation with strain. InGaN has an indium-rich surface, while InAlN has an indium-poor surface.

5.4 Discussion

Our findings can be explained in the context of the recent theoretical framework of J. Zhu et al. showing that impurity formation energy decreases monotonically when the host lattice is strained in the same direction as the volume change induced by the dopant [165]. For InAlN, we can treat the indium atoms as impurities in an AlN host lattice. Because the volume change induced by the impurity (indium) is positive due to the longer In-N bond length in comparison to Al-N, for tensile-strained InAlN, the direction of strain is in the same direction of the volume change. Therefore, the indium formation energy is decreased and the indium incorporation is increased with increasing strain. On the surface of InAlN, when the layer is partially relaxed the strain is reduced and therefore the formation energy is increased which reduces the indium incorporation, thus creating an indium poor surface. For InGaN we treat indium again as an impurity incorporating in a GaN lattice. Here, the In-N bond length is longer than that of Ga-N. Because the films are compressively strained, the strain is in the opposite direction of the volume change so the impurity formation energy increases with larger
strain producing an indium-rich InGaN surface. This explanation is only valid for InGaN with compressive strain and InAlN with tensile strain (In<17\%-18\%) as studied in this work.

For compressively-strained InAlN (In>17\%-18\%), the strain should hinder the incorporation of In so that the layer at the surface will be In rich while the layer closest to the InAlN/GaN interface should contain less In. However, several groups have reported that this prediction is not observed and, in fact, lower In content is found at the surface of compressively-strained InAlN [160-162]. A number of mechanisms leading to this anomalous phenomenon have been proposed. One possible mechanism was articulated by Lorenz et al. [160] with the conjecture that compressively-strained InAlN may obey a mechanism wherein the in-plane lattice parameter remains similar to that of the GaN buffer layer, and strain is relieved via a compositional change towards the lattice matched condition. The same author observed relaxation that could be induced by composition change or lattice-parameter change for similar growth conditions [162].

As there is currently no agreement on mechanism, we here propose a possible mechanism. T. Ive et al. [166] studied MBE-grown InAlN and discovered that InAlN films with In composition larger than or equal to the lattice-matched condition can experience a tensile strain instead of a compressive strain. This tensile strain comes from the nanocolumnar microstructure observed in InAlN films. If these films therefore experience tensile strain, the strain should encourage the incorporation of In, and
therefore the predicted compositional pulling is consistent with the experimental results. This unusual pulling phenomenon for InAlN with In larger than 17~18% is observed in MBE-grown InAlN [161]. A nanocolumnar microstructure was observed to be present in MBE-grown InAlN films [167]. In our MBE-grown InAlN samples, we observe this phenomenon as well. Figure 5-5 shows the plane-view dark field transmission electron microscopy (TEM) images of one InAlN films [168]. Since TEM is sensitive to atomic number, the bright image regions correspond to the In-rich boundaries, while the dark parts correspond to Al-rich centers with diameters of ~10 nm.
Figure 5-5: TEM results of nanocolumnar microstructure in our MBE grown InAlN. (a) High Angel Angular Dark Field (HAADF) planeview image with g=0001 of sample (b) HAADF Cross-section image with g=1100 of sample.

For MOCVD-grown InAlN, this phenomenon exists only for synthesis under low growth temperature less than 800 °C [160, 162]. The low temperature growth condition is conjectured to encourage the formation of a nanocolumnar microstructures [167]. Even for lattice-matched InAlN films, some find that the pulling effect exists [163]. Considering that lattice-matched InAlN films are found to contain tensile strain for specific growth conditions, this could explain the pulling that appeared in the lattice-matched InAlN/GaN system.
5.5 Conclusions

In conclusion, the characterization of compressively-strained InGaN and tensely-strained InAlN shows a relationship between the strain and vertical compositional variation resulting from a variation in indium incorporation. Relaxation can result in an indium-rich InGaN surface layer and an indium-poor InAlN surface layer. The mechanism associated with InAlN having an In composition larger than 17%-18% can be attributed to the tensile strain within the film resulting from the formation of nanocolumnar microstructure.
6. Optical properties of InAlN measured by spectroscopic ellipsometry

6.1 Introduction

Optical characteristics of ternary nitrides, especially an accurate determination of the dielectric function, is crucial in order to gain a better understanding of the basic properties of nitrides including band structure details. Moreover, a better understanding of the dielectric function is essential for the design of photonic devices such as optical waveguides for laser diodes [169] and Bragg reflectors [170] with high reflectivity. Despite its importance, attention to the determination of the dielectric function has been lacking, especially for the ternary alloys. Accurate determination of the dielectric function normally requires a high-quality bulk material, however, ternary nitrides are commonly grown epitaxially on foreign substrates. Thus, good characterization of the dielectric function involves the understanding and modeling of non-ideal materials with surface roughness, interfaces, etc. MOCVD-grown Al-rich InAlN [171, 172] and MBE-grown In-rich InAlN [173] has been studied. Herein, we characterize and analyze MBE-grown Al-rich InAlN, focusing on employing parametric dielectric function model for the InAlN layers with modeling consider non-idea factors to accurately determine absorption edges in InAlN films.
6.2 Dielectric function

The dielectric function of a material describes its response to an applied electric field, for example oscillating light, as a function of the light’s energy, $E$ (wavelength $\lambda$). The complex dielectric function, $\varepsilon$, is composed of a real part, $\varepsilon_1$, and an imaginary part, $\varepsilon_2$, and is expressed as

$$\varepsilon_j(E) = \varepsilon_{j,1}(E) + i \varepsilon_{j,2}(E), \ j = o, e. \quad (6.1)$$

in which, $j$ stands for the two polarization directions, ordinary and extraordinary, corresponding to light polarized either perpendicular or parallel to the optical axis. The real part, $\varepsilon_1$, characterizes the magnitude of the dipole in the material induced by the applied electric field. The imaginary part, $\varepsilon_2$, describes the amount of energy absorbed by the material. The two quantities are related to each other through the Kramers-Kronig relation:

$$\varepsilon_1(E) = 1 + \frac{2}{\pi} \int_{0}^{\infty} \frac{E' \varepsilon_2(E')}{E'^2 - E^2} \, dE' \quad (6.2)$$

where $P$ denotes the Cauchy principal value. The complex refractive index, $N$, is related to $\varepsilon$ through

$$N = \sqrt{\varepsilon} \quad (6.3)$$

With the real part is the refractive index and the imaginary part is the extinction coefficient.
It should be noted that the complex parameter, $\varepsilon$, here represents the pseudo-dielectric properties of the whole sample including the InAlN, the interface, and the GaN buffer and substrate etc.; the real dielectric function of the InAlN layer can only be obtained by modeling and fitting the spectrum. Comparison between real and pseudo-dielectric function of InAlN films is shown in Figure 6-1 [21]. For the pseudo-dielectric function (Figure 6-1 (b)), the part of the spectrum below the GaN band gap (3.42 eV) shows interference characteristics within the film. The peak around 3.42 eV illustrates absorption by the GaN band gap. The InAlN is too thin (2.5-25 nm) for any obvious peak associated with the epitaxial layer to be detected.

![Graphs showing dielectric function of InAlN and InAlN/GaN](image)

**Figure 6-1:** Comparison between (a) True dielectric function of InAlN. (b) Pseudo-dielectric function of InAlN/GaN structure.

The first step in modeling is to choose an appropriate dispersion equation to describe the material, in this case the InAlN. Dispersion equations are mathematical representations of the dielectric function, which can be used to generate a simpler
description of the dielectric function with using minimal parameters. The dispersion
equation commonly used for semiconductors is the Tauc-Lorentz formula [174] which is
applied in this work. The imaginary part, $\varepsilon_2$, in this model is described by multiplying
the Tauc joint density of states by the Lorentz oscillator model. The real part, $\varepsilon_1$, is
determined using the Kramers-Kronig relation relating the real and imaginary parts
following equation (6.2). Sakalauskas et al. [171] showed that three high-energy critical
points (CPs) are found around 7–9 eV. Considering these CPs, we use the Tauc-Lorentz
formula with two oscillators to describe the dielectric function of InAlN, one accounting
for band gap absorption, the other accounting for the tail of the higher energy CPs
considering they are located relatively close to each other. Thus the imaginary and real
part is expressed as:

$$
\varepsilon_2 = \begin{cases} 
\sum_{i=1}^{2} \frac{A_i \cdot E_i \cdot C_i \cdot (E - E_g)^2}{(E^2 - E_i^2)^2 + C_i^2 \cdot E^2}, & E > E_g \\
0, & E \leq E_g 
\end{cases}
$$

$$
\varepsilon_1 = \varepsilon_\infty + \sum_{i=1}^{2} \frac{2}{\pi} \cdot P \cdot \int_{E_g}^{\infty} \frac{\xi \cdot \varepsilon_1(\xi)}{\xi^2 - E^2} \, d\xi
$$

Eight parameters are included in this model with $\varepsilon_\infty$ denoting the high frequency
dielectric constant, $E_g$ denoting the optical band gap, $A_{1,2}, E_{1,2}, C_{1,2}$ representing the
intensity, energy position, and broadening of the first and second oscillator peaks,
respectively. Fittings are processed by feeding this parametric model of InAlN’s
dielectric function and each layer’s thickness into the HORIBA DeltaPsi 2 software [75]

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and optimizing the eight parameters and thicknesses so that the spectrum fit is close to measured data.

### 6.3 Non-ideal factors

The previous discussion focuses on an ideal clean, good-quality semiconductor film sitting on a substrate with a perfect interface. However, the real situation calls for fitting using a more complicated structure which includes non-idealities such as surface roughness, interface roughness, etc. In order to know how these factors influence the measured spectra, a sensitivity analysis based on an AlGaN/GaN heterostructure is shown below. We used AlGaN instead of InAlN since the dielectric function of AlGaN is relatively well known [21]. Moreover, InAlN shares similar optical properties with AlGaN. The dielectric function of GaN used here is obtained experimentally using *in situ* SE. The dielectric function of AlGaN is described by an analytical model developed by R. Goldhahn et al. [21] for Al$_{0.3}$Ga$_{0.7}$N, a composition typical for AlGaN/GaN HEMT applications. The model describes the imaginary part, $\varepsilon_2$, with both a low-energy and a high-energy terms. The low-energy term originates from contributions around band gap including the bound exciton states below the band gap and the exciton continuum term. The high-energy term arises from the high-energy critical points. Parameters used in the model are extrapolated from AlN and GaN with a bowing parameter [21]. The dielectric function of a HEMT structure grown on a SiC substrate and comprised of a 2µm GaN buffer layer and a 25 nm Al$_{0.3}$Ga$_{0.7}$N barrier layer is simulated (see Figure 6-2).
Figure 6-2: AlGaN/GaN HEMT structure used in the dielectric function simulations.

