ABSTRACT

BRYAN, ISAAC S. Al-rich AlGaN and AlN Growth on Bulk AlN Single Crystal Substrates (Under the direction of Dr. Zlatko Sitar).

Al-rich AlGaN and AlN epitaxial thin films were grown by metalorganic chemical vapor deposition (MOCVD) on both vicinal (0001)-oriented native single crystal AlN substrates and AlN templates grown on vicinal (0001)-oriented sapphire to develop the first all-inclusive surface kinetic framework for the control of surface morphology in the III-nitrides. The role of dislocation density on the surface morphology of these thin films is discussed. A Burton, Cabrera, and Frank (BCF) theory-based model was formulated and utilized to understand the dependence of the surface kinetics on the vapor supersaturation, $\sigma$, and substrate misorientation angle, $\alpha$. Transitioning from a surface with 2D nuclei to one with bilayer steps required a decrease in $\sigma$ or an increase in $\alpha$, whereas the suppression of step-bunching required an increase in $\sigma$ or a decrease in $\alpha$. Furthermore, there are many surface defects that exist on these layers which have not yet been properly classified. These defects, namely cracks, pits, and hillocks, will be studied and methods for preventing the formation of them will be presented. Ultimately, having the ability to achieve defect free and atomically smooth surfaces will be made possible through these results and allow for much better device performance due to an enhancement in interface smoothness and a reduction in scattering events both optically and electrically.

The first high quality non-polar Al-rich AlGaN and AlN epitaxial thin films were realized by MOCVD growth on (1-100)-oriented single crystalline AlN substrates. The dependence of the surface morphology, structural quality, and unintentional impurity concentrations on the growth temperature was studied in order to determine the most
appropriate growth conditions for high quality epitaxial layers. Optically smooth surfaces (RMS roughness of 0.4 nm) and high crystalline quality, as demonstrated by the presence of FWHM values for (10-10) rocking curves along [0001] of less than 18 arcsec, were achieved for films grown above 1350 °C. Furthermore, sharp (FWHM values less than 550 μeV) and intense near band edge luminescence was observed in homoepitaxial (1-100) AlN films. A reduction in unintentional oxygen impurity levels was seen with an increase in growth temperature. These high crystalline quality films are suitable for device applications and hold great potential for providing an ideal platform for deep UV emitters without polarization related effects.

The electrical and optical properties of Si- and Mg-doped AlGaN epitaxial thin films spanning the entire composition range from GaN to AlN were studied. A clear onset of over compensation was observed in the free carrier concentration and photoluminescence for high doping concentrations above 1 to 3 x 10^{19} cm^{-3} for both Si and Mg doping. The role of dislocations on the compensation levels was investigated by growing films on both native (single crystalline AlN and GaN) and foreign (sapphire) substrates. Hybrid density functional theory calculations were implemented to provide further insight on the identification of point defects which incorporated during growth. Point defect identification made it possible to reduce the concentration of compensating defects in Si-doped AlGaN providing a means of improving the conductivity. These results further the current understanding of the role of extended and point defects on the material properties of AlGaN and offer guidance for improving the performance of future devices.
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Al-rich AlGaN and AlN Growth on Bulk AlN Single Crystal Substrates

by
Isaac S. Bryan

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DEDICATION

To my wife, parents and siblings,

your love, patience and support has made this endeavor possible.
BIOGRAPHY

Isaac Bryan was born on November 25, 1988 and raised in Maiden, North Carolina. He earned a BS in Physics and in Mathematics from Appalachian State University in May of 2011. In August of 2011, he enrolled into the doctoral program in the Materials Science and Engineering Department at North Carolina State University.
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CHAPTER 1: Introduction

1.1 Dissertation Overview

AlN single crystalline substrates provide an excellent platform for fabricating Al-rich AlGaN based deep-UV emitting optoelectronic and high-frequency, high-power electronic devices.\textsuperscript{1-6} Many recent studies have been reported in a push towards the successful fabrication of highly efficient light emitting diodes (LEDs) and electrically pumped laser diodes (LDs), which emit at wavelengths below 300 nm.\textsuperscript{3,7} This wavelength range is near the absorption edge of many biological species and provides an opportunity for sterilization and biochemical identification applications. The high thermal conductivity and low lattice mismatch of the native AlN substrate with Al-rich AlGaN make it suitable for such devices. In order to exploit its full potential, the ability to grow low defect density homoepitaxial AlN and heteroepitaxial Al-rich AlGaN layers on single crystalline AlN substrates, which serve as a base for the subsequent growth of device structures, is essential, as defects within the layers can be detrimental to the overall performance of III-nitride based technologies.\textsuperscript{8-11} Furthermore, reduction of dislocation density and identification and reduction of compensating defects are necessary to obtain highly conductive Al-rich AlGaN and AlN for these devices. Most of these devices are implemented on c-plane surfaces and potentially suffer from large internal electric fields due to the effects of the inherent spontaneous and piezoelectric polarizations. It is expected that these polarizations cause a spatial separation of the charge carriers in quantum confinement structures, limiting radiative recombination efficiencies.\textsuperscript{12, 13} Therefore, eliminating these effects of the polarization fields through growth of films in directions
perpendicular to the polar axis, i.e. a non-polar orientation, is of interest to the III-nitride community.

This dissertation will be primarily focused on the growth by metalorganic chemical vapor deposition (MOCVD) of high quality and purity Al-rich AlGaN and AlN thin films on native AlN substrates. The present chapter will provide an overview of the material properties of III-nitrides along with some of the basic principles and concepts that will be referred to throughout the entire dissertation. Growth of epitaxy along the metal-polar orientation will be discussed in Chapter 2 with a primary focus of developing an understanding of the surface dynamics in order to consistently produce atomically smooth and homogeneous thin films. Chapter 3 will include studies of non-polar growth with a similar focus to Chapter 2. Doping, both n- and p-type, will be investigated in Chapter 4 with an emphasis on identifying the unintentional point defects that incorporate during growth. Finally, Chapter 5 will provide a summary of all the results discussed and suggestions for future work.

1.2 Properties of III-nitrides

The III-nitrides are comprised of InN, GaN, and AlN, along with their ternary and quaternary alloys. These semiconductors have direct bandgaps which span a range of 0.7 eV for InN to 3.4 eV for GaN to 6.0 eV for AlN.\textsuperscript{14,15} This wide range of direct bandgaps make the III-nitrides prime candidates for optoelectronic devices that emit and absorb in the infrared, visible, and deep ultraviolet spectral regions. In addition to their direct bandgaps, the III-nitrides are also readily known for their relatively high thermal conductivities, thermal
stabilities, electric breakdown fields, and electron mobility making them ideal for high power electronic devices.\textsuperscript{16} Table 1-1 gives some room temperature properties of the III-nitrides.

Table 1-1: Room temperature properties of the III-nitrides.\textsuperscript{14, 17}

<table>
<thead>
<tr>
<th></th>
<th>InN</th>
<th>GaN</th>
<th>AlN</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity</td>
<td>0.8</td>
<td>2.3</td>
<td>3.4</td>
<td>W/cm K</td>
</tr>
<tr>
<td>Electric breakdown field</td>
<td>3.3</td>
<td>11.7</td>
<td></td>
<td>MV/cm</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>3200</td>
<td>1800</td>
<td>300</td>
<td>cm$^2$/V s</td>
</tr>
<tr>
<td>Lattice constants: $c_0/a_0$</td>
<td>5.703 / 3.545</td>
<td>5.185 / 3.189</td>
<td>4.982 / 3.112</td>
<td>Å</td>
</tr>
<tr>
<td>Bandgap</td>
<td>0.7</td>
<td>3.4</td>
<td>6.0</td>
<td>eV</td>
</tr>
</tbody>
</table>

There are two primary crystal structures observed for the III-nitrides; a metastable cubic zincblende structure and a stable 2H wurtzite structure. Figure 1-1 (a) shows an incomplete unit cell of the stable wurtzite phase, which is the most natural and common crystal form of the III-nitrides. Due to the differences in electronegativity of the N and III-atom, the crystal structure is non-centrosymmetric. This break in symmetry exists along the c-axis and promotes a built in spontaneous polarization field. Because of this polarization, there are two types of orientations when looking along the c-axis, a N-polar and a III-atom polar (metal-polar) orientation. The polarization points in the direction of the N-polar surface. Symmetry does exist along the a-axis and this introduces non-polar ($m$- and $a$-) and semi-polar ($s$- and $r$-) planes, which are denoted in Figure 1-1 (b). The surface energies of these planes are different.
and causes there to be intrinsic differences in how adatoms incorporate and move on the growing surfaces, which will be discussed throughout later chapters in terms of impurity incorporation and surface morphology. These intrinsic differences make it important to have the ability to distinguish between these orientations, which can be done efficiently through selective etching or x-ray diffraction studies.