6.3.1 Surface oxides

Surface oxides are known to readily form on nitride surfaces under ambient conditions in just seconds, and it has been shown experimentally that the presence of an oxide can significantly change the pseudo-dielectric function of nitrides [102]. A comparison of the pseudo-dielectric function of AlGaN/GaN HEMT with a 1 nm Al₂O₃ added to the simulation structure and without Al₂O₃ is simulated in Figure 6-3. It shows that with only a 1 nm oxide layer, the higher energy term has a decreased real part and the imaginary part is increased significantly. Thus, the impact of the oxide on the dielectric function should be considered in simulations.
6.3.2 Surface roughness

Surface roughness is another important factor affecting the ellipsometry spectrum. To achieve a simulation of the roughness, the structure is simulated by replacing 1 nm of the AlGaN layer at the surface with “roughness” obtained by mixing 50% AlGaN with 50% voids. Results are shown in Figure 6-4. It is revealed that with only 1 nm of surface roughness, the spectrum is changed: the real part decreased in the energy range higher than band gap, and the imaginary part increased across the entire energy range.
Figure 6-4: Surface roughness effects on the real and dielectric part of the pseudo-dielectric functions.

6.3.3 Non-abrupt interlayer

A non-abrupt interlayer is always present due to machine limitations in switching between materials. In order to simulate this effect, a 1 nm intermixing layer comprised of 50% AlGaN and 50% GaN is added to the AlGaN/GaN interface. The simulation results are shown in Figure 6-5. With the intermixing layer added, the interference characteristics in the lower energy range change while the higher energy range part is not affected.
Figure 6-5: Non-abrupt interface effect on the real and imaginary parts of the pseudo-dielectric functions.

### 6.3.4 InAlN nanocolumnar microstructure

MBE-grown InAlN is observed by many to possess a lateral composition modulation or nanocolumnar microstructure [167, 175, 176] as mentioned in Chapter 5. This structure is honeycomb-like with Al-rich centers on the order of 5-10 nm in diameter and In-rich boundaries of 1-2 nm. Zhou et al. [176] suggested that the lateral and vertical honeycomb structure may form in order to efficiently relax during coalescence of nuclei on the initiation of growth possessing non-uniform (in-plane) composition due to the large difference in Al-N and In-N bond strengths and lattice-constants. Figure 6-6 shows dark field TEM images of two of our MBE-grown InAlN films grown at a temperature of 400 °C and 540 °C [168]. The bright image regions are...
In-rich boundaries and the dart regions are Al-rich based on the mechanism that TEM is sensitive to atomic number. It is interesting to observe that the sample grown at 400 °C with indium composition of 12% has larger contrast in the plane-view TEM with the nanocolumnar microstructure starting from the InAlN/GaN interface. This is in contrast to the sample grown at 540 °C with indium composition of 17% which has less contrast and the nanocolumnar microstructure starting at a later depth in the epitaxial film, i.e. not at the substrate/buffer interface. These observations are considered in the following simulation.

Figure 6-6: TEM results of nanocolumnar structure in our MBE grown InAlN in different growth conditions. High Angel Angular Dark Field (HAADF) planeview image with g=0001 of sample (a) InAlN grown in 400°C and (b) InAlN grown in 540 °C. HAADF Cross-section image with g=1100 of sample (c) InAlN grown in 400 °C and (d) InAlN grown in 540 °C.
6.4 Results

6.4.1 InAlN/GaN structure

The fitting of SE data involves several steps as described earlier. In this case, the surface oxide is not included in the model since our ellipsometry is in situ, and the samples are measured right after growth and are not oxidized.

The pseudo-dielectric function of the GaN buffer together with the GaN template/sapphire substrate was measured in situ after the GaN buffer growth. The InAlN is described using a Tauc-Lorentz dispersion formula with two oscillators, as discussed above. The parameters of the Tauc-Lorentz dispersion, layer thicknesses, and percentage of InAlN phases were estimated. Then, the pseudo-dielectric functions were calculated based on the layer structure and compared to the experimental data. The unknown parameters were fit so that the calculated spectrum is as close to the experimental data as possible. The fitting process shows that it is impossible to fit the samples properly with only one compositional phase. Considering the TEM results shown above, a two-phase model was utilized wherein phase 1 refers to the in-poor regions inside the nanocolumns and phase 2 refers to the In-rich regions at the boundaries. Thus, phase 1 is expected to have a higher volume percentage and larger band gap since it is more Al-rich. The phase 1 volume percentage varies from 77% to 87% as obtained from fitting different samples. Interface and/or surface roughness was
added to the models when necessary. The final model for InAlN/GaN heterostructures is shown in Figure 6-7.

![Diagram of InAlN + Air mixture, showing InAlN Phase 1, InAlN Phase 2, GaN + AlN mixture, GaN Buffer, and GaN/Sapphire Substrate]

**Figure 6-7: Model for InAlN SE fitting.**

Three samples of 15 nm thicknesses were grown under conditions shown in Chapter 2 and Table 6-1.

<table>
<thead>
<tr>
<th>Sample series</th>
<th>Growth Temp (°C)</th>
<th>BEP ratio Al/In</th>
<th>III/V</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>400</td>
<td>1.27</td>
<td>0.60</td>
<td>0.169</td>
</tr>
<tr>
<td>B</td>
<td>450</td>
<td>1.23</td>
<td>0.62</td>
<td>0.182</td>
</tr>
<tr>
<td>C</td>
<td>540</td>
<td>1.01</td>
<td>0.33</td>
<td>0.098</td>
</tr>
</tbody>
</table>

**Table 6-1: Growth condition for A, B, C set of samples.**

The dielectric functions of phase 1 from the InAlN obtained from the SE fitting is shown in Figure 6-8. It can be seen that the imaginary part, \( \varepsilon_2 \), red-shifts with increasing In composition. Similar behavior is observed for phase 2.
Figure 6-8: Real and imaginary part of phase 1 dielectric function for A, B, and C series. Inset presenting a zoomed-in view of imaginary part showing red shift of with increasing indium composition.

The absorption energy, $E_A$, corresponding to both phases is obtained by plotting $(\alpha n E)^2$ as a function of $E$, and performing a linear extrapolation to zero, in which $\alpha$ is the absorption coefficient, $n$ is the refractive index, and $E$ is the photon energy [177]. The process is shown in Figure 6-9.
Figure 6-9: $(\alpha n E)^2$ as a function of photon energy. Dotted line shows how absorption energy $E_A$ is determined.

The calculated $E_A$ for phase 1 and phase 2 for each sample is shown in Table 6-2 and Figure 6-10(a). Both phases 1 and 2 show red shifts of the adsorption edge with increasing bulk indium composition determined by XRD, indicating that the indium composition both inside and outside of the honeycomb structure follows the same trend. Figure 6-10(b) shows the $E_A$ difference of phases 1 and 2 as a function of growth temperature. It is interesting to see that this difference decreases almost linearly with increasing growth temperature. We speculate that at higher growth temperatures, the film is more uniform and the two phases have more similar compositions. From the TEM images shown in Figure 6-6, it can be observed that the film grown at 540 °C with 17% indium composition has a less well developed nanocolumnar microstructure.
compared with the film grown at 400 °C with 12% indium. Since SE is a measurement that averages the properties of the entire film, it is speculated that the less well developed and therefore smaller volume of the nanocolumnar microstructures causes the average characteristics of the two phases to be relatively similar. Strain might also play a role here due to compositional difference but is not studied in this research.

Table 6-2: Simulated results for phase 1 and phase 2.

<table>
<thead>
<tr>
<th>Growth temp (°C)</th>
<th>Indium composition x</th>
<th>Phase 1 $E_A$ (eV)</th>
<th>Phase 2 $E_A$ (eV)</th>
<th>$E_A$ difference (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 400</td>
<td>0.169</td>
<td>4.57</td>
<td>2.75</td>
<td>1.82</td>
</tr>
<tr>
<td>B 450</td>
<td>0.182</td>
<td>4.42</td>
<td>2.75</td>
<td>1.67</td>
</tr>
<tr>
<td>C 540</td>
<td>0.098</td>
<td>4.95</td>
<td>3.95</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Figure 6-10: (a) $E_A$ of phase 1 and phase 2 for three series as a function of indium composition x. (b) $E_A$ separation of phase 1 and 2 for three series as a function of growth temperature.
6.4.2 InAlN/AlN/GaN structure

Apart from the growth conditions of InAlN, it is believed that the initiating layer for InAlN growth is also an important characteristic affecting InAlN properties. AlN layer can induce extra strain stress due to its lattice mismatch with GaN affecting InAlN. Also, the surface roughness might change with AlN added. Moreover, surface reconstruction is changed thus might alter atom binding condition or migrate properties.

To understand this better, a set of samples were prepared with structures shown in Figure 6-11.

![Sample structures for studying AlN interlayer's influence on optical properties.](image)

**Figure 6-11:** Sample structures for studying AlN interlayer’s influence on optical properties.

All three samples have 20 nm InAlN grown under the same growth conditions at \( T_g = 400 \degree C \). D2 has a 300 nm GaN buffer grown at 750 \degree C compared to D1 with a 50 nm GaN buffer grown at 680 \degree C. D3 has the same GaN buffer with D2 and is the only sample in the set that has a 1 nm AlN interlayer inserted between the InAlN and GaN.
buffer. A HRXRD (0002) $\omega$-2θ scan performed on D3 showed that the InAlN has an In composition of 15.89% and the AlN layer has a thickness of 0.8 nm (Figure 6-12).

Figure 6-12: HRXRD (0002) $\omega$-2θ scan and fitting of D3 film.

The calculated absorption edges for both InAlN phases are shown in Figure 6-13. D1 and D2 show similar absorption edges for both phase 1 and phase 2. However, D3 with an AlN layer inserted shows red shift of phase 1 and blue shift of phase 2, demonstrating the two phases have closer absorption edge energies compared with D1 and D2. This indicates that the two phases should contain closer compositions.
Figure 6-13: Simulated $(\alpha n E)^2$ as a function of photon energy showing the absorption edge of (a) phase 1 and (b) phase 2.

VDP Hall measurements were performed for these three samples and the results are shown in Table 6-3 and Figure 6-14. It can be seen that by including the AlN layer the 2DEG density increases slightly while the mobility of the 2DEG is almost five times larger than that without AlN insertion layer. The sheet resistance of D3 is greatly reduced due to the increase in the mobility.

Table 6-3: VDP results of D1, D2 and D3 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_s$ (ohm/sq)</th>
<th>$n_e$ ($10^{13}$ cm$^{-2}$)</th>
<th>Mobility (cm$^2$/VS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>2531</td>
<td>2.210</td>
<td>112</td>
</tr>
<tr>
<td>D2</td>
<td>2950</td>
<td>1.579</td>
<td>134</td>
</tr>
<tr>
<td>D3</td>
<td>552.4</td>
<td>1.820</td>
<td>621</td>
</tr>
</tbody>
</table>
Figure 6-14: Sheet resistance and mobility of D1, D2, and D3 samples measured from VDP.

The possible mechanisms responsible for the improvement of 2DEG mobility with the AlN layer insertion are listed in the following.

First, without the AlN layer, the 2DEG penetrate into the InAlN experiencing alloy disorder scattering [178]. Also, poor quality InAlN may degrade the mobility through additional scattering. The AlN separates the 2DEG from the InAlN and should reduce scattering. Second, SE results show that without the AlN layer, InAlN possesses more severe compositional non-uniformity possibly related to the nanocolumnar microstructure. From the TEM results (Figure 6-6), it can be observed that the nanocolumnar microstructure is randomly distributed through the film, i.e. it is not a strict periodic structure. It is shown in Table 1-2 that InN has a spontaneous polarization value only half of that of AlN. Thus, in the indium-rich boundaries, the polarization
dipole is less than that in the middle as shown in Figure 6-15. Thus, localization of the 2DEG in the middle of the microstructure will degrade the mobility. Moreover, Jena et al. [179] demonstrated a scattering mechanism named dipole scattering which is caused by random fluctuations in the distributed dipoles. The 2DEG will experience dipole scattering which degrades mobility as well.

![Figure 6-15: Model of nanocolumnar microstructure in InAlN showing localized 2DEG and randomly distributed dipoles.](image)

### 6.5 Conclusions

In this chapter, we showed that SE is a non-destructive and sensitive method useful for nitride material characterization even when nonidealities exist. The true dielectric function of InAlN is extracted by modeling the pseudo-dielectric functions of InAlN/GaN with a two-phase model likely due to the nanocolumnar microstructure observed in MBE-grown InAlN. An increase in growth temperature is shown to minimize this effect.
The AlN insertion layer positively impacts the InAlN layer by increasing its compositional uniformity and increasing the mobility of 2DEG by five fold in the GaN channel.
7. Surface states and the bare surface barrier height characteristics of InAlN/GaN heterostructures

7.1 Introduction

InAlN/GaN heterostructures have attracted significant interest for electronics since Kuzmik et al. reported on its promise for HEMTs in 2001 [8]. Its unique advantage lies in making HEMTs that could provide better electrical, mechanical, and thermal characteristics than traditional AlGaN/GaN HEMTs.

Among all the properties of HEMTs, the 2DEG characteristics are key to device performance. The most widely accepted theory on the origin of the 2DEG states that the abrupt polarization change at the heterostructure interface causes a positive polarization sheet charge, attracting a 2DEG to the GaN close to the interface. The source of the electrons comprising the 2DEG is surface donor states [180, 181]. Possible sources of charges in the HEMT structure include (Figure 7-1):

1. Spontaneous polarization-induced charge at the InAlN surface and at the InAlN/GaN interface. Since our structure is grown on [0001] direction, the surface charge is negative and denoted as $-\sigma_{SP}$, while the interface charge is positive and denoted as $\sigma_{SP}$

2. Negative 2DEG charge $n_s$ at GaN surface close to InAlN

3. Ionized surface states charge $\sigma_{Surface}$

4. Buffer charge in GaN $\sigma_{Buffer}$
Charge neutrality requires:

\[ n_s + \sigma_{Surface} + \sigma_{Buffer} + \sigma_{SP} - \sigma_{SP} = 0 \]  
\[(7.1)\]

In Chapter 3 the Hall measurements show that the buffer charge \(\sigma_{Buffer}\) in GaN is very small in comparison to the 2DEG (~0.1%) so this term can be omitted.

Considering the positive and negative polarization charges cancel each other, we have:

\[ n_s = -\sigma_{Surface} \]  
\[(7.2)\]

The 2DEG density should be equal to the number of ionized positive donor surface states.

![Figure 7-1: Sources of charge in InAlN/GaN HEMT structure.](image)

Donor-type surface states are charge-neutral when occupied, and positive when emptied. The Fermi level position relative to the energy of the surface states determines their occupation. The states above the Fermi level are empty and therefore positive,
while the states below the Fermi level are occupied and therefore neutral. If all of the states are below the Fermi level, there should be no 2DEG. This is the case for the InAlN/GaN structure when the InAlN layer is less than ~2 nm (Figure 7-2).

The spontaneous polarization induces an internal electric field in the InAlN or AlGaN layer so that their bands bend upwards naturally. This causes the Fermi level to move to a lower energy within the band gap with increasing barrier layer thickness as seen in Figure 7-2. Eventually, the Fermi level will meet the energy of the surface states ionizing them resulting in electron donation to the 2DEG. This model is supported experimentally wherein it was shown that the 2DEG concentration in an AlGaN/GaN structure increased with the AlGaN barrier thickness [182].

Figure 7-2: The 2DEG originates from surface states donation.
Thus, to understand the origin, density, and energies of surface states and how surface states can affect the 2DEG properties and device performance is of significant importance.

Although the relationship between surface donor states and the 2DEG is generally accepted, the energy distribution and density of surface states remain unclear. Studies report a variety of surface states properties. For AlGaN, two different distributions have been revealed experimentally described herein.

1) Surface states reside at a single energy level with relatively high density [180, 183, 184]. For example, Al$_{0.34}$Ga$_{0.66}$N is found to have surface states residing 1.65 eV below conduction band minimum (CBM) [180].

2) Surface states distribute over a large energy range with a relatively low density [181, 185-188]. For example, Al$_{0.35}$Ga$_{0.65}$N is found to have surface states residing in the energy 1.0-1.8 eV below CBM [182].

For InAlN, only one study by Pandey et al. on Schottky junctions fabricated on InAlN/AlN/GaN heterostructure indicating distributed surface states is found. The density of surface donor state is estimated to be $2.7 \times 10^{13}$ cm$^{-2}$eV$^{-1}$ by simulating 2DEG density as a function of Schottky barrier height. No bare InAlN/GaN heterostructure samples have been studied to author’s best knowledge. Thus, in this work, we studied the properties of surface states of InAlN/GaN heterostructures. Moreover, InAlN with different indium compositions are studied.
7.2 Surface states and bare surface barrier height on clean InAlN/GaN surfaces

7.2.1 Experimental

In this work, the properties of surface states at a clean InAlN/GaN heterostructure without oxidation are studied first. InAlN/GaN were grown by PAMBE with a structure shown in Figure 7-3.

![Figure 7-3: MBE grown InAlN/GaN heterostructure.](image)

Three series of InAlN samples discussed in Chapter 3 were used for surface states study with detailed growth conditions listed in Table 7-1.

<table>
<thead>
<tr>
<th>Sample series</th>
<th>Growth Temp (°C)</th>
<th>BEP ratio Al/In</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>400</td>
<td>1.27</td>
<td>2.5, 7, 15</td>
</tr>
<tr>
<td>B</td>
<td>450</td>
<td>1.23</td>
<td>2.5, 7, 15, 20, 25</td>
</tr>
<tr>
<td>C</td>
<td>540</td>
<td>1.01</td>
<td>2.5, 5, 7, 15</td>
</tr>
</tbody>
</table>
In each series, the only difference between samples is the InAlN epi-layer thickness, all of the other growth conditions are kept same. The as-grown samples were prepared for characterization with standard solvent cleaning procedures followed by a 10-minute etch in BOE.

HRXRD was used to characterize the indium incorporation in the InAlN films using a Philips X’Pert PRO HR XRD System with a Cu Ka1 (1.5405 Å) x-ray source and Ge (220) hybrid monochromator. SE measurements over the range of 1.5 eV to 6.0 eV were carried out in situ after the films were grown and cooled to room temperature. XPS was conducted using a Kratos Axis UltraTM instrument with a monochromatic Al Kα source of kinetic energy of 1486.6 eV. Both survey scans and regional scans of In 3d, Al 2p, N 1s, C 1s, and O 1s are obtained. The instrument was calibrated to and Au 4f7/2 binding energy of 84.00 eV.

### 7.2.2 Results

To obtain the dielectric function of InAlN layers, a systematic simulation of SE is conducted for these samples using HORIBA DeltaPsi 2 software [75]. Details of SE analysis can be found in Chapter 6. The calculated band gaps of the samples are listed in Table 7-2.

The energy separation between the Fermi level and VBM was extracted using XPS. The linear extrapolation of the valence band edge to the background was fit. The XPS spectra was calibrated to the C 1s at 285.0 eV.
The bare surface barrier height (BSBH) is defined as the distance between the conduction band minimum and the Fermi level at the surface when no metal or other materials are deposited on the surface as shown in Figure 7-4.

![Figure 7-4: Schematic band diagram showing BSBH relations to band gap and VBM](image)

The BSBH was calculated by subtracting the VBM from the band gap for each sample. The measured data and calculated BSBH values are summarized in Table 7-2.
Table 7-2: Calculated BSBH and measured data of InAlN films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$x$</th>
<th>Thickness (nm)</th>
<th>$E_A$ (eV)</th>
<th>VBM (eV)</th>
<th>BSBH (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.169</td>
<td>2.5</td>
<td>4.57</td>
<td>2.02</td>
<td>2.55</td>
</tr>
<tr>
<td>A2</td>
<td>0.169</td>
<td>7</td>
<td>4.56</td>
<td>1.61</td>
<td>2.95</td>
</tr>
<tr>
<td>A3</td>
<td>0.169</td>
<td>15</td>
<td>4.57</td>
<td>1.69</td>
<td>2.88</td>
</tr>
<tr>
<td>B1</td>
<td>0.182</td>
<td>2.5</td>
<td>4.35</td>
<td>2.29</td>
<td>2.06</td>
</tr>
<tr>
<td>B2</td>
<td>0.182</td>
<td>7</td>
<td>4.37</td>
<td>1.9</td>
<td>2.47</td>
</tr>
<tr>
<td>B3</td>
<td>0.182</td>
<td>15</td>
<td>4.36</td>
<td>1.91</td>
<td>2.45</td>
</tr>
<tr>
<td>B4</td>
<td>0.182</td>
<td>20</td>
<td>4.35</td>
<td>1.87</td>
<td>2.48</td>
</tr>
<tr>
<td>B5</td>
<td>0.182</td>
<td>25</td>
<td>4.39</td>
<td>1.85</td>
<td>2.54</td>
</tr>
<tr>
<td>C1</td>
<td>0.098</td>
<td>2.5</td>
<td>4.88</td>
<td>2.41</td>
<td>2.47</td>
</tr>
<tr>
<td>C2</td>
<td>0.098</td>
<td>5</td>
<td>4.88</td>
<td>2.09</td>
<td>2.79</td>
</tr>
<tr>
<td>C3</td>
<td>0.098</td>
<td>7</td>
<td>4.85</td>
<td>1.97</td>
<td>2.88</td>
</tr>
<tr>
<td>C4</td>
<td>0.098</td>
<td>15</td>
<td>4.92</td>
<td>1.90</td>
<td>3.02</td>
</tr>
</tbody>
</table>

7.2.3 Modeling the bare surface barrier height

From Table 7-2 we can tell, for all three series, that all of the BSBH values have the tendency to increase at first and then saturate at a certain thickness. If surface states reside at a single energy level, when the thickness of InAlN is small, the Fermi level is higher than the surface states level (Figure 7-5 (a)), and no 2DEG is formed. As the thickness of the InAlN increases, the donor states rises due to polarization caused by band bending until it reaches the Fermi level and starts to donate electrons to the 2DEG. Since the concentration of donors is high, a small movement of the Fermi level donates a large concentration of electrons to the 2DEG, and the Fermi level is pinned at the donor level, resulting in constant BSBH with thickness. If the surface states are distributed over
a specific energy range (Figure 7-5 (b)), once the Fermi level reaches the donor level, it is not pinned and the BSBH changes as a function of InAlN thickness. From our data, we can see that Fermi level is not pinned and increases with InAlN thickness. This is an indication that the surface states density is relatively low. The slope of the BSBH provides insight into the distributed surface states density.