![Diagram](image)

Figure 1-1: An incomplete wurtzite unit cell (a) along with a depiction of the common planes (b) found in the III-nitrides.
For optoelectronic devices, this spontaneous polarization can be seen as problematic due to the quantum confined Stark effect. When III-nitride quantum wells are grown along the polar axis, both the piezoelectric and spontaneous electric fields cause the bands to bend, as shown in Figure 1-2. The band bending results in a poor overlap of the electron and hole wavefunctions, which causes a reduction of the internal quantum efficiency and a shift of the emission wavelength. This problem could be mitigated by using a non-polar orientation, also shown in Figure 1-2, however, growth along this direction has yet to be developed to the extent of the polar orientations.¹⁹

Figure 1-2: Schematic representation (from Reference ¹⁹) of the band structure and electron and hole wavefunctions for GaN/AlGaN quantum wells grown along the polar and non-polar orientations.
The preferential polarization of photons that emit from GaN and AlN are different due to a shift in the highest energy hole state from the heavy-hole to split-off-hole, respectively. Therefore, light that emits from GaN or AlN is preferentially transverse electric (TE) or transverse magnetic (TM) polarized, respectively. Moreover, for AlGaN based optoelectronics, studies show that as the Al-concentration increases, there is a transition for the polarization of emission from TE to TM because of the crossover of the top most valence band. For efficient light extraction in top and bottom emitting structures, the light that propagates along the polar axis needs to be TE polarized, which is depicted in Figure 1-3. TM polarized emission is more difficult to extract than TE polarized emission due to the typical light extraction cone perpendicular to the multiple quantum well (MQW) plane which has a critical angle of total internal reflection of ~20°. Therefore, the emission along the polar axis is greatly hindered for any structures implementing high Al-concentration AlGaN, where TM polarization exists. For the non-polar orientation, light extraction is not imposed by the type of polarization, i.e. Al-concentration.
1.3 Growth of Al-rich AlGaN and AlN

1.3.1 Single Crystalline AlN Bulk Substrates by PVT

Al-rich AlGaN and AlN thin films are typically grown on foreign substrates such as sapphire, silicon carbide or even silicon due to the lack of a readily available native substrate. These films exhibit high dislocation densities (10^7 to 10^{10} cm^{-2}) due to the large lattice mismatch between the substrate and film. The high dislocation densities hinder the overall performance of the thin films, making it desirable to reduce them. Recently, the development and availability of AlN single crystal substrates with low dislocation densities (< 10^3 cm^{-2}) has made it possible to grow Al-rich AlGaN and homoepitaxial AlN with low densities of extended
defects.\textsuperscript{22, 23} These epi-ready substrates have many advantages over the foreign substrates besides just the significant decrease in dislocation density of thin films grown on them. By having AlN as a substrate, one can use the high thermal conductivity to improve thermal management for high power devices. Furthermore, growing epitaxial films requires no additional buffer layers or transition layers which are typically used to account for the large lattice mismatch between the substrate and film. This simplicity of growth saves time and materials.

These substrates are grown by physical vapor transport (PVT). The AlN source powder used for PVT growth is sintered at temperatures above 2150 °C for about 20 hrs. in order to reduce oxygen and carbon impurities, which would result in the deposition of Al$_2$O$_3$ and Al$_4$C$_3$.\textsuperscript{24} During PVT growth, this AlN source powder is sublimed within a tungsten or tantalum carbide crucible. Once in the vapor form, a temperature gradient transfers the vapor to an AlN seed crystal, which is held at a lower temperature than the source powder. Recrystallization occurs at the seed crystal and growth proceeds in this manner. Growth temperatures between 2200 and 2500 °C are typically used with growth rates of around 500 µm/hr.\textsuperscript{1} These PVT systems must be designed to withstand these high temperatures and more importantly control the temperature gradients with great precision. The temperature profile control across the crucible directly affects the successful growth of a symmetric crystal boule like that shown in Figure 1-4 (a).
The highest quality AlN single crystals are grown using a high crystalline quality seed crystal (typically the top of a previously grown boule). Thus, the diameter of a boule is directly dependent on the lateral growth rate of the m-planes. There are ways to increase the lateral growth rate but this can only be done at the expense of the crystalline quality. This results in a
painfully slow expansion rate of the crystal boules and is one reason for limitations in available wafer diameters and for the high cost of currently available AlN single crystal substrates. To fabricate an epi-ready substrate, these boules are taken and sliced by a diamond wire saw along the desired crystal direction. The most common type of substrate are c-plane substrates like that shown in Figure 1-4 (b). Once the boule is cut, the slices are first mechanically polished to remove the plastic deformation caused by the saw. It is at this step that the substrate misorientation is fixed. The substrate misorientation from the c-axis plays an important role in the subsequent growth of thin films as will be discussed throughout this dissertation. The final step of fabrication is a chemomechanical polish (CMP) which plays three important roles; first it removes subsurface damage, second it produces an atomically smooth surface, and third it passivates the surface with a stable hydroxide layer that can be easily removed prior to growth.\textsuperscript{1, 23, 25} The passivation is key because AlN tends to spontaneously oxidize and this can result in difficulty later when trying to grow epitaxially on the oxide layer.

PVT grown AlN substrates are often amber in color, as shown in Figure 1-4. This is surprising when the bandgap of around 6.0 eV is taken into account, which should make substrates transparent to visible light. The origin of the apparent color of the AlN substrates is the incorporation of undesirable impurities. Carbon, oxygen, and silicon are common impurities which exist in AlN crystals that incorporate during growth. These impurities form deep level states and result in absorption bands within the bandgap. In particular, carbon has been found to incorporate readily in the PVT grown substrates at significant levels of around $10^{19}$ cm\textsuperscript{-3}. Collazo et al. showed that carbon is responsible for the absorption at 265 nm.\textsuperscript{26} This absorption band is one of the most important seen in AlN, since most optoelectronic devices
which would utilize the AlN native substrate emit between 230 and 280 nm. Therefore, the substrate absorbs a significant amount of the emitted light and prevents light extraction through the substrate of such devices. This absorption band along with the high expense of growing these AlN substrates have hindered their overall success and spot in the mainstream of nitride growth processes in industry. Ultimately, however, the only way to produce high quality and efficient devices will be through growth on a native substrate as has been seen in other materials systems throughout history. All of the work that will be discussed in this dissertation will serve to strengthen the position of AlN substrates in the III-nitride community.

1.3.2 Al-rich AlGaN and AlN Epitaxy by MOCVD

The most common technique used today for the growth of Al-rich AlGaN and AlN thin films is MOCVD. Other techniques include molecular beam epitaxy (MBE) and hydride vapor phase epitaxy (HVPE). The main reasons for the popularity of MOCVD for Al-rich AlGaN and AlN growth is that it provides a way to grow films with relatively low impurity levels while maintaining manageable growth rates for device structures.

The thin film samples studied for this dissertation research were grown using a vertical, cold-walled, rf-heated, low-pressure MOCVD reactor. Figure 1-5 shows the reactor during a growth where the glowing hot susceptor can be seen in the center of the reactor. For this reactor, trimethylaluminum (TMA), triethylgallium (TEG), and ammonia (NH$_3$) are used as the Al, Ga, and N precursors, respectively. Silane (SiH$_4$) and bis-cyclopentadienyl magnesium (Cp$_2$Mg) are used as the Si and Mg dopant sources. As compared to PVT, which relies solely on the physical transport of the AlN from the source to the seed crystal, this deposition
technique relies on a chemical reaction taking place near the hot substrate during growth. The following reaction occurs for the growth of AlN or AlGaN, where M represents either Al or Ga species.

\[
M (g) + NH_3 (g) \rightleftharpoons MN (s) + \frac{3}{2} H_2 (g)
\]  

(1)

The metalorganic sources, TEG and TMA, are not included in this reaction because thermolysis of the sources into the Ga and Al gas phase is highly spontaneous.

Figure 1-5: MOCVD chamber (top) and complete reactor system (bottom), which is used for the growth of all the samples studied.
The driving force behind MOCVD growth can be described by a single universal parameter called the vapor supersaturation. The vapor supersaturation is given by the following expression for AlN, where $P_{Al}$ is the equilibrium vapor pressure of Al and $P_{Al'}$ is the input partial pressure of the Al species.

$$\sigma = \frac{P_{Al'} - P_{Al}}{P_{Al}}$$

This parameter describes the deviation of the system from thermal equilibrium conditions. The vapor supersaturation determines the growth rate, surface morphology and defect incorporation of the thin film and can be controlled by adjusting different growth parameters. $P_{Al'}$ is affected by the total flow of all the gas species, total pressure, and the gas flow of TMA. $P_{Al}$ is primarily dependent on the growth temperature, but is also affected by the diluent gas composition, cracking efficiency of the NH$_3$, and the partial pressures of all the gaseous species. This vapor supersaturation is directly linked to the surface supersaturation which will be discussed in later sections.

1.4 Defects in Al-rich AlGaN and AlN

1.4.1 Point Defects

Point defects are zero dimensional defects which consist of missing atoms, i.e. vacancies or vacancy complexes, or atoms sitting on non-intrinsic lattice sites within the crystal. Point defects prevent the crystal from being 100% pure. These defects can influence the electrical conductivity of semiconductors. Without point defects, Al-rich AlGaN and AlN would be insulating at room temperature due to their wide bandgaps. Therefore, a clear
understanding of all intentionally and unintentionally incorporated point defects in this material is necessary.

There are many techniques for studying point defects, but each one has its own limitations. Impurities can be quantified by secondary ion mass spectroscopy (SIMS). This technique assumes that appropriate standards exist for calibration and that the impurity level is above some threshold or detection limit. For AlGaN, this becomes very difficult to achieve since there are no such appropriate standards available. The concentration of native defects, such as vacancies and vacancy-impurity complexes, are very difficult to quantitatively determine. For native defects, typically positron annihilation spectroscopy is used as a qualitative measure, but this technique can only identify negatively charged defects. Positron analysis requires theoretical input as a reference as well and is very poor in predicting the concentration of such defects.

With any point defect, the presence of the defect within the crystal will cause defect bands to form within the bandgap. These additional states cause the material to have characteristic optical properties. Therefore, another practical method for qualitatively studying point defects is by studying the optical properties, such as absorption and luminescence. For relatively new material systems like AlN and Al-rich AlGaN, photoluminescence (PL) and cathodoluminescence (CL) can provide information on the relative position of point defect bands within the bandgap, but additional reference information is needed to identify the point defects and their associated emission lines. With the advances made possible through the work that will be presented in this dissertation, new qualities have been achieved that for the first
time allow for observation and identification of defects using PL. PL will be used extensively in conjunction with theoretical modeling to study the point defects in Al-rich AlGaN and AlN.

Hybrid density functional theory (DFT) calculations provided by Dr. Benjamin Gaddy and Dr. Douglas Irving will be used in this dissertation to model point defects in Al-rich AlGaN and AlN. DFT is a quantum mechanical method, typically carried out computationally, for determining the electronic wavefunction within a many atom system. In the studies to follow, the formation energies of defects were calculated using hybrid DFT in the plane wave expansion as implemented in VASP 5.2 in order to determine the likelihood of defect formation. Hybrid functionals, which mix a standard exchange-correlation functional with a fraction of exact Hartree-Fock exchange, were used in an attempt to better capture the experimental bandgap of the AlGaN and AlN materials. With the formation energies determined, as a function of the accessible growth conditions and Fermi level, the concentration of a defect can be determined. All of these calculations can be closely tied to experimental measurements such as PL, SIMS, or positron measurements to better understand the role of point defects in these wide bandgap semiconductors.

In the case of conductive thin films, the number of compensating point defects can be determined indirectly through temperature dependent Hall effect measurements. The subsequent discussion will give a brief overview on the theoretical background.

Consider a n-type semiconductor with a concentration of \( n \) free electron carriers. The law of mass action states that the number of positive charges must be equal to the number of negative charges through the following expression

\[
p + N_D^+ = n + N_A^-
\]  

(3)
where $p$, $N_{D^+}$, and $N_{A^-}$ are the free hole carrier, ionized donor, and ionized acceptor concentrations, respectively. Assuming Fermi-Dirac statistics, the concentration of ionized donors can be found using

$$N_{D^+} = N_D [1 - f(E_D)] = \frac{N_D}{1 + e^{\frac{E_F - E_D}{k_B T}}}$$  \hspace{1cm} (4)$$

where $f(E_D)$ is the probability of an electron occupying the donor energy state, $E_D$, and $N_D$, $E_F$, and $g$ are the donor concentration, Fermi level, and charge degeneracy factor, respectively. But if we let $E_a$ equal the difference between the conduction band minimum and $E_D$ then the equation can be rewritten into the following form.

$$N_{D^+} = \frac{N_D}{1 + \frac{n}{N_C} e^{\frac{E_a}{k_B T}}}$$  \hspace{1cm} (5)$$

where $N_C$ is the density of states for the conduction band. For a n-type semiconductor, the free hole carrier concentration is very small. Also, the concentration of ionized acceptors must equal the concentration of acceptors, $N_A$, since every free electron will occupy the lower energy acceptor states at all temperatures. Using these assumptions along with Equations 3 and 5, Equation 6 can be used to determine the concentration of compensating defects, i.e. acceptors, by knowing the temperature dependence of the free carrier concentration.

$$\frac{n(n+N_A)}{N_D-N_{A^-} - n} = \frac{N_C}{g} e^{\frac{E_a}{k_B T}}$$  \hspace{1cm} (6)$$

Equation 6 will be used to calculate the degree of compensation and the Si donor activation energy in Si-doped Al-rich AlGaN and AlN in Chapter 4.
1.4.2 Extended Defects

In contrast to point defects, extended defects are defects which extend in one or more dimensions. The two types of extended defects that will be discussed in this dissertation are dislocations and stacking faults which are line and planar defects, respectively. The presence of extended defects in a material can hinder the materials potential in device structures. Some extended defects have been shown to act as scattering centers, which can potentially reduce the conductivity of a material by reducing the mobility. Others are known to act as nonradiative recombination centers which reduces quantum efficiencies in optoelectronic devices. There are even some extended defects which are conductive and act as electrical leakage paths in vertical devices. Lastly, these defects distort the crystal and induce strain fields which can attract point defects due to a local change in the chemical potential.

Since the III-nitrides have a wurtzite crystal structure, the dislocations in Al-rich AlGaN and AlN are classified into three different types; \( a \) type, \( b=(1/3)<11 \bar{2}0> \), \( a+c \) type, \( b=(1/3)<11 \bar{2}3> \), and \( c \) type, \( b=<0001> \). By definition of edge and screw type dislocations, if a film is grown epitaxially in the [0001] direction, i.e metal-polar, and the dislocation line is given by [0001], then these three types would be denoted as edge, mixed, and screw type dislocations, respectively. These dislocations would also be known as threading dislocations since the dislocation line is parallel to the growth direction. Dislocations can be annihilated by either terminating at a free surface or by forming loops among each other. In later chapters, both heteroepitaxial films grown on foreign and native substrates will be studied. In the case of using a foreign substrate, techniques will be used to reduce dislocation densities by increasing the surface area through three dimensional growth in order to increase the
probability of dislocation annihilation. For AlGaN films grown on native AlN substrates, the critical thickness will be considered.\textsuperscript{34, 35} By growing pseudomorphically, no additional dislocations will be introduced beyond those already present in the substrate. Above the critical thickness, relaxation will occur to reduce the mismatch strain potentially introducing additional dislocations.

Stacking faults (SFs) are associated with partial dislocations, which have Burgers vectors that are not equivalent to a lattice vector. There are two primary classifications for SFs in a wurtzite structure, prismatic stacking faults (PSFs) and basal plane stacking faults (BSFs). For III-nitride epitaxial films, SFs are most commonly observed and studied in non-polar films. In fact, a high density of SFs remains one of the primary issues for realizing high quality non-polar III-nitride materials. Of the observed SFs in non-polar III-nitrides, BSFs tend to prevail and be only intrinsic $I_1$ type which can be formed with a displacement of the lattice of $1/3 \times 1\overline{1}00$ plus the insertion or removal of a basal plane resulting in $\ldots AaBbAaBbCcBbCcBb \ldots$ stacking.\textsuperscript{36, 37} Contrary to extended defects formed with polar growth, the density of these BSFs in non-polar films do not significantly reduce with an increase in film thickness.\textsuperscript{38} Therefore, in order to achieve high quality non-polar films, the formation of such defects to begin with must be mitigated. One way to potentially do this is through growth on non-polar native substrates, which will be discussed in Chapter 3.

There are two techniques that will be used to study extended defects in this dissertation, high resolution x-ray diffraction (HRXRD) and transmission electron microscopy (TEM). HRXRD is an indirect technique and is used to study the tilt and twist of the mosaicity of a crystal, which can be related to the dislocation density type and density.\textsuperscript{39} HRXRD is also used
to determine lattice constants through the use of the basic Bragg’s Law. This technique is nondestructive and relatively fast, however, it is limited by the lack of an ability to detect clusters of dislocations or determine the behavior of dislocations in multilayered structures. A more direct technique is to study these defects by conventional TEM. TEM is a destructive technique, which requires the ability to prepare a sample that is thin enough for electron transparency. However, once the sample is properly prepared, this technique can image any type of extended defect and determine the exact type through using the diffraction invisibility criterion and direct detection of atomic displacements.

1.5 Surface Dynamics of Crystal Growth

Epitaxial thin film deposition or growth can proceed on a substrate surface by 2D or 3D nucleation growth, step flow growth, or a combination of these growth modes. In all cases, deposition requires that there be a deviation of the system from thermodynamic equilibrium. This deviation can be expressed through the surface supersaturation. The surface supersaturation determines which of the growth modes is the most favorable. In the sections to follow, different growth modes will be discussed along with classical theory which is commonly used to describe each of them.

1.5.1 Nucleation

During thin film growth, if the supersaturation is large then growth can proceed by nucleation. The formation of stable nuclei requires that the nuclei be sufficiently large so that the energy released to form its volume is enough to create its surface. The critical size where
this occurs is governed by thermodynamics where the change in Gibbs free energy must be favored. The following expression describes the change in Gibbs free energy, $\Delta G_{2D}$, for a circular two dimensional nucleation process like that shown in Figure 1-6

$$\Delta G_{2D} = 2\pi rh \gamma_s - \frac{\pi r^2}{A} \Delta \mu$$

(7)

where $r$, $h$, $\gamma_s$, $A$, and $\Delta \mu$ are the nucleus radius, nucleus height, surface free energy of the step, projected area of an adatom, and change in chemical potential, respectively. For this case, it has been assumed that the nuclei are of the same material as the substrate so that there is no need to consider the change in interface energy or strain energy. The change in free energy for this process is plotted in Figure 1-6 (b). From this plot, it is clear that $\Delta G_{2D}$ initially increases due to the unfavorable creation of the new step edge. It is during this increase that the formation of a stable nucleus cannot occur spontaneously. The nucleus will become stable once the critical radius, $r^*$, is reached which is associated with the maximum of $\Delta G_{2D}$. 


Figure 1-6: Schematic of a circular two dimensional nucleus (a) and the change in free energy for the nucleation process plotted as a function of the nucleus radius (b).