An analytical physical model is used to calculate the concentration of distributed surface states [186]. This model relates the BSBH to thickness and is given by:

$$q\Phi_b = \frac{(n_0E_d + \sigma_{pz}/q)d + \epsilon_{InAIN}\Delta E_c/q^2}{n_0(d + \epsilon_{InAIN}/q^2n_0)}$$  \hspace{1cm} (7.3)

in which, $q\Phi_b$ is the BSBH, $n_0$ is the density of surface states per unit area and energy, the energy distribution of surface states start from $E_d$ below the CBM as shown in Figure 7-5, $\sigma_{pz}$ is the positive density surface charge at the heterojunction interface, $q$ is the electron charge, $d$ is the barrier thickness, $\epsilon_{InAIN}$ is the permittivity of InAlN, $\Delta E_c$ is the

![Figure 7-5: Two models of surface states distribution. (a) Surface states reside in single energy position with high density. (b) Surface states span an energy range with relatively low density.](image)
conduction band offset (CBO) between InAlN and GaN. In this equation, the BSBH and thickness are given by experimental data and $E_d$ and $n_0$ are fitting parameters. To get a better idea of how this model works, different $n_0$ and $E_d$ values are tried as shown in Figure 7-6. We can observe that the slope of BSBH significantly affected by the $n_0$ value (Figure 7-6 (b)). Higher $n_0$ leads to earlier saturation of the BSBH which shows a flatter BSBH slope. The final saturated BSBH is determined by both $n_0$ and $E_d$: higher $n_0$ leads to a lower BSBH saturation value, while higher $E_d$ leads to larger BSBH saturation value. This can also be confirmed with equation (7.3): for sufficiently large thickness $d$, BSBH will finally saturation at a value $E_d + \sigma_{pz} / qn_0$, which is a function of both $E_d$ and $n_0$.

![Figure 7-6: Simulation of BSBH as a function of InAlN layer thickness. (a) Various $E_d$ values. (b) Various $n_0$ values.](image)

Fitting constants are chosen as shown in Table 7-3. The CBO is calculated using

$$\text{CBO} = \text{Band Gap}_{\text{GaN}} - \text{Band Gap}_{\text{InAlN}} - VBO$$

(7.4)
with a GaN band gap of 3.42 eV, the band gap of InAlN determined by SE simulation, and the valence band offset (VBO) is measured and calculated as explained in detail in Chapter 8. The spontaneous polarization charge difference between InAlN and GaN $\sigma$ and the InAlN permittivity $\varepsilon$ values are obtained from Gonschorek et al. [189].

**Table 7-3: Chosen simulation parameters, spontaneous polarization charge and permittivity values from Ref. [189].**

<table>
<thead>
<tr>
<th>Series</th>
<th>CBO (eV)</th>
<th>$\sigma/e$ ($10^{13}$cm$^{-2}$)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.02</td>
<td>3.4499</td>
<td>11.3917</td>
</tr>
<tr>
<td>B</td>
<td>0.84</td>
<td>3.3403</td>
<td>11.5339</td>
</tr>
<tr>
<td>C</td>
<td>1.25</td>
<td>4.6506</td>
<td>10.8655</td>
</tr>
</tbody>
</table>

A fitting of our data yielded the results listed in Table 7-4 and Figure 7-7. A detailed description of the Matlab codes used for this purpose is presented in Appendix B. In this table, the surface states density $n_0$ and $E_d$ are fitting parameters to best fit the experimental data. The saturation energy is obtained by calculating the BSBH with InAlN having a thickness of 30 nm. At this thickness, the BSBH is saturated and pinned. The energy distribution is calculated by subtracting the saturation energy by $E_d$, indicating the energy range of the surface states affecting the BSBH and responsible for the 2DEG.
Table 7-4: Surface states distribution simulation results with clean InAlN surfaces.

<table>
<thead>
<tr>
<th>Sample series</th>
<th>$n_0 \times 10^{13} \text{cm}^{-2}\text{eV}^{-1}$</th>
<th>$E_d \text{ (eV)}$</th>
<th>Saturation energy (eV)</th>
<th>Energy distribution (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8.27</td>
<td>2.63</td>
<td>3.00</td>
<td>0.37</td>
</tr>
<tr>
<td>B</td>
<td>6.81</td>
<td>2.10</td>
<td>2.54</td>
<td>0.44</td>
</tr>
<tr>
<td>C</td>
<td>4.64</td>
<td>2.17</td>
<td>3.09</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Figure 7-7: Simulation of BSBH as a function of thickness for series A, B, and C.

Set A samples are characterized using VDP Hall measurements. With increasing thickness, the 2DEG density increases at first and then saturates. The measured 2DEG density is plotted as a function of the BSBH in Figure 7-8.
Figure 7-8: The 2DEG as a function of BSBH, fitted line given surface donor states density.

If the surface states are distributed with a constant density, increasing BSBH, which changes the occupation of the state, the 2DEG density will increase. To maintain charge neutrality, the emptied surface states charge equals the increased 2DEG population. Thus, the slope of the fitted linear line represents the surface states charge change related to the BSBH change, which is the density of surface donor states \([182]\). A density of \(8.47 \times 10^{13} \text{ cm}^{-2} \text{eV}^{-1}\) was obtained by this method which is consistent with BSBH modeling with a density of \(8.27 \times 10^{13} \text{ cm}^{-2} \text{eV}^{-1}\) shown in Table 7-4.

From the results in Table 7-4, we can first observe that the surface states density \(n_0\) varies from \(4.64\) to \(8.27 \times 10^{13} \text{ cm}^{-2} \text{eV}^{-1}\). Compared with the literature, the density of surface states is higher than that for AlGaN, which is around \(1 \times 10^{13} \text{ cm}^{-2} \text{eV}^{-1}\) [187] and higher than that for MOCVD-grown InAlN/AlN/GaN with density of \(2.7 \times 10^{13} \text{ cm}^{-2} \text{eV}^{-1}\) [190]. Additionally, surface states density and energy distribution from 2DEG.
Table 7-4 are plotted in Figure 7-9 for comparison.

![Figure 7-9: Surface states density and energy distribution of set A, B, and C films. Surface indium composition x are calculated using XPS.](image)

It can be observed that the surface states density and energy distribution vary with different growth conditions. In incorporation x is expected to be the main factor impacting properties of surface states due to material difference between AlN and InN. However, the bulk indium incorporation does not directly relate to surface states distribution. XPS region scan peak intensities are used for calculating the surface indium composition x with results shown in Figure 7-9. It shows surface states distribution are more related to surface indium composition instead of the bulk indium composition. With more indium composition on the surface, surface states have higher density and narrower energy distribution.
7.3 Surface states and the bare surface barrier height on oxidized InAlN/GaN surfaces

7.3.1 Introduction

At this point we have an idea of how surface donor states are energetically distributed at clean InAlN/GaN surfaces. Moreover, oxides have been found to play a significant role in the formation of surface states for III-N compounds. For example, Dong et al. studied distributed surface states around the mid-gap of GaN resulting from an amorphous oxide layer [94], Al_{0.4}Ga_{0.6}N oxidized at a high temperature is found to have its Fermi level pinned approximately 3 eV below the CBM [191], possibly due to pinning by surface states. Similar observations are found by Masataka et al. [101]. Thus, the oxidation conditions and their effect on surface states are studied in this section.

7.3.2 Experiments and results

In order to study the origin of surface states of MBE-grown InAlN, we prepared series C sample surfaces under the following conditions: 1) Clean surfaces with oxides removed by BOE etching. 2) Surfaces with native oxides. 3) Surfaces with thermal oxides formed using RTA.

Series C samples were treated following these four steps: 1) After growth, they were cleaned with a standard solvent cleaning procedure, and soaked in BOE for 10 minutes to remove any oxides that form on the sample surfaces. 2) Samples were stored in ambient lab environments for a couple of months to provide ample time for the native
oxide to form. 3) Native oxides were removed by BOE etch. 4) Samples were annealed in air environment in RTA at 800 °C for 1 minute. XPS data was obtained after each step for comparison.

The BSBH as a function of InAlN layer thickness is plotted for series C samples after the BOE etch, with native oxides, and with thermal oxides. It can be seen that with a native oxide and a thermal oxide, the BSBH is higher than that without oxides (after BOE etch). A similar observation from Hasan et al. [192] shows that the decomposition of oxides can lower the BSBH.

![BSBH vs Thickness Plot](image)

**Figure 7-10:** Experimental data and simulation of BSBH as a function of thickness for series C samples under different treatment conditions.
All data is simulated using the analytical model described by equation (7.3) to obtain the surface states density and their energy distribution. The results are shown in Table 7-5.

**Table 7-5: Simulation results for series C InAlN samples with different surface oxide conditions.**

<table>
<thead>
<tr>
<th></th>
<th>( n_0 ) ( \times 10^{13} \text{cm}^{-2} \text{eV}^{-1} )</th>
<th>( E_d ) (eV)</th>
<th>Saturation energy (eV)</th>
<th>Energy distribution (eV)</th>
<th>Simulation error (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without oxide</td>
<td>4.22</td>
<td>2.10</td>
<td>3.11</td>
<td>1.01</td>
<td>0.0348</td>
</tr>
<tr>
<td>Native oxide</td>
<td>3.45</td>
<td>2.17</td>
<td>3.39</td>
<td>1.22</td>
<td>0.0897</td>
</tr>
<tr>
<td>Thermal oxide</td>
<td>10.1</td>
<td>2.61</td>
<td>3.04</td>
<td>0.43</td>
<td>0.0522</td>
</tr>
</tbody>
</table>

In this table, the surface states density \( n_0 \) and \( E_d \) are fitting parameters adjusted to best fit the experimental data. The saturation energy equals the BSBH at a thickness of 30 nm. The energy distribution is calculated by subtracting the saturation energy by \( E_d \). Simulation errors are determined using the square root of the sum of the square of the differences between the fitted values and measured data.