This critical point can easily be determined and gives the critical free energy of nucleation, $\Delta G_{2D}^*$, and $r^*$ as the following expressions

$$ r^* = \frac{hAy_s}{k_B T \ln (\sigma_s^* + 1)} $$

(8)

$$ \Delta G_{2D}^* = \frac{\pi h^2 Ay_s^2}{k_B T \ln (\sigma_s^* + 1)} $$

(9)

where $\Delta \mu$ has now been expressed in terms of the critical surface supersaturation, $\sigma_s^*$.

Classical nucleation theory establishes that the critical nucleation rate, $R_{2D}^*$, is proportional to the rate at which the molecules attach to the supercritical nucleus, $j^*$, the probability of a nucleus overcoming the critical energetic barrier (Zeldovich nonequilibrium factor, $Z$), and the equilibrium concentration of critical nuclei, $N_s^*$.\(^{40}\) This can be approximated for AlN as shown
\[ R_{2D}^* = j^* Z N^* \approx e^{65 - \frac{\Delta G_{2D}}{k_B T}} \]  

(10)

By combining Equation 9 with Equation 10, the critical surface supersaturation, where the onset of nucleation should be favored, is given as

\[ \sigma_s^* = e^{\frac{\pi h^2 A_y^2}{k_B T^2 [65 - \ln(R_{2D}^*)]}} \]  

(11)

This expression is important to realize since as will be shown in Chapter 2, this critical point can be observed experimentally and can resolve kinetic properties of adatoms during Al-rich AlGaN and AlN thin film growth.

1.5.2 Surface Diffusion

The well-known Burton, Cabrera, and Frank (BCF) theory for crystal growth can be used to better understand the kinetics of adatoms on a step and terrace morphology during step-flow growth.\(^{41}\) The source of steps can be from a misoriented cut of the substrate, dislocations or both. The following discussion will present a technique for determining the surface diffusion properties of Al for the growth of AlN epitaxy. For the case of an ideal step, each step is isotropic in nature and free of nuclei. This allows one to consider only a one dimensional case for surface diffusion. An atom approaches a step of height, \( h \), normal to the surface and either diffuses and incorporates at the step edge, adsorbs to form a nucleus on the step, or desorbs. Figure 1-7 depicts the resulting fluxes, where \( J_s, J, n_s, \tau_s \), and \( \lambda_0 \) are the surface diffusion flux, adatom arrival flux, adatom density on the surface, mean residence time, and terrace width, respectively.
Using Einstein’s relation, the surface diffusion length, $\lambda_s$, is directly related to the diffusion coefficient on the surface, $D_s$, and $\tau_s$. It can also be expressed in terms of the diffusion barrier energy, $E_d$, and the energetic barrier to be surmounted for desorption which is the same as the adsorption energy, $E_{ad}$:\[^{42}\]

$$
\lambda_s = \sqrt{D_s \tau_s} = \lambda_e e^{\frac{E_{ad} - E_d}{2k_B T}}
$$

(12)

Here, $\lambda_e$ is the effective elementary jump distance on the surface.

In absence of nucleation, the net flux adsorbing to the surface, $J_s(x)$, must be equal to the diffusion flux toward the steps. Therefore, if the steps are assumed to be perfect sinks, i.e. the capture probability at the steps is unity, then the following continuity equation describes the system:
\[ \frac{dJ_s(x)}{dx} = J - \frac{n_s(x)}{\tau_s} = J_v(x) \quad (13) \]

Fick’s first law states that the diffusion flux is proportional to the change in adatom concentration. Therefore, Equation 13 can be rewritten as follows:

\[-D_s \frac{d^2n_s(x)}{dx^2} = J - \frac{n_s(x)}{\tau_s} \quad (14)\]

A solution to the second order differential equation is used to determine the adatom density as a function of the position on the surface, using the step edge as a boundary condition. It is assumed that the step edge is at equilibrium and has an adatom density of \( n_{s0} \).

\[ n_s(x) = J \tau_s + (n_{s0} - J \tau_s) \frac{\cosh \left( \frac{x}{\lambda_s} \right)}{\cosh \left( \frac{L_0}{2 \lambda_s} \right)} \quad (15) \]

The surface supersaturation, \( \sigma_s \), is given as the relative difference between \( n_s \) and \( n_{s0} \). Therefore, Equation 15 can be used to derive the surface supersaturation as a function of the position on the surface.

\[ \sigma_s(x) = \frac{n_s(x) - n_{s0}}{n_{s0}} = \left( \frac{J \tau_s}{n_{s0}} - 1 \right) \left( 1 - \frac{\cosh \left( \frac{x}{\lambda_s} \right)}{\cosh \left( \frac{L_0}{2 \lambda_s} \right)} \right) \quad (16) \]

With this expression, \( \sigma_s \) is sketched as a function of position on a step and terrace surface in Figure 1-8.
Figure 1-8: Schematic representing the surface supersaturation as a function of position on an ideal step and terrace morphology.

Through the original BCF treatment, $\sigma_s$ is directly related to $\sigma$. Considering the relationship proposed, the net adatom arrival flux going from the vapor to the surface, which was already described in Equation 13, can be rewritten as:

$$J_v(x) = \frac{n_{s0}}{\tau_s} (\sigma - \sigma_s(x))$$

(17)

Therefore, through this relationship, Equations 13 and 16 can be considered in order to express $\sigma_s$ in terms of $\sigma$.

$$\sigma_s(x) = \sigma \left(1 - \frac{\cosh \left( \frac{x}{\lambda_s} \right)}{\cosh \left( \frac{\lambda_0}{2 \lambda_s} \right)} \right)$$

(18)
Equation 18 indicates the direct connection between the vapor and surface kinetics. Having this relationship allows for a better understanding of how growth conditions will affect the dynamics of the adatoms on the surface. This expression indicates that $\sigma_s$ reaches a maximum somewhere near the center of the terrace. It is important to note that this kinetic theory treatment assumes a symmetric $n_s$, however an asymmetric condition is probably more likely to exist due to the fact that the probability of uphill and downhill adatom diffusion occurring at a step edge is usually not the same. For simplicity the symmetric condition is used since this does not change the overall trends that will be discussed and supported through experimental results in later Chapters. If the maximum of the surface supersaturation profile across a step exceeds a critical surface supersaturation value, $\sigma_s^*$, then nucleation will occur. The maximum of Equation 18 gives the maximum surface supersaturation as follows:

$$\sigma_{s,\text{max}} = \sigma \left(1 - \frac{1}{\cosh \left( \frac{4\pi}{\sigma_{s}} \right)} \right)$$

(19)

Finally, Equation 11, can be used for $\sigma_s^*$ and the surface diffusion properties can be realized, which will be shown in detail throughout Chapter 2.

1.5.3 Alloy Composition

Section 1.5.2 described a system where only one adatom was considered. This simplified model can be used for AlN in order to understand general trends observed experimentally, but for AlGaN both the Al and Ga adatoms must be considered. The surface diffusion flux as a function of position on a step for each species can be formulated from Equation 15.
The arrival and desorption flux will not necessarily be the same for Ga as it is for Al. Knowing the diffusion flux at the step edge for both species allows for the composition to be estimated.

\[
J_{s,Al}(x) = \lambda_{s,Al} \left[ J_{Al} - \left( \frac{n_{s0}}{\tau_s} \right)_{Al} \right] \frac{\sinh \left( \frac{x}{\lambda_{s,Al}} \right)}{\cosh \left( \frac{2b}{\lambda_{2s,Al}} \right)}
\]

\[
J_{s,Ga}(x) = \lambda_{s,Ga} \left[ J_{Ga} - \left( \frac{n_{s0}}{\tau_s} \right)_{Ga} \right] \frac{\sinh \left( \frac{x}{\lambda_{s,Ga}} \right)}{\cosh \left( \frac{2b}{\lambda_{2s,Ga}} \right)}
\]

(20)

(21)

The arrival and desorption flux will not necessarily be the same for Ga as it is for Al. Knowing the diffusion flux at the step edge for both species allows for the composition to be estimated.

\[
x = \frac{J_{s,Al} \left( \frac{\lambda_0}{2} \right)}{J_{s,Ga} \left( \frac{\lambda_0}{2} \right) + J_{s,Al} \left( \frac{\lambda_0}{2} \right)} = \frac{R_{Al}}{R_{Al} + R_{Ga}}
\]

(22)

where \( R \) is the growth rate. The growth rate is given by the product of the step velocity and \( h/\lambda_0 \). The step velocity, \( v \), can be expressed in the following manner where adatoms diffusing from both the left and the right of the step edge has been considered:

\[
v = 2 \frac{J_{s} \left( \frac{\lambda_0}{2} \right)}{n_0}
\]

(23)

Here \( n_0 \) is the density of adatom sites on the surface.

With an alloy, there is always going to be a difference in the mobility of the different species. In particular, it is expected that Ga adatoms during GaN growth have a much larger diffusion length than Al adatoms during AlN growth.\(^{43, 44}\) However, these diffusion lengths were determined considering different growth conditions. Furthermore, this could be altered when Al and Ga are both on a surface simultaneously and deposited with the same growth conditions, for example during AlGaN growth. Notice that when \( \lambda_s \) is much greater than \( \lambda_0 \), the hyperbolic tangent term in \( J_s(\lambda_0/2) \) tends to \( \lambda_0/2\lambda_s \). Conversely, if \( \lambda_s \) is much smaller than \( \lambda_0 \),
then the hyperbolic tangent term in $J_s(\lambda_0/2)$ tends to 1, which gives the following relationships for $R_{Al}$ and $R_{Ga}$.

\[
R \approx \begin{cases} 
\frac{2h\lambda_S}{n_0\lambda_0} \left( f - \frac{n_{s0}}{\tau_s} \right), & \lambda_0 > \lambda_S \\
\frac{h}{n_0} \left( f - \frac{n_{s0}}{\tau_s} \right), & \lambda_0 < \lambda_S 
\end{cases} 
\]

(24)

Therefore, if either Al, Ga, or both species exhibits a small diffusion length relative to the terrace width, then the composition of AlGaN will be substrate misorientation dependent.

1.5.4 Step Bunching

As mentioned in Section 1.5.3, the Al and Ga adatoms will have different surface kinetics, therefore any evolution of the surface morphology, such as step bunching, has the potential of leading to nonuniform compositions.\textsuperscript{45} The surface supersaturation plotted in Figure 1-8 assumed the boundary conditions that when approaching the step edge from the left (top) and the right (bottom), the same equilibrium adatom concentration exists. This assumption is a good approximation for a step and terrace morphology free of step bunching. However, when step bunching is favorable, one must consider the significant Schwoebel barrier effect that exists at the step edge as depicted in Figure 1-9 (a).\textsuperscript{46,47} $E_{ES}$ and $E_S$ represent the Ehrlich-Schwoebel barrier and step edge binding energies, respectively, and arrive from the difference of coordination for atoms at the top and bottom of the step. This barrier will require the adatoms that travel toward the top of the step edge to undergo a less probable diffusion down the step edge in order to incorporate. Therefore, the adatom concentration should be different at the top of the edge versus the bottom.
The exact reason for the onset of step bunching is still under debate. Usually, it is attributed to the surface kinetics of adatoms through the Schwoebel effect, however, others have suggested the cause to be from short range attractions between steps and some from partial relaxation of a strained vicinal layer. Through the surface kinetics approach, the
onset of step bunching can be described as shown in Figure 1-9 (b). The Schwoebel barrier causes the rate of step advancement to vary from step to step due first to the attachment probability differences and second to the length differences of the adjacent steps. This instability will result in some steps shrinking and others expanding until bunching occurs. The advantages and disadvantages of having a step bunched morphology will be discussed throughout this dissertation.

1.5.5 Surface Roughening

There are three traditional growth modes for heteroepitaxial growth, where some degree of mismatch strain exists between the film and substrate, which are Frank-van der Merwe (FM)\textsuperscript{51}, Volmer-Weber (VW)\textsuperscript{52}, and Stranski-Krstanow (SK)\textsuperscript{53}. These are commonly referred to as layer by layer, island, and layer by layer plus island growth, respectively. The type of growth mode depends directly on the interface, surface, and mismatch strain energies. For the case of a system where the mismatch strain is negligible, VW growth will occur when the sum of the film surface free energy and the interface energy is greater than the substrate surface free energy. If the contrary is true then FM growth will tend to initially take place. If the mismatch strain is not negligible, as a FM grown film gets thicker, mismatch strain will build up and drive the system to form islands, i.e. SK growth.

More generally, surface modulation or roughening can occur during growth of elastically strained epitaxial layers. Surface roughening can be in the form of islands\textsuperscript{54}, surface cusps\textsuperscript{36}, cracks\textsuperscript{38}, or even pits\textsuperscript{55}. Of particular interest for this dissertation is island and pit formation, which are analogous to each other in terms of energetics. Conventionally, during
SK growth, the total energy of the system is reduced by island formation where the strain energy is relaxed by misfit dislocation formation. Therefore, by tradition, islands were dislocated, however, more recent experiments have shown that dislocation-free SK growth can occur which indicates that there exists some kind of coherent mechanism for reducing the elastic strain locally.\textsuperscript{54}

Vanderbilt et al. first developed a theory which compares these two mechanisms for reducing elastic strain during SK growth for elongated prisms.\textsuperscript{56} Later, Ratsch et al. extended this theory for pyramid shaped islands, which are more applicable to the surface defects that will be discussed in Chapter 2.\textsuperscript{57} In both cases, the formation of an island on a flat surface results in, first, a relaxation of the volumetric elastic strain energy, and, second, a change in the surface area.\textsuperscript{58} This increase in surface area is associated with an increase in surface energy which must be less than the reduction of the strain energy in order for the process to be spontaneous. The competition between dislocation and dislocation free island formation is governed by the relationship between the change in surface energy, $\Delta E_s$, and the energy of the dislocated interface, $E_{di}$. Figure 1-10 shows the general trend for preferred morphologies without islands, with dislocation free islands, and with dislocated islands as a function of film thickness, $t$, and the energetic ratio, $\Psi = E_{di}/\Delta E_s$. 
Figure 1-10: Sketch of a phase diagram for the preferred morphologies of a strained epitaxial layer (adopted from reference 58).

This phase diagram indicates that if $\Delta E_s$ is small relative to $E_{di}$ then the film will transition from no islands to dislocation free islands with increased film thickness. Eventually, there is a possibility of dislocated island formation with continued film deposition. To conclude, the driving force for coherent pit or island surface roughening is a partial relaxation of the total strain energy by purely elastic deformation even though there is an increase in the surface area and associated surface energy.
CHAPTER 2: Polar Growth

2.1 Motivation

Al-rich AlGaN alloys possess great potential as materials for deep-UV optoelectronic and high-power electronic devices due to their direct wide bandgaps and high electric breakdown fields.\(^6\),\(^7\) To realize such devices, high quality epitaxial films are necessary in order to reduce nonradiative events and current leakage pathways.\(^{59}\) This chapter will provide the necessary knowledge for producing such high quality epitaxial films. High densities of threading dislocations are present in films grown on typical foreign substrates, such as sapphire and silicon carbide.\(^4\),\(^{60}\) To achieve high crystalline quality films, the use of a high crystalline quality native substrate is essential due to the low lattice mismatch of the substrate with Al-rich AlGaN.\(^{22}\) Furthermore, the relatively high thermal conductivity of AlN makes the use of such a substrate ideal for thermal management in these devices.\(^{17}\)

Aside from dislocation reduction, it is crucial to obtain atomically smooth AlGaN thin films to acquire high quantum efficiencies in quantum well structures that require compositional uniformity.\(^{61}\) Also, efficient electron transport properties in high electron mobility transistors is directly dependent on the interface roughness.\(^{62}\) Finally, the importance of atomic thickness uniformity has been demonstrated in resonant tunneling devices such as resonant tunneling diodes and quantum cascade lasers, where the nonuniformity caused by large steps hindered the overall performance of such devices.\(^{63,64}\) For these reasons, the surface morphology and roughness of epitaxial films is very important and must be controlled. The only way to do this is through an understanding of the fundamental surface properties of the material species involved during growth.
It is known that different substrate misorientations and growth modes will result in characteristically rough or smooth surfaces in other material systems such as GaAs and SiC.\textsuperscript{65, 66} These material systems have been thoroughly investigated in terms of their surface kinetic properties using the well-known BCF theory for crystal growth.\textsuperscript{41} The surface kinetics of adatoms in vapor phase epitaxial growth of AlN or AlGaN on AlN vicinal surfaces has yet to be reported on. The effect of substrate misorientation on surface morphology has been observed for AlN and AlGaN epitaxy grown on foreign sapphire substrates.\textsuperscript{67, 68} However, these surfaces are influenced heavily by spiral growth due to high dislocation densities on the order of $10^9$ to $10^{10}$ cm$^{-2}$. The spiral growth makes it difficult to directly measure the surface kinetics related purely to the step flow growth mode. Furthermore, the spiral-mediated growth introduces additional roughness that must be mitigated.

Recently, growth of high-quality homoepitaxial AlN layers by MOCVD has been achieved.\textsuperscript{22, 23, 69} These films had defect-free surfaces and similar crystalline quality to those of the substrates, demonstrating the superiority of AlN bulk substrates for this purpose. However, the perfect epitaxial relationship depends on the condition of the polished surface of the substrate and, to some extent, the applied growth conditions. Interfacial layers between the epitaxial layer and substrate, small strain gradients, and surface defects such as pits or hillocks can be present in non-ideal cases. For the quick development of an innovative technology, it is important to recognize the manifestations of these effects and understand their origins to enable isolation and adjustments of relevant processes.

Small strain gradients in epitaxial layers can be partially relaxed during growth through various mechanisms such as misfit dislocation formation, surface roughening, and cracking.
Each relaxation mechanism requires different amounts of strain energy for initiation, which is dependent on the material system and crystallographic orientation. An assortment of relaxation-related defect structures has been found in strained epitaxial AlN layers on sapphire. In thick AlN layers on sapphire, large amounts of tensile strain exist which results in strain relaxation by means of crack formation. Furthermore, the formation of pits intrinsic to strained epitaxial layers has been shown to be a mechanism for partial local relaxation of strain. Therefore, pits and hillocks on AlN and AlGaN epitaxial layers must be investigated keeping this in mind.