We know from previous analysis that the slope of BSBH as a function of film thickness is determined by \( n_0 \) values. As can be seen in Figure 7-10, compared with sample after BOE etch, samples with native oxides have a steep slope, while samples with a thermal oxide have a shallow slope. This means that with a native oxide, the BSBH increases fast with growing thickness, showing that the density of surface states is
low and the BSBH is not pinned. On the other hand, surfaces with a thermal oxide show a much flatter slope, indicating a higher density of surface states, which pin the Fermi level. This is confirmed with the simulated surface states density $n_0$. The thermal oxide surfaces have a density three times greater than that of a surface with a native oxide. However, the energy distribution of the surface states is much narrower for the thermal oxide as compared to native oxides. Moreover, the surface states with a native oxide start at a higher energy in the band gap compared to those from the thermal oxide.

Surface states densities and energy distributions are plotted in Figure 7-11.

Figure 7-11: Surface states densities and distributions of series C samples (a) Without oxide. (b) With native oxide, and (c) With thermal oxide.

To better understand the sensitivity of the simulation, the surface states density $n_0$ is changed to double the simulation error while $E_d$ is kept the same. Next, $E_d$ is changed to double the simulation error with surface states density $n_0$ kept the same. The calculated data is shown in Table 7-6.
Table 7-6: Sensitivity check for \( n_0 \) and \( E_d \) with values to double error.

<table>
<thead>
<tr>
<th></th>
<th>Decreased ( n_0 ) to double error</th>
<th>Increased ( n_0 ) to double error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value ( (x 10^{13} \text{ cm}^{-2} \text{ eV}^{-1} \text{ eV}) )</td>
<td>Percentage (%)</td>
</tr>
<tr>
<td>BOE etch</td>
<td>4.02</td>
<td>-4.7</td>
</tr>
<tr>
<td>Native oxide</td>
<td>3.09</td>
<td>-10.4</td>
</tr>
<tr>
<td>Thermal oxide</td>
<td>8.6</td>
<td>-14.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Decreased ( E_d ) to double error</th>
<th>Increased ( E_d ) change percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value ( (x 10^{13} \text{ cm}^{-2} \text{ eV}^{-1} \text{ eV}) )</td>
<td>Percentage (%)</td>
</tr>
<tr>
<td>BOE etch</td>
<td>2.06</td>
<td>-1.9</td>
</tr>
<tr>
<td>Native oxide</td>
<td>2.06</td>
<td>-5.1</td>
</tr>
<tr>
<td>Thermal oxide</td>
<td>2.56,</td>
<td>-1.9</td>
</tr>
</tbody>
</table>

It can be observed that the error is more sensitive to \( E_d \) than to \( n_0 \). For example, in the BOE etch set, a \( \sim 2\% \) change of \( E_d \) can lead to a doubled error, while a \( \sim 5\% \) change of surface states density \( n_0 \) is needed to double the error.

7.3.3 Oxide characteristics

The observation that surface states with thermal oxides have a higher density, narrower energy distribution, and a larger \( E_d \), thus occupying a deeper position in band gap than would be observed from native oxide is a very interesting phenomenon. We
used XPS to check the composition of the oxides on our nitride surfaces to develop a conjecture about this difference.

In 3d 5/2 peaks were fitted as shown in Figure 7-12 (a)(b), the main component is In-N bonding, the component on the higher binding energy side is In-O bonding, and In metallic bonding states can be observed on the lower energy side. Native oxide and thermal oxide sets have similar In-O component percentages.

Figure 7-12: (a)(b) In 3d 5/2 XPS peaks fitting with different surface oxides. (c)(d) Al 2p XPS peaks fitting with different surface oxides.
Al 2p peaks are fitted with Al-N bonding on the lower binding energy side and Al-O bonding on the higher energy side with a 0.8 eV separation and 0.2 eV FWHM difference as shown in Figure 7-12 (c)(d). Clearly, the annealed set has a much higher oxide percentage than native oxide set, which is different from the conclusion drawn from the In fitting.

Finally, O 1s peak fitting is shown in Figure 7-13 with similar procedures applied as described in Chapter 4. In oxides cannot be seen due to their relative small amount. Akazawa et al. pointed out that the peak related to OH is closer to surface [193], while we do not see this phenomenon in our results. With annealing, the lower energy peak rises, indicating increasing Al-O-Al. The hydroxide peak decreased with annealing.

![Figure 7-13: O 1s fitting for C2 sample with (a) Native oxide. (b) Thermal oxide.](image)

With all three peaks studied, we have come to the conclusion that native oxides and thermal oxides both have a very small amount of In₂O₃, or hydroxide InOOH or
In(OH)$_3$, but are mostly comprised of Al$_2$O$_3$, AlOOH or Al(OH)$_3$. In addition, the thermal oxides contain mostly aluminum oxide, while the native oxides are comprised primarily of aluminum hydroxides. The same oxide layer thickness estimation method is used as discussed in Chapter 4. Considering the Al$_2$O$_3$ density, a ML of oxide has a thickness around 3.6 Å. Using these parameters, the oxide coverage on our samples with native oxide is estimated to be ~0.4 ML, while on samples with the thermal oxide it is estimated to be ~2.5 ML.

### 7.3.4 The oxidized InAlN surface reconstruction

At this point, the surface oxide composition is clear. However, to understand how surface oxidation can affect surface states and the microstructures of the oxides, i.e. surface reconstruction models on oxidized InAlN should be considered.

The bare surface of semiconductors are well known to follow the electron counting (EC) rule [194]. Semiconductors cleaved at a polar surface will result in a net charge on top of the surface, with dangling bonds leading to surface states formation in the band gap. Empty donor states have a positive charge, while occupied acceptor states have a negative charge. To compensate non-neutral charge on the surface, the surface bands will bend. In addition, reconstruction of the surface atoms can compensate charge by removing surface states from the bulk gap. The EC model explains the rules that reconstructions must follow: all the dangling bonds of the electropositive element (Al, Ga, In) are empty, and the dangling bonds of the electronegative element (N) are full,
resulting in no net surface charge. Surface reconstructions based on this model have been studied for AlN [195, 196], GaN [197-199], and InN [197-199] using first-principle computational methods based on density function theory.

However, surface states at bare nitride surfaces reside close to the valence band [195-199]. This is inconsistent with experimental results showing that the surface states reside in the upper part of the band gap [180, 182-184]. Moreover, nitride surfaces are quickly oxidized under ambient conditions, therefore surface reconstruction including oxygen should be considered in calculations.

Two different reconstruction models are considered here. The first one is the EC rule applied to the nitride elements plus oxygen. The calculation by Miao et al. [134] shows that to follow the EC rule, for GaN or AlN, the first layer of nitrogen atoms must be replaced with oxygen. This can be applied to all [0001]-direction binary and ternary nitrides. The second model is the oxide-stoichiometry (OS) matching rule. The OS matching reconstruction can be formed by adding Al/In/Ga and O layers at the nitride surface in a 2/3 ratio to follow the Al$_2$O$_3$, In$_2$O$_3$, and Ga$_2$O$_3$ stoichiometry [134]. One thing to notice is that EC rule and OS rule are not compatible on [0001] nitride surfaces, meaning that oxides that follow the OS rule does not obey the EC rule.

Our samples have oxides on top of the surface, thus they could follow either the EC rule or the OS rule. Currently, no theoretical or experimental work has been done for InAlN surface reconstructions. The AlN surface reconstruction calculation [134, 196] is...
compared with our results here. Our speculation is that the native oxides are more likely to follow the OS rule, while the thermal oxides possibly follow the EC rule because of the following reasons.

One reason for this conjecture is that the EC rule requires replacement of nitrogen atoms with oxygen. The AlN surface reconstructions with 1 ML OS oxide, 2 ML OS oxide, 1 ML EC oxide, and 2 ML OS oxide are shown in Figure 7-14 [134] and show that EC oxides have nitrogen atoms in the first layer replaced by oxygen atoms. A similar phenomenon applies to InAlN. This will cause a nitrogen deficiency at the surface of InAlN. The nitrogen amount can be extracted by calculating the XPS N 1s peak intensity normalized by In 3d and Al 2p peak intensities. We plot the nitrogen amount measured at a TOA = 30° in Figure 7-15.
Figure 7-14: AlN surface reconstruction of 1 ML OS; 2 ML OS; 1 ML EC; 2 ML EC oxides. Blue balls represent Al atoms, grey balls represent N atoms, and red balls represent O atoms. The numbers 1 and 2 refer to the oxide layer in which atom stays, with 1 denoting the layer closer to nitride. Plot taken from Ref. [134].

Figure 7-15: Nitrogen amount on the surface of the series C samples measured by N 1s intensity normalized by In 3d plus Al 2p peaks intensities.
From Figure 7-15, with the exception of the 2.5 nm samples, all of the other samples show that on an annealed sample surface, the nitrogen amount is lower than that of the native oxide sample surface. The annealed samples have a lower ratio, possibility due to the replacement of nitrogen on the surface by oxygen. The 2.5 nm samples show abnormal behavior due to the fact that they are so thin that signal from the underlining GaN template is being detected thus showing an anomalously high nitrogen amount. This result shows that the native oxide is formed possibly without nitrogen replacement, thus obeying the OS rule; while the thermal oxide shows nitrogen deficiency implying that the EC rule could apply.

Moreover, since EC requires N replacement at room temperature, it is possible that kinetic limitations exist, hindering the EC oxide formation. Thus native oxides are more likely to obey the OS rule. At higher temperatures, enough energy is provided to form the most energetically favorable EC oxides, thus a thermal oxide is more likely to obey the EC rule.

Finally we consider the surface states energy distribution in the band gap. It is shown in Table 7-5 that the C set samples with a band gap around 4.9 eV have surface states starting at position $E_d$ of 2.17 eV (upper half in the band gap) for samples with native oxides, while $E_d$ is 2.61 eV (lower half in the band gap) for samples with thermal oxides. To compare these findings to reconstruction studies on AlN [134], we show
selected calculated starting energy positions for surface states with different oxide types and coverage in Table 7-7.

<table>
<thead>
<tr>
<th></th>
<th>0.5 ML OS</th>
<th>1 ML OS</th>
<th>2 ML OS</th>
<th>1 ML EC</th>
<th>2 ML EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_d$ (eV)</td>
<td>1.99</td>
<td>2.39</td>
<td>1.86</td>
<td>3.35</td>
<td>4.93</td>
</tr>
</tbody>
</table>

It is interesting to notice that independent of the oxide coverage, all of the OS oxides provide surface states starting energies in the upper half in the band gap, while all the EC oxides have starting energies in the lower half in the band gap. This is consistent with our findings for InAlN.