Moreover, the compositional uniformity of ternary alloys has been shown to be directly related to the surface roughness. This is due to the fact that the surface diffusion properties of all the adatom species of the alloy differ and depend on local energetic barriers associated with the steps. In particular, step bunched surface morphologies have been seen to contain seemingly abrupt and undesirable compositional gradients that have been correlated with the differences in step densities across such a surface. The local variations in alloy composition observed in rough surfaces are not desirable since these variations can scatter carriers, broaden emission, and shift threshold voltages. Therefore, in order to achieve uniform compositions in alloy films and ultimately improve device performance, controlling the surface morphology during AlGaN growth is critical.
2.2 AlN and Al-rich AlGaN Growth

2.2.1 Preparation and Growth

Metal-polar AlN and Al-rich AlGaN films were deposited by MOCVD on vicinal c-plane sapphire and AlN substrates. It is important to mention that epitaxial growth on native bulk AlN is still a relatively new field of study primarily due to the availability and size of appropriately polished substrates.\textsuperscript{22,23,69,72-74} Even though devices have been demonstrated on these bulk AlN substrates, a comprehensive understanding of how growth proceeds on these substrates has not been presented.\textsuperscript{3,75} In particular, the substrate polishing process must result in a surface that is atomically smooth, properly passivated (to ensure longer term stability), free of subsurface polishing damage, flat (surface and lattice radius of curvature > 10 m for a 1” substrate), and oriented to the desired plane with an accuracy of ~ 0.1°, which has proven to be a difficult task for AlN substrates available to date. Rice et al. demonstrated the importance of chemomechanical polishing of the substrate for the epitaxial film growth and developed a surface preparation technique for reducing the amount of surface hydroxide on the substrate surface.\textsuperscript{23}

The AlN substrates used were processed from single crystalline AlN boules grown by PVT, as described in Section 1.3.1.\textsuperscript{24,76,77} All of the AlN substrates were nominally (0001) oriented and were received with a chemomechanically polished, atomically smooth surface, free of surface defects such as scratches or pits unless otherwise noted. Figure 2-1 gives a 5x5 μm\textsuperscript{2} atomic force microscope (AFM) image of a typical polished (0001) AlN substrate free of polishing damage where clear steps can be discerned. The steps were measured to have a step-height of 2.5 ± 0.1 Å, which matches nicely with the theoretical height of one c-plane bilayer.
\( c/2 \approx 2.49 \, \text{Å} \). The RMS roughness of the substrates was consistently below 100 pm for 5x5 \( \mu m^2 \) scan areas.

Figure 2-1: 5x5 \( \mu m^2 \) AFM image representing a typical as-received (0001) AlN substrate with an RMS roughness of about 60 pm.

The step/terrace ratio was used to determine the misorientation angle relative to [0001]. These measurements were further supported using standard HRXRD techniques. Before epilayer growth, the AlN substrates were put through a treatment procedure which fit within the criteria presented by Rice et al.\textsuperscript{23} The treatment began with cleaning the substrates using organic solvents. After cleaning, a wet etch using a 3:1 sulfuric:phosphoric acid mixture was implemented to reduce the amount of surface oxide and hydroxide. The substrates were then loaded into the MOCVD reactor and ramped to 1100 °C with 45 mmol/min flow of NH\(_3\) at a total pressure of 20 Torr. Once 1100 °C was achieved, epitaxial growth was initiated. This nitridation step is thought to promote the transformation of the surface to AlN.
The growth of AlN and AlGaN on the foreign sapphire substrate required multiple steps to account for the large lattice mismatch between the substrate and film and are as follows. First, the sapphire substrates were annealed at about 1100 °C under vacuum of around 10⁻⁶ Torr. This was followed by a treatment of H₂ annealing at 1100 °C and nitridation at around 950 °C, as described by Mita et al.[78] A 10 nm AlN buffer layer was deposited at 650 °C and annealed at around 1050 °C in order to control the polarity of the film. Next, an intermediate high temperature AlN layer was deposited using a growth condition that promoted 3D growth. The 3D growth is thought to promote annihilation of dislocations by causing dislocation bending towards the additional free surfaces. This intermediate layer reduced the dislocation density and allowed for thicker films to be realized without cracking. Finally, the growth conditions were changed to promote step flow growth, which provided an AlN template for all the AlN and AlGaN growth that will be discussed for foreign substrate growth.

All of the AlN and Al-rich AlGaN epitaxial films had final layers that were either deposited on the AlN template on sapphire or on the nitridated native AlN substrate, unless otherwise noted. The growth parameters follow. A pressure of 20 Torr was maintained during the entire epilayer growth and H₂ was used as the diluent gas with a flow of approximately 450 mmol/min. TMA, TEG, and NH₃ were used as the Al, Ga, and N precursors, respectively. The NH₃ flow was fixed at around 13 mmol/min while the TMA and TEG were varied from 7 to 28 µmol/min and 2 to 12 µmol/min, respectively. A TMA flow of 7 µmol/min during AlN growth resulted in a growth rate of about 500 nm/hr. The AlN epitaxial films were grown at temperatures between 1100 and 1250 °C, whereas all AlGaN epitaxial films were grown at 1100 °C. The growth was mass transport limited for all the conditions mentioned. Figure 2-2
shows the temperature profile for a typical AlGaN growth on both the sapphire and AlN substrates, with each of the above-mentioned growth steps being denoted.
Figure 2-2: Temperature profiles for a typical AlGaN growth on AlN substrates (top) and sapphire substrates (bottom). (a) AlN substrate nitridation, (b) AlN growth, (c) AlGaN growth, (d) vacuum anneal, (e) H₂ anneal, (f) sapphire substrate nitridation, (g) AlN buffer growth, (h) AlN buffer anneal, and (i) intermediate AlN layer growth.
2.2.2 Crystalline Quality

The epitaxial layers and substrates were characterized for extended defects by conventional TEM using a JEOL 2000FX operating at 200 kV. TEM samples were prepared by mechanical wedge polishing followed by Ar$^+$ ion milling with a Fischione Model 1010 Ion Mill. For the films grown on the native substrates, TEM analysis confirmed that no new dislocations were introduced in the epitaxial layers, which indicates that the high quality of the substrate was maintained through the MOCVD growth. In particular, all of the AlGaN films were grown pseudomorphically on the native AlN substrates. For films grown on sapphire, similar TEM analysis provided a consistent dislocation density of around $1 \times 10^{10}$ cm$^{-2}$.

HRXRD was also used to characterize the structural quality of the epitaxial layers. The full width at half maximums (FWHMs) of the (00.2), (10.2), and (30.2) XRD $\omega$-rocking curves of the AlN were measured to be as low as 26, 1070, and 1320 arcsec, respectively, for the films on sapphire and 12, 13, and 36 arcsec, respectively, for the films on AlN substrates. The $\omega$-rocking curves were indistinguishable from those of the substrate for the films grown on AlN substrates and the FWHMs did not deviate by more than 15 arcsec among all the films. For films grown on sapphire, $\omega$-rocking curve FWHMs had larger deviations of up to 200 arcsec. These deviations did not significantly affect the surface morphology, however. These results coincide well with the TEM results and shows the reproducibility of the growth procedure.
Figure 2-3: HRXRD triple axis (0002) ω-2θ curves of a (0001) AlN substrate, AlN homoepitaxial film and heteroepitaxial AlN film.

Representative (0002) ω-2θ spectra are given in Figure 2-3 for homoepitaxial and heteroepitaxial AlN films. The homoepitaxial films exhibited symmetric peaks that matched that of the substrate indicating the absence of a strained AlN layer. Pendellösung fringes were present in the ω-2θ line scans for the heteroepitaxial films grown on sapphire due to the abrupt change in electron density at the sapphire/AlN interface. Furthermore, the spacing between these interference fringes could be used to determine the thickness of the heteroepitaxial layers. The thickness of the layers could also be determined by the pyrometer interference pattern seen in Figure 2-2. These thicknesses were further confirmed by TEM and scanning transmission electron microscopy (STEM) studies in order to bring confidence to the growth rates given by various growth conditions for the AlN and Al-rich AlGaN films that were used for the studies presented in this dissertation.
2.3 Overview of All Possible Surface Morphologies

It is well known that for smooth surface morphologies, the step flow growth mode is necessary. This growth mode typically requires the presence of steps with a width on the order of or smaller than the diffusion length of the adatoms on the growing surface. The two primary sources of steps are dislocations and an intentionally misoriented substrate. When the dislocation density is very low, as in the case of epitaxial films deposited on native AlN substrates, the surface kinetics are dominated by the growth condition and the step density caused by the intentional misorientation of the substrate. No V-defect pitting, step pinning, or spiral growth exists in such a case. Figure 2-4 shows the six primary types of surface morphologies observed for AlN and Al-rich AlGaN epitaxial layers grown on native AlN single crystal substrates. Al-rich AlGaN surfaces were studied with an Al-content ranging from 60 to 100%.
Figure 2-4: 5x5 µm² AFM images representing the 6 types of surface morphologies attainable for both AlN and Al-rich AlGaN epitaxial layers free of dislocation mediated growth.
Figure 2-4 (a) represents a surface comprised of macro-sized islands made up of 2D nuclei stacked one on top of the other. This surface is a result of a 2D nucleation growth mode as compared to the step flow growth mode present in Figure 2-4 (b)-(f). Figure 2-4 (b) consists of bilayer steps that have a step height of ~2.5 Å. These epitaxial surfaces are the smoothest type of surface with an RMS roughness of less than 50 pm. The RMS roughness is even smoother than that of the as-received polished AlN substrates, shown in Figure 2-1. This is because the small protrusions occasionally seen on the AlN substrate surfaces, which are thought to be related to the surface passivation, are not present on freshly grown epitaxial film surfaces. Figure 2-4 (c) contains bilayer steps that are separated enough so that 2D nucleation is favorable on the steps. Figures 2-4 (e) and (f) are step bunched morphologies where the step heights are many times greater than the bilayer height. The edges of the step bunches in Figure 2-4 (e) are predominantly straight as compared to the jagged step bunch edges in Figure 2-4 (f). This difference was found to be due to the differences in the misorientation direction. Figures 2-4 (e) and (f) are misoriented close to the [1-100] and [11-20] direction, respectively. In fact, the degree of jaggedness was directly correlated to the deviation of the misorientation direction from the [1-100] direction. Finally, Figure 2-4 (d) represents a meandering step morphology which is a transitional stage between bilayer and step bunched morphologies.