Next we consider the density of surface states. From the simulated results in Table 7-5, the density of surface states with thermal oxides is almost three times larger than that with native oxides. We’ve calculated a rough estimation of the coverage of oxides and found that of the native oxide to be $\sim$0.4 ML and that of a thermal oxide to be $\sim$2.5 ML. For comparison, we show the theoretically calculated AlN surface states distribution for 0.5 ML OS oxides and 2 ML EC oxides [134] (Figure 7-16).
Figure 7-16: (a)(c) Density of states of AlN with 0.5 ML OS oxides and 2 ML EC oxides. Blue area being the unoccupied acceptor states and red area being occupied donor state. (b)(d) Simulated surface states density and energy distribution of our InAlN films with 0.4 ML native oxide or 2.5 ML thermal oxide.

Although the theoretical calculation does not show a distribution of surface states with constant density, our results should be considered an average of the surface states density. The comparisons show that native oxide and OS oxide both have surface states with lower density and wider energy distribution while the thermal oxide and EC oxide have narrower energy distribution with higher density.
7.4 Conclusions

In this chapter, the properties of surface states on clean InAlN/GaN heterostructures with various indium incorporation are first studied. Samples having higher surface indium composition show surface states with larger density and narrower energy distribution.

Surface oxidation is studied in order to determine its effect on the surface states. Thermal oxides and native oxides are compared and show that annealing likely creates EC oxides, leading to higher density surface states distributed over a narrower energy range. Meanwhile, the native oxides appear to be OS oxides, leading to lower density surface states distributed over a wider energy distribution.
8. InAlN/GaN heterostructure valence band offsets

8.1 Introduction

A fundamental understanding of the properties of InAlN/GaN heterostructure, for example the band alignment of InAlN to GaN, is still lacking. Very few studies have measured the CBO and the VBO of this heterostructure [200-203] and only one of them [200] is experimental, the others are theoretical. To the author’s best understanding, no MBE-grown InAlN/GaN has been previously studies. Since the CBO and VBO are crucial parameters for HEMT device performance and, therefore, design, we herein studied these parameters for several InAlN/GaN heterostructures with various indium compositions grown by MBE.

8.2 Experimental

XPS is by far the most reliable method [204] for determining the band offset between two semiconductors in contact. Typically three samples are needed for InAlN/GaN band offset measurements. These are (1) an ultrathin InAlN/GaN sample with the InAlN layer less than 3 nm so that electrons from the underlying GaN layer can pass through the InAlN layer to be detected by XPS, (2) a thick InAlN sample, and (3) a thick GaN sample. In this study, ultrathin InAlN/GaN samples were grown with an InAlN thickness of 2.5 nm using three different growth conditions as shown in Table 8-1 and discussed in Chapter 3. Thick InAlN samples were grown under the same three growth conditions with a thickness of 15 nm. A GaN buffer grown on top of a GaN
template without InAlN was prepared to fulfill the thick GaN sample measurements. First, a commercial semi-insulating GaN template was used which is grown on top of sapphire with a very thin AlN interlayer buffer. A 50 nm GaN buffer was then grown under 680 °C using Ga-rich growth conditions on top of the GaN template. InAlN films were finally grown on top of the GaN buffer.

Table 8-1: Growth conditions for A, B, C set of samples.

<table>
<thead>
<tr>
<th>Sample series</th>
<th>Growth Temp (°C)</th>
<th>BEP ratio Al/In</th>
<th>Thickness (nm)</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>400</td>
<td>1.27</td>
<td>2.5, 15</td>
<td>16.9%</td>
</tr>
<tr>
<td>B</td>
<td>450</td>
<td>1.23</td>
<td>2.5, 15</td>
<td>18.2%</td>
</tr>
<tr>
<td>C</td>
<td>540</td>
<td>1.01</td>
<td>2.5, 15</td>
<td>9.8%</td>
</tr>
</tbody>
</table>

High resolution (10I5) asymmetric RSM XRD was used to determine that the indium composition is x=16.90% for series A, x=18.20% for series B, and x=9.8% for series C as shown in Chapter 3.

Before loading the samples into the XPS system, they were solvent cleaned and etched in BOE for ten minutes to remove any remaining native oxide. XPS survey and region scans for In 3d, Al 2p, N 1s, C 1s, O 1s, Ga 2p, Ga 3d core levels and valence band spectra were captured and analyzed with calibration of the C 1s to be 285 eV. XPS showed that the oxides are effectively removed from the InAlN surface.
### 8.3 Valence band offset X-ray photoelectron spectroscopy measurements model

VBO is the offset of the valence bands between two semiconductors: here InAlN and GaN. Following the band diagram in Figure 8-1, the VBO can be calculated as follows [205]:

\[
VBO = -\Delta E_{\text{CL, thin InAlN}} + \Delta E_{\text{Ga 2p, thick GaN}} - \Delta E_{\text{Al 2p, thick InAlN}}
\]  
\[
\Delta E_{\text{Ga 2p, thick GaN}} = E_{\text{Ga 2p, thick GaN}} - E_{\text{V, thick GaN}}
\]  
\[
\Delta E_{\text{Al 2p, thick InAlN}} = E_{\text{Al 2p, thick InAlN}} - E_{\text{V, thick InAlN}}
\]  
\[
\Delta E_{\text{CL, thin InAlN}} = E_{\text{Ga 2p, thin InAlN}} - E_{\text{Al 2p, thin InAlN}}
\]

where \(\Delta E_{\text{CL, thin InAlN}}\) is the core level difference measured with ultrathin InAlN/GaN samples. \(\Delta E_{\text{Ga 2p, thick GaN}}\) and \(\Delta E_{\text{Al 2p, thick InAlN}}\) is the core level and valance band difference measured with thick GaN and InAlN samples. There are several possible core level choices to use for the calculation. In our XPS measurements, we took region scans of Ga 2p, O 1s, In 3d5/2, N 1s, C 1s, Al 2p and Ga 3d. O 1s and C 1s come from surface contamination. N 1s is obtained from both GaN and InAlN. The possible choices for core levels are Ga 2p, Ga 3d in GaN, and In 3d, Al 2p in InAlN. Use of either of these core levels should provide similar results for the VBO. Here, we choose Ga 2p and Al 2p as the core levels to use for the calculation. Figure 8-1 shows a schematic band diagram of InAlN/GaN heterostructure with Al 2p and Ga 2p chosen as the core levels.
This calculation method is based on the assumption of a flat band heterostructure. However, if the bands are bent, this method no longer applies and an additional correction is needed. For nitride materials, spontaneous polarization and piezoelectric polarization exist, and their impact on the band bending at the InAlN/GaN interface cannot be ignored. The polarization direction points to the substrate, leading to an upward band bending as shown in Figure 8-2. A uniform electric field is commonly assumed inside the InAlN layers [42].
Figure 8-2: Upward band bending in InAlN caused by spontaneous polarization.

With the bending of the conduction and valence bands as shown in Figure 8-2, the core levels in the InAlN shift in energy alongside the bands while preserving their magnitude. The core level photoelectrons captured by XPS need to overcome this barrier to escape the material. Due to this, the kinetic energy of the detected electrons is lowered and the binding energy is shifted to a larger energy. Because the magnitude of the barrier to overcome depends on the electron’s initial depth, peaks from different depths will experience different shifts of binding energies. According to Akazawa et al. [200], the apparent shape of the measured XPS peak is a convolution of all the true peaks coming from different depth up to several nanometers. The various positions of the true peaks yield an apparent shape with broadened FWHM. The equation describing the measured core-level spectrum as a function of the binding energy $E$ is shown here [206]:
\[ I(E) = \int_0^d I_0(E, z)e^{-z/\lambda}dz \]  

(8.5)

where \( z, \lambda, d, \) and \( I_0(E, z) \) are the depth from the surface, the escape depth of the photoelectrons, the barrier thickness, and the spectrum generated at each depth point. 

\( I_0(E, z) \) is assumed to have a pseudo-Voigt function considering both machine broadening and physical broadening:

\[ V(E, z) = I_{00} \left[ \alpha e^{-\ln 2 \left( \frac{E-E_0(z)}{F^2} \right)^2} + (1-\alpha) \frac{1}{1 + \left\{ -\frac{(E-E_0(z))^2}{(F^2)^2} \right\}} \right] \]  

(8.6)

in which \( I_{00} \) is the intensity of core level, \( \alpha \) is the ratio of the Gaussian function, \( E_0 \) is the binding energy of the core level, and \( F \) is the FWHM of the core level. Using these two equations yields information on the true positions of core levels and true FWHM considering the internal electric field (Matlab codes are given in Appendix C).

**8.4 Results**

**8.4.1 Characterization of bulk material properties**

First, the core level and VBM difference in the bulk GaN buffer sample is extracted. Ga 2p, Ga 3d peaks and the VBM spectrum are fit in order to determine this separation as shown in Figure 8-3. The Ga 2p peak is fit with Ga-N bonding and Ga-O bonding since the surface of the GaN buffer is slightly oxidized in the atmosphere. The
Ga 3d peak is fit with Ga-N, Ga-O, metallic Ga and the N 1s peak. The VBM is extracted by using a linear extrapolation of the valence band edge to the background.

Figure 8-3: Thick GaN XPS spectrums and fittings of (a) Ga 2p (b) Ga 3d (c) VBM.

A Ga 2p and VBM separation of 1115.29 is calculated from the spectra. The Ga 3d peak overlaps with the N 1s peak making it not a good candidate for the separation calculation. Also, according to King et al. [207], Ga 3d is very shallow and hybridizes with the valence band structure, making fitting using conventional methods challenging. In this study we use Ga 2p instead of Ga 3d. A correction of this separation shows that is
negligible since the GaN band is almost flat. A similar phenomenon also exists in MOCVD GaN [200].

For thick InAlN, the Al 2p core level and VBM are measured and fit as shown in Figure 8-4.

Figure 8-4: Thick InAlN XPS spectrums and fitting (a) Al 2p (b) VBM.

A separation between the Al 2p core level and the VBM of 71.23 eV is obtained for all three sets of samples with the correction applied due to the band bending in thick InAlN films.

8.4.2 Measurements of band offset

To measure the band offset, we need to get the core level difference in the thin InAlN/GaN structure. Al 2p and Ga 2p core level spectra for Set B are shown in Figure 8-5 as an example using XPS data acquired at different TOAs. Sets A and C have similar spectra.
Figure 8-5: Ultrathin InAlN/GaN XPS spectrums and fittings under various XPS TOA for set B.

A summary of the measured peak separations and calculated VBO is shown in Table 8-2 and Figure 8-6.

Table 8-2: Calculated core level separation and corresponding VBM for samples under different TOA.

<table>
<thead>
<tr>
<th>Series</th>
<th>TOA</th>
<th>$\Delta E_{Cl}^{Thin\text{InAlN}}$</th>
<th>VBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>15</td>
<td>1044.08</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1044.06</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1044.00</td>
<td>0.06</td>
</tr>
<tr>
<td>B</td>
<td>15</td>
<td>1044.11</td>
<td>-0.05</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1044.05</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1044.07</td>
<td>-0.01</td>
</tr>
<tr>
<td>C</td>
<td>15</td>
<td>1044.73</td>
<td>-0.67</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1044.70</td>
<td>-0.64</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1044.67</td>
<td>-0.61</td>
</tr>
</tbody>
</table>
Figure 8-6: VBO without correction for A, B, and C sets as a function of TOA.

It can be seen that without using the correction, the VBO values are not consistent with different TOAs. Moreover, the VBO values are positive as reported in the literature which is not the case for our analysis without the correction. Thus, we next apply the correction model to these results.

8.4.3 Valence band offset analysis with correction

To apply the correction model, the inelastic mean free path $\lambda_0$ is calculated using the NIST electron effective-attenuation-length database [72] following the theoretical equation developed by S. Tanuma et al. [148]. The calculated inelastic mean free paths and escape lengths for different TOAs are shown in Table 8-3 where the escape length is determined using:
\[ \lambda = \sin(\theta) \lambda_0 \] (8.7)

Table 8-3: Escape length of samples with different TOA

<table>
<thead>
<tr>
<th>TOA</th>
<th>A (nm)</th>
<th>B (nm)</th>
<th>C (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.734</td>
<td>0.731</td>
<td>0.751</td>
</tr>
<tr>
<td>30</td>
<td>1.418</td>
<td>1.412</td>
<td>1.451</td>
</tr>
<tr>
<td>50</td>
<td>2.173</td>
<td>2.163</td>
<td>2.223</td>
</tr>
</tbody>
</table>

The peak positions and FWHM before and after applying the correction at three different TOAs are listed in Table 8-4.

Herein, we show the processes for correction of the Al 2p peaks. First, a constant electric field \( E_F \) is assumed in each sample. The FWHM \( F \) of the peaks coming from any depth of the sample is assumed to be constant. The position of the core level peak \( E_{00} \) coming from depth \( z = 0 \) is assumed. The peak shape from a specific depth \( z \) is described by a pseudo-Voigt function with FWHM \( F \) and peak position \( E_{00} + E_F \cdot z \) since the electric field in InAlN shifts the peaks. Thus, the experimental measured peak is a convolution of all these peaks from different depths, \( z \). By adjusting \( E_F, F \) and \( E_{00} \), we can adjust the apparent convoluted peak to be as close to the experimental result as possible.

Before applying the correction, the experimental data shows that the positions and FWHM increase for the Al 2p core level with increasing TOA (Table 8-4) indicating sharp band bending. After applying the correction, a constant position and FWHM is
obtained. The apparent peak resulting from the convolution is very close to experimental results.

Table 8-4: Al 2p peak position and FWHM before and after correction.

<table>
<thead>
<tr>
<th>TOA</th>
<th>Position of Al 2p</th>
<th>FWHM of Al 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Apparent</td>
<td>Corrected</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>73.45</td>
<td>73.39</td>
</tr>
<tr>
<td>30</td>
<td>73.48</td>
<td>73.39</td>
</tr>
<tr>
<td>50</td>
<td>73.48</td>
<td>73.39</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>73.70</td>
<td>73.64</td>
</tr>
<tr>
<td>30</td>
<td>73.72</td>
<td>73.64</td>
</tr>
<tr>
<td>50</td>
<td>73.73</td>
<td>73.64</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>73.11</td>
<td>72.86</td>
</tr>
<tr>
<td>30</td>
<td>73.19</td>
<td>72.86</td>
</tr>
<tr>
<td>50</td>
<td>73.28</td>
<td>72.86</td>
</tr>
</tbody>
</table>

To calculate the corrected VBO, the corrected Al 2p position is used instead of the non-corrected position. Correction of the Ga 2p position is calculated to be negligible. Moreover, since the Ga photoelectrons need to overcome the entire InAlN barrier before escaping from the sample, a potential barrier correction using the electric field multiplied by the InAlN thickness is applied to Ga 2p assuming a constant electric field in InAlN film similar to AlGaN [42]. Considering all of these corrections, the VBO and simulated electric field values are shown in Table 8-5 and Figure 8-7.
Table 8-5: VBO and internal electric field of A, B, and C sets after correction.

<table>
<thead>
<tr>
<th>Series</th>
<th>$x$</th>
<th>VBO (eV)</th>
<th>Electric field (MV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16.90%</td>
<td>0.15</td>
<td>0.9</td>
</tr>
<tr>
<td>B</td>
<td>18.20%</td>
<td>0.12</td>
<td>0.9</td>
</tr>
<tr>
<td>C</td>
<td>9.8%</td>
<td>0.23</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Figure 8-7: VBO values before and after correction.

After applying the correction, the VBO obtained for all angles have the same positive values.

8.4.4 Discussion: literature review

To compare our experimental results with literatures, the band edges of binary nitrides and InAlN valence band edges are plotted in Figure 8-8.
Figure 8-8: Comparison of InAlN/GaN VBO from literatures.

In this plot, all of the data are referred to the charge neutrality level (E_{CNL}), which is defined as the position for the Fermi level that renders the surface uncharged. The absolute value is not important since we are only concerned about the offsets here. Data for the CBM and VBM of the binary nitrides AlN, GaN, and InN are referenced to King [208]. The green dots show our experimental results. Four main methods were used in the literatures to obtain the InAlN/GaN heterostructure VBO.

The magenta triangles referenced to Akazawa et al. [200] are from the only experimental work available focusing on MOCVD-grown InAlN. Their calculation
suggests a VBO of $0.2 \pm 0.2$ eV for lattice-matched InAlN/GaN. Compared with our VBO result for the lattice-matched A set, our determined VBO of 0.15 eV is within the result range of theirs. An improvement using Ga 2p peaks instead of Ga 3d peaks should yield a more reliable choice as mentioned above for their work.

The blue line represents the theoretical estimation of the InAlN valence band edges by King et al. [201]. They assume that the InAlN’s valence band’s position is a linear extrapolation from InN and AlN based on Monch et al.’s work [209]. A VBO of $\sim 0.68$ eV for lattice-matched InAlN/GaN was obtained.

The yellow circle represents theoretical work by Walukiewicz et al. [202]. They predicts a VBO of $\sim 0.3$ eV with an indium composition of 20%. Their results are obtained by extrapolation from InN and AlN with a bowing parameter term added. Generally, the band gaps of compound semiconductors follow Vegard’s law:

$$\text{Band gap}(\text{In}_x\text{Al}_{1-x}N) = x \cdot \text{Band gap}(\text{InN}) + (1 - x) \cdot \text{Band gap}(\text{AlN})$$

(8.8)

Sometimes, however Vegard’s law is not enough for the estimation of band gap, thus a third term is added:

$$\text{Band gap}(\text{In}_x\text{Al}_{1-x}N) = x \cdot \text{Band gap}(\text{InN}) + (1 - x) \cdot \text{Band gap}(\text{AlN}) - b \cdot x \cdot (1 - x)$$

(8.9)
Parameter $b$ is called bowing parameter. It has been shown in InAlN the bowing parameter varies from 3 to 6 eV [171, 210, 211]. Thus, it is possible that this reduction term characterized by the bowing parameter is also affected by the valence band edge.

The orange circle represents work by Kim et al. [203]. They estimated the InAlN VBM by assuming that InAlN/GaN has the same CBO/VBO ratio of 1.08 as AlN/GaN following work of Waldrop et al. [212].

From Figure 8-8 it is shown that our results are close to the prior experimental work and theoretical work which includes a bowing parameter. The theoretical work using linear extrapolation or assuming a CBO/VBM ratio is not close to our findings. A fit of our results is shown by the green line using the following equation:

\[
VBO(In_xAl_{1-x}N/GaN) = x \cdot VBO(\text{InN/GaN}) + (1 - x) \cdot VBO(\text{AlN/GaN}) - b(x)
\]

(8.10)

\[
\cdot x \cdot (1 - x)
\]

The bowing parameter $b$ is a nonlinear function of composition $x$ referencing Sakalauskas et al. [171]'s result:

\[
b(x) = \frac{A}{1 + C \cdot x^2}
\]

(8.11)

with A and C being fitting parameter. Our fit with A being 9.31 and C being 49.26 describes the experimental results well.
8.5 Conclusions

AR-XPS is used in this work to experimentally determine the VBO of InAlN/GaN heterostructures with different indium compositions. The application of a correction to the analysis which considers the internal electric field resulting from polarization is applied. VBOs of 0.15 eV for In$_{0.17}$Al$_{0.83}$N, 0.12 eV for In$_{0.18}$Al$_{0.82}$N, and 0.23 eV for In$_{0.098}$Al$_{0.902}$N are obtained.
9. Conclusions and Perspectives

9.1 Conclusions

In this work, MBE is used for the growth of In-based III-N ternary alloys. We successfully demonstrated the growth of good quality GaN buffers under Ga-rich conditions achieving smooth surfaces without Ga droplets and low residual donor concentrations of \( \sim 6 \times 10^{11} \text{ cm}^{-2} \). Thin AlN layers with AFM RMS = 0.748 nm are achieved with accurate determination of layer thicknesses by SE. InAlN with different indium compositions is grown with RMS \( \sim 0.28 \text{ nm} \) and XRD FWHM less than 400 arc-sec under almost stoichiometric growth conditions. Finally, good quality InAlN/(AlN)/GaN HEMT structures are also demonstrated using MBE.

The surface properties of InAlN are studied using AR-XPS. Native oxides are comprised primarily of AlOOH or Al(OH)\(_3\), together with In(OH)\(_3\), Al\(_2\)O\(_3\) and In\(_2\)O\(_3\). BOE is shown to effectively remove most of native oxides with only a small amount of AlOOH or Al(OH)\(_3\) remaining. Finally, RTA is demonstrated as a reliable growth approach of thermal oxides on InAlN surfaces. These oxides are comprised primarily of Al\(_2\)O\(_3\).

We show that the unintentional compositional grading in InAlN results during growth from strain and relaxation especially for tensile-strained InAlN. It is found that strain and relaxation can cause tensilely-strained InAlN to have an indium-poor surface,
consistent with our observation that compressively-strained InGaN develops an indium-rich surface.

The optical characterization of InAlN was carried out using SE. A compositional model of InAlN possessing two phases is shown to successfully describe the optical properties of InAlN likely due to the observed nanocolumnar microstructure. Insertion of an AlN interlayer mitigates the development of this microstructure. Moreover, AlN interlayer greatly improve the structure’s mobility by fivefold.