For AlN and Al-rich AlGaN, the 2D nuclei are triangular in shape due to anisotropic step edges for the [0001] growth direction. To help explain why this occurs, Figure 2-5 gives a plan view of the atomic configuration for a bilayer step, taken from work by Xie et al. Here a surface without reconstruction, i.e. identical to the bulk, is assumed. By making this assumption, atomic sites will represent potential resting spots for diffusing adatoms along the
surface. There are two types of step edges, Type A and B edges which are normal to [10-10] and [1-100], respectively, or equivalent directions. The Type A edge has two adjacent empty sites as compared to the Type B edge which has one adjacent empty site, therefore there is a greater tendency for an adatom to incorporate on a Type A edge. Moreover, it would make sense that the growth rate of a Type A edge is faster than a Type B edge, which was suggested by Xie et al.\textsuperscript{79} The faster growth rate of a Type A edge forces the nucleus to take a triangular shape with vertices pointing along the [10-10] and equivalent directions. Furthermore, since the Type A step edge will rotate 60° with a descent of a single bilayer height, so will the 2D triangular nuclei. This is represented in Figure 2-5 where both macro-sized island and bilayer step morphologies are given. Notice how the 60° rotation of the 2D nuclei is clearly visible from one bilayer step to the next.
Figure 2-5: Plan view atomic configuration of a bilayer step (a) (from Reference 79) and two 2x2 µm² AFM images demonstrating the 60° rotation of 2D nuclei on a bilayer step (b) and macro-sized island (c) morphology.
2.4 AlN Homoepitaxy and Heteroepitaxy

2.4.1 (0001) AlN Surface Energy

As shown in Figure 2-4, AlN homoepitaxial films can possess well defined bilayer steps, which are free of surface pinning by dislocations. This type of morphology is ideal for studying fundamental ideal step and terrace morphology concepts like those discussed in Sections 1.5.1 and 1.5.2. In this section, those concepts will be used and applied to the AlN materials system in order to extract the (0001) AlN surface energy. To do this, $\sigma_{s,\text{max}}$ and $\sigma_s^*$ must be calculated.

To determine $\sigma_{s,\text{max}}$, simply using thermodynamics to determine $\sigma$ would result in a value representative of the ideal case where no pre-reactions take place and no other transport losses take place. To more accurately capture the effective $\sigma$ near the surface, the growth rate, $R$, must be considered since this can be measured experimentally and depicts the adatom incorporation at the step edge.

$$R = v \frac{h}{\lambda_0} = \frac{2h\lambda_s}{\lambda_0 n_0} \left( J - \frac{n_{s0}}{\tau_s} \right) \tanh \left( \frac{\lambda_0}{2\lambda_s} \right)$$  \hspace{1cm} (1)

By accounting for $R$, $\sigma_{s,\text{max}}$ can be reformulated to the following form using Equations 13, 17, and 19 from Chapter 1.

$$\sigma_{s,\text{max}} = \frac{R\lambda_0 n_0}{2h\lambda_s n_{s0}} \tanh \left( \frac{\lambda_0}{4\lambda_s} \right)$$  \hspace{1cm} (2)

In Equation 2, $R$, $\lambda_0$, $\lambda_s$, and $h$ can be determined experimentally. Also, $n_0$ is an intrinsic material parameter that is already known. However, $\tau_s$ and $n_{s0}$ must be determined in some other manner. Even though it is difficult to separately quantify $n_{s0}$ and $\tau_s$, the ratio between the
two can be determined through the Knudsen equation, which can be expressed for AlN growth as:

\[
\frac{n_{s0}}{\tau_s} = \frac{p_{Al}}{\sqrt{2\pi m_{Al} k_B T}}
\]

where \(m_{Al}\) is the Al atomic mass. For the case of AlN step flow growth, only the metal species have to be considered under typical growth conditions since the V/III ratio is much greater than unity and the growth rate is limited by the supply of metal atoms.

The equilibrium vapor pressure can be calculated by considering the chemical reaction that takes place during growth:

\[
\text{Al (g) + NH}_3\text{ (g)} \rightleftharpoons \text{AlN (s)} + \frac{3}{2} \text{H}_2\text{ (g)}
\] (4)

Thermolysis of the TMA source into the Al gas phase is highly spontaneous therefore it is not included in this reaction. The corresponding equilibrium equation is:

\[
K_{Al} = \frac{a_{AlN} p_{H_2}^{3/2}}{p_{Al} p_{NH_3}}
\]

where \(a_{AlN}, p_{H_2},\) and \(p_{NH_3}\) are the activity of AlN, partial pressure of H\(_2\), and partial pressure of NH\(_3\), respectively, and \(\log_{10}K_{Al} = -14.24 + (3.17 \times 10^4)/T + 2.33 \log_{10} T\). \(^{80}\) By using the methodology previously described by Mita et al., a fourth order polynomial equation can be derived for determining the equilibrium vapor pressure:

\[
p_{Al}^4 + \left[2C_1 + 8 \frac{a_{AlN}^2}{K_{AlN}^2} \right] p_{Al}^3 + \left[C_1^2 - 12 \frac{a_{AlN}^2}{K_{AlN}^2} C_2 \right] p_{Al}^2 + 6 \frac{a_{AlN}^2}{K_{AlN}^2} C_2 p_{Al} - \frac{a_{AlN}^2}{K_{AlN}^2} C_2^2 = 0
\] (6)
where \( C_1 = P^\circ_{NH3} - P^\circ_{Al} \), \( C_2 = P_T + P^\circ_{Al} - P^\circ_{NH3} \), and \( P^\circ_{NH3} \) and \( P_T \) are the input partial pressure of \( NH_3 \) and total pressure, respectively.\(^{78}\) Knowing this, \( \sigma_{s,max} \) can be quantified using Equations 2, 3, and 6.

The transition between step flow and 2D nucleation growth can be observed by AFM, as shown in Figure 2-4. This transition point represents when the surface supersaturation is large enough for 2D nucleation to be favorable on the step terrace, i.e. \( \sigma_{s,max} \geq \sigma_{s}^* \). By setting \( \sigma_{s,max} \) equal to each other, the diffusion properties can be realized by determining this transition point experimentally. Furthermore, it is clear now that growth parameters such as growth rate and temperature will directly affect this transition point, as will the misorientation angle, i.e. the terrace width of the growing surface.

By considering the theory, \( \lambda_s \) should be quantifiable, however, this is not straightforward due to the fact that \( \gamma_s \) has never been experimentally determined. Therefore, another method for determining \( \lambda_s \) is considered and used to indirectly arrive at \( \gamma_s \). Figure 2-4 (c) shows a surface where the terraces are large enough such that 2D nuclei form. This is representative of the onset for the transition from 2D nucleation to the step flow growth mode. The mean distance between the nuclei should be approximately twice \( \lambda_s \). Using this approach, 1-\( \mu \)m thick AlN homoepitaxial films were deposited on a range of misoriented substrates with a growth rate and temperature of 500 nm/hr and 1250 °C, respectively in order to determine the critical point for 2D nucleation. From these results, the surface diffusion length was determined to be approximately 46 ± 13 nm. This value is reasonable since the denuded zone at the step edge was measured to be between 60 to 110 nm long.
Figure 2-6: The surface energy of the (0001) polar plane of AlN plotted as a function of the chosen surface diffusion length.

With the diffusion length known, the surface energy was calculated to be 149 ± 8 meV/Å². Figure 2-6 shows how the calculated $\gamma_s$ changes as a function of the chosen $\lambda_s$. This plot clearly indicates that the surface energy does not change much with a large deviation in $\lambda_s$ helping to validate the calculated $\gamma_s$ value. According to these results, the surface energy of the (0001) polar plane of AlN is on the same order as that of the (1-100) and (11-20) planes, which were predicted from density functional theory by Jindal et al. to be 175 and 187 meV/Å², respectively. Additionally, it is interesting to note that this $\gamma_s$ value is close to 139 meV/Å², the $\gamma_s$ value reported for (111) 3C-SiC (Si face), which has the same atomic configuration near the surface as (0001) 6H-SiC (Si face).
2.4.2 2D Nucleation and Step Flow Growth

With $\gamma_s$, the derived theory can now be used in a quantitative and predictive manner. Equation 19 from Chapter 1 indicates that the critical point between 2D nucleation and the step flow growth mode will be directly dependent on $\sigma$. Figure 2-7 shows the theoretical curves for $\sigma$, assuming the same thermodynamic methodology reported by Mita et al., for AlN growth as a function of growth rate for $T = 1050, 1150, \text{ and } 1250 \, ^\circ\text{C}$ and growth temperature for $R = 500, 1000, \text{ and } 2000 \, \text{nm/hr}$. These growth conditions were chosen here to represent typical conditions that are met by most MOCVD systems. These curves indicate that the vapor supersaturation increases and decreases with an increase in the growth rate and temperature, respectively. Therefore, it should be that with a large/small enough growth rate/temperature, 2D nucleation growth should be observable.
Figure 2-7: Al vapor supersaturation as a function of growth rate (red) for $T = 1050^\circ C$ (dotted), 1150°C (dashed), and 1250°C (solid). Also plotted is the Al vapor supersaturation as a function of growth temperature (black) for $R = 500$ nm/hr (dotted), 1000 nm/hr (dashed), and 2000 nm/hr (solid).