The density and energy distribution of surface donor states is studied supporting the model of a constant distribution of states in the band gap with a relatively low concentration. Higher surface indium composition is shown to create surfaces with a higher density of surface states and narrower distribution energy. Furthermore, the oxide is shown to be related to surface states properties. Annealed and native oxides are compared and we show that annealing likely provides EC oxides, leading to higher density surface states in a narrower energy distribution. Native oxides are similar to OS oxides, leading to a lower density of surface states over a wider energy distribution.

The VBO’s of InAlN/GaN structures with various In compositions are studied considering the effects of the internal electrical filed caused by polarization. This is the first work characterizing the VBO of this kind. VBOs of 0.15 eV for In_{0.17}Al_{0.83}N, 0.12 eV for In_{0.18}Al_{0.82}N, and 0.23 eV for In_{0.098}Al_{0.902}N are obtained.
9.2 Perspectives

Throughout this work, the properties of InAlN and InAlN/(AlN)/GaN heterostructures have been discussed. Still, much more work could be done in order to develop a more detailed understanding of this material.

1. In Chapter 4, the oxidation of InAlN is studied using RTA-synthesized thermal oxides. Further work with annealing at different temperatures and ambient is needed. Oxidation of nitrides remains a problem and reliable oxidation methods compatible with device fabrication process are needed. Different oxidation methods should be further studied such as ALD, MOCVD deposition, MBE deposition, photoelectronchemical oxidation, hydrogen peroxide oxidation with oxides SiN, MgO, ZrO, SiO₂, HfO₂, Al₂O₃ etc. on top of nitrides.

2. In Chapter 5, tensilely-strained InAlN’s unintentional compositional grading is studied and explained consistently with that occurring for InGaN due to strain. On the other hand, compressively-strained InAlN was studied with controversial results that cannot be explained solely by strain [160-162]. Although, we hypothesize that the nanocolumnar microstructure structure impacts this phenomenon, more experimental studies are needed to complete the picture.
3. As discussed in Chapter 6, we show that the nanocolumnar microstructure may degrade InAlN’s electrical properties such as electron mobility. At this point, this microstructure is ubiquitous in MBE-grown InAlN [175, 176, 213]. Very recently, Kaun et al. achieved a homogeneous InAlN film using MBE by employing a slow growth rate (~1nm/min) and N-rich growth conditions (III/V = 0.3) [62]. More work should be done to optimize material quality of InAlN through eliminating this microstructure. Also, models of the impact of the microstructure on InAlN’s electrical, optical, and structural properties are needed.

4. In Chapter 7, our findings on the oxide characteristics are compared with an AlN surface reconstruction model which includes oxide formation and bonding. This analogy and model should be further developed with surface reconstruction modeling on InAlN surfaces.

5. In Chapter 7, a model is applied to study the relationships between oxide formation, oxide types, and surface states. As a starting point, this method could also be applied to InAlN grown by MOCVD or oxides grown by alternative methods. Moreover, the modeling of the BSBH is applied without considering strain. Strain is believed to affect the BSBH at large thicknesses [186]. Although our samples are very thin and may not experience a strong
strain influence, this remains an important and interesting topic to explore in the future.

6. To date the insertion of an AlN barrier layer in InAlN/GaN HEMTs has enabled significantly improved device characteristics. Very recently, AlN together with an GaN insertion layer has been explored by Kaun et al. [62]. By adding a 2 nm GaN layer, device structures have improved sheet resistance (163 Ω/□ compared with 241 Ω/□), with increasing 2DEG electron density and mobility. This method should be further studied.
Appendix A: Experimental procedure for InAlN synthesis using MBE

All the materials in this work are prepared using MBE system. Here, we record the basic procedure. Before growth, commercial GaN templates (GaN on sapphire) are cleaned, diced, and back-coated with 1.2 µm titanium using e-beam evaporation. Nitrides are transparent and therefore cannot directly absorb the radiation energy from the substrate heater, therefore, titanium coating is needed. Then, the templates are loaded into the introduction chamber on a substrate holder. After the introduction chamber is pumped down to a pressure lower than $10^{-8}$ torr, the sample holder is moved into the buffer chamber. The substrate is heated in the buffer chamber up to 500 °C to remove moisture and other impurities from the template surface.

The substrate heater, ion gauge (for flux measurements), In cell, Al cell, and Ga cell are heated to high temperatures so that impurities can be removed and pumped out of the system. The cells are then lowered to the temperatures required for growth.

Flux is measured for growth at this point. After that, the template is transferred to the growth chamber once ensuring the buffer chamber pressure is lower than $10^{-8}$ torr.

A pyrometer is used to monitor the real temperature of the substrate. It is heated up to 710 °C and kept at this temperature for 10 minutes to remove any residual surface oxide or contaminants. Reflection high-energy electron diffraction (RHEED) is used to monitor the oxide removal process. The RHEED pattern changes from a (1x1) to a (2x1)
streak pattern indicating that the oxide is removed and the surface is smooth. The template temperature is then lowered to that required for GaN buffer layer growth. The Ga cell together with the N\textsubscript{2} plasma source are both opened for buffer layer growth. After that, the Ga cell is closed, and the In cell, and the Al cell are opened together for InAlN layer growth.
Appendix B: Matlab codes for BSBH fitting

% 
INSTRUCTION: 
Change fitting parameter n0, ed so that calculated error is minimized. 
%

clear all;
clc;

%----------------------------------------------PARAMETERS ASSIGNING-----------------------------------------------%
q = 1.6E-19; 
%Electron charge (C)
sigma_pz = 4.65E13; 
%Positive density surface charge at the interface (ecm^-2)
sigma_pz = 4.65E13; 
epsilon = 10.87*8.85E-14; 
%Permittivity of InAlN (f/cm)
deltaEc = 1.25; 
%CBO for InAlN/GaN (eV)

%----------------------------------------------CHANGE FITTING PARAMETERS HERE---------------------------------------------%
Ed = 2.1; 
%Surface states energy distribution position Ed (eV)
n0 = 4.22E13/q; 
%Density of surface states (cm^-2eV^-1)

%----------------------------------------------CALCULATE BSBH----------------------------------------------------------% 
d = 0:0.1:20; 
%Thickness of barrier layer (nm)
qphiB=((n0*Ed+sigma_pz/q)*(d/10^7)+epsilon*deltaEc/q^2)./(d/10^7)+epsilon/q^2/n0)./n0; 
%BSBH (eV)
qsat=((n0*Ed+sigma_pz/q)*(30/10^7)+epsilon*deltaEc/q^2)./(30/10^7)+epsilon/q^2/n0)./n0; 
%BSBH at d = 30 nm (eV)

%---------------------------------------------- INPUT EXPERIMENTAL DATA -----------------------------------------------%
d_expe = [2.5 7.15]; 
%Thickness of barrier layer (nm)
BSBH_expe = [2.47 2.79 2.88 3.02]; 
%Experimental BSBH (eV)

%---------------------------------------------- CALCULATE ERROR -------------------------------------------------%
qphiB_com=((n0*Ed+sigma_pz/q)*(d_expe/10^7)+epsilon*deltaEc/q^2)./(d_expe/10^7)+epsilon/q^2/n0)./n0; 
%Calculated BSBH at each experimental d
Sum=0;
for i=1:1:4;
    Sum=Sum+(qphiB_com(i)-BSBH_expe(i))^2;
end

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end
error = sprintf('%0.6f',sqrt(Sum));

%------------------------------------------------------------------ PLOT *------------------------------------------------------------------%
plot(d,qphiB,'LineWidth',3,'Color',[0 1 1]);
hold on;
%title('Plot of BSBH as a function of thickness','fontsize',25)

ylim([0.9,3.5]);
scatter(d_expe,BSBH_expe,220,'ro','filled','MarkerFaceColor',[0 1 1]);
hold on;

xlabel('Thickness(nm)','fontsize',25)
ylabel('Bare surface barrier height (eV)','fontsize',25)
set(gca,'fontsize',20,'Linewidth',2)

legend('BOE simulaiton','Native oxide simulaiton','Thermal oxide simulaiton','BOE experiment','Native oxide experiment','Thermal oxide experiment');
Appendix C: Matlab codes for band offset correction

%{ 
Instruction:
Change fitting parameter F, E00 and EF so that calculated Emax and FWHM matches experimental data.
}%

clear all;
clc;

%----------------------------------PARAMETERS ASSIGNING----------------------------------%
% \texttt{thetadegree} = [15 30 50]; %Take-off-angle $\theta$
% \texttt{Emax} = [0 0 0]; %Matrix to store calculated peak position
% \texttt{FWHM} = [0 0 0]; %Matrix to store calculated FWHM

%--------------------------------SIMULATION LOOP FOR EACH TOA-----------------------------%
for i = 1:3

%----------------------------------PARAMETERS ASSIGNING----------------------------------%
alpha =0.73; %Ratio of Gaussian to Lorentz function
\texttt{d}=2.5; %Thickness $d$
\texttt{theta} = degtorad(\texttt{thetadegree}(i)); %Inelastic mean free path (nm)
\texttt{lamda0} = 2.902;

%----------------------------------CHANGE FITTING PARAMETERS HERE----------------------%
\texttt{F}=0.97; %Actual value of FWHM
\texttt{E00}=72.86; %Correct value of core level position
\texttt{EF}=4.6; %Internal electric field

%----------------------------------CALCULATE CONVOLUTED PEAK-----------------------------%
\texttt{lamda} = \texttt{lamda0}\times\sin(\texttt{theta}); %Depth of information (nm)
\texttt{E}=70:0.001:80; %Energy position

%Intensity from one depth multiply by weakening factor
\texttt{Q}=@(z) (\texttt{alpha}\times\exp(-4*\log(2)*((\texttt{E}-\texttt{(E00+0.1*\texttt{EF}\times\texttt{z})})/\texttt{F})^2)+(1-\texttt{alpha})./(1+(2*(\texttt{E}-\texttt{(E00+0.1*\texttt{EF}\times\texttt{z})})/\texttt{F})^2)).\times\exp(-\texttt{z}/\texttt{lamda});
%Convoluted intensity
\texttt{I}=quadv(\texttt{Q},0,\texttt{d});
%----------------------------------FIND CONVOLUTED PEAK POSITION AND FWHM-----------------%
[M,index]=max(I); %Find the largest index in I
Emax(i)=E(index); %Find E corresponds to largest I

%Plot to make sure E covers the proper range, whole peak is shown
plot(E,I);
hold on;

%Calculate FWHM
A=find(I > M/2);
FWHM(i) = E(A(end))-E(A(1));

end

%-----------------------------------------DISPLAY RESULTS-----------------------------------------
format short
display(Emax);
display(FWHM);
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