2.4.2.1 Observation of the Critical Supersaturation for Nucleation on (0001) AlN

To demonstrate the dependence of the critical point on growth rate, Figure 2-8 shows the surfaces of AlN films grown at different growth rates. The misorientation angle and growth temperature were kept constant at 0.3° and 1150 °C, respectively. At a growth rate of 2000 nm/hr a 2D nucleation growth mode was present and resulted in islands of 2D nuclei, similar to those shown in Figure 2-4 (a). The islands are slightly tilted in Figure 2-8 due to a higher misorientation angle as compared to the surface shown in Figure 2-4 (a). With a reduction in
the growth rate to 500 nm/hr, the growth transitioned to a purely step flow growth mode resulting in an atomically smooth bilayer step morphology. This observation is understood from Figure 2-7, since a reduction in $R$ requires that $\sigma_{s,max}$ is reduced, making nucleation on the step terraces less likely. In other words, by sufficiently reducing $R$, $\sigma_{s,max}$ was lowered to below the value for $\sigma_s^*$.

Figure 2-8: 2x2 $\mu$m$^2$ AFM images representing AlN homoepitaxial films grown at different growth rates.

Figure 2-9 demonstrates another way of transitioning from 2D nucleation to the step flow growth mode. The AlN homoepitaxial films shown in Figure 2-9 had a fixed misorientation angle and growth rate of 0.08° and 1000 nm/hr, respectively. Increasing the growth temperature from 1100 to 1250 °C increased the surface diffusion length of the Al adatoms, reducing the maximum surface supersaturation. These results indicate that this reduction in $\sigma_{s,max}$ must have been larger than the reduction that occurs in $\sigma_s^*$ with the increase
in growth temperature. Notice how the critical point found through adjusting the growth rate and growth temperature both correlate with about the same $\sigma$, as can be seen in Figure 2-7. This indicates that other parameters that affect $\sigma$ could also be considered, such as the V/III ratio, diluent gas, and total pressure during growth. More importantly, bilayer step morphology can be achieved by understanding surface kinetic concepts, determining which growth regime is present, and by appropriately adjusting the vapor supersaturation.

2.4.2.2 Implications for Other AlN Surface Orientations

All of these results provide a predictive method for determining growth conditions that would be needed for different growth modes on N-polar, semi-polar, and non-polar AlN surfaces. These surfaces have associated surface energies that have not been determined.
experimentally and will be different from $\gamma_s$ of the Al-polar surface. For example, the surface energy of the (0001) 6H-SiC (Si face) and (000-1) 6H-SiC (C face) have been reported to be 139 and 19 meV/Å$^2$, respectively, indicating nearly an order of magnitude difference.\textsuperscript{66} Accurately calculating the surface energies for these polar, semi-polar, and non-polar surfaces from first principles is quite difficult since this requires a precise depiction of the surface reconstruction during growth. This reconstruction of the surface depends on the thermodynamics of the growth system; therefore, growing under N-rich as opposed to III-rich conditions will result in different surface reconstructions.\textsuperscript{81} It is important to note that these conditions represent thermodynamic extremes that may not be reached within a particular growth process. In particular, the role of hydrogen in the surface reconstruction of polar AlN is thought to be significant through thermodynamic considerations, yet this has not been verified experimentally.\textsuperscript{82} For these reasons, only the implications for surface energies different than 149 meV/Å$^2$, which serve to represent N-polar, semi-polar, and non-polar surfaces, should be considered.

Based on the proposed model, the transition from 2D nucleation and the step flow growth mode is directly dependent on $\sigma_s^*$. For a surface with $\gamma_s$ lower than 149 meV/Å$^2$, $\sigma_s^*$ would be smaller than it is for (0001) AlN meaning that using the same growth conditions as was used for (0001) AlN growth would result in a higher probability of 2D nucleation growth. Therefore, such a surface would require a lower vapor supersaturation during growth to achieve atomically smooth surfaces by the step flow growth mode. This could be realized by growing at higher temperatures or with lower growth rates, following the process parameters used in this work. In addition to using a lower vapor supersaturation, the substrate
misorientation could be increased to reduce $\sigma_{s,max}$ below the value for $\sigma_s^*$. This technique has been used for achieving smooth N-polar GaN epitaxial film surfaces.\textsuperscript{83} Other parameters such as diluent gas, total pressure, and V/III ratio could also be considered for reducing the vapor supersaturation as discussed by Mita et al. and Rice et al.\textsuperscript{23,78,84} As an example, a decrease in $\gamma_s$ of one order of magnitude would result in a subsequent decrease in $\sigma_s^*$ of over three orders of magnitude suggesting the significant growth condition changes that would be required to achieve atomically smooth surfaces. Conversely, with $\gamma_s$ greater than 149 meV/Å\textsuperscript{2}, the step flow growth mode will be easier to achieve for the growth conditions that otherwise would favor 2D nucleation growth on (0001) AlN. In such a case, a significant increase in the vapor supersaturation would be necessary to transition into the 2D nucleation growth mode.

2.4.3 Step Bunching

2.4.3.1 AlN Homoepitaxy

Another surface morphology transition that is of interest is the one from a bilayer step to step bunched morphology, which has been shown in other materials systems to be dependent on the substrate misorientation angle.\textsuperscript{85} The effect of substrate misorientation angle, $\alpha$, was investigated by keeping the homoepitaxial AlN growth conditions constant with a growth rate of 500 nm/hr and temperature of 1250 °C. Intentional substrate misorientation was shown to modify the step morphology from bilayer to step bunched with increasing $\alpha$. By growing AlN on vicinal (0001)-oriented substrates misoriented from 0 to 4°, the critical misorientation angle, $\alpha^*$, for the transition from bilayer steps to step bunches was determined to be ~0.25°. Figure 2-10 demonstrates this transition, where an abrupt increase in step height represents the onset
of step bunching. For quantification of the step bunching morphology, the step height and width were taken from the entire step bunch, even though bilayer steps were present, as shown in Figure 2-4. Below a misorientation angle of 0.25°, the bilayer step height was consistently measured to be 2.5 ± 0.1 Å and the step width deviated as $\lambda_0 = h / \tan(\alpha)$. The step bunch height increased with an increase in $\alpha$. The step width of the step bunches remained relatively constant in the range from 0.25 to 0.62° misorientation. A film grown with 4° misorientation (not shown in Figure 2-10) resulted in a step bunch height and width of 14 nm and 300 nm, respectively. This observation demonstrated that the step bunch height continues to increase and the width begins to decrease beyond the misorientation angle of 0.62°. All of these general trends were found to be independent of the misorientation direction. The only differences observed for misorientations toward [1-100] compared to [11-20] was the step edge shape, as discussed earlier.
Figure 2-10: Step height and width as a function of misorientation angle for AlN homoepitaxial films grown with a growth rate and temperature of 500 nm/hr and 1250 °C, respectively.
2.4.3.2 AlN Heteroepitaxy

The critical misorientation angle was found to be independent of the substrate used. This study was also carried out on AlN films grown on AlN templates on sapphire with a constant growth rate of 500 nm/hr and temperature of 1250 ºC. Interestingly, $\alpha^{*}$ was determined to be around 0.25° for these films as well. Even though film growth was initiated through 3D nucleation on the hetero-interface and followed by coalescence of these nuclei, once the film was coalesced and step flow growth proceeded; the effect of the absolute step density of the substrate still had the effect of changing the type of surface morphology that existed. This demonstrates that this transition from bilayer step to step bunched morphology is solely dependent on the adatom surface kinetics during the final step flow growth stage. More importantly, the strain state of the heteroepitaxial AlN films is significantly different from that of the homoepitaxial AlN films. In particular, the heteroepitaxial films are in tension whereas the homoepitaxial films are strain-free. These results indicate that the surface morphology transition is likely not initiated by strain. HRXRD studies determined that these AlN films on sapphire had undetectable differences in their strain state further indicating that the notion of step bunching as a form of sufficient bulk strain relaxation can be ruled out. This will be further discussed in Section 2.5 with AlGaN growth. Bilayer step fronts were always uniformly parallel and straight for AlN growth on AlN because of the low dislocation densities of < 10$^3$ cm$^{-2}$; however with higher dislocation densities in the AlN heteroepitaxial films, step pinning occurred. Figure 2-11 shows this step pinning through representative AFM images of the surface of a bilayer step and step bunched morphology for AlN films grown on AlN templates on sapphire. This step pinning roughened the surface, however, it did not affect $\alpha^{*}$.
2.4.3.3 Critical Misorientation Angle Dependence on the Supersaturation

The surface diffusion length of the adatoms was altered by changing the growth temperature. AlN films with a growth rate of 500 nm/hr were grown on substrates with a fixed $\alpha$ of 0.35°. At a growth temperature of 1250 °C, the surface was step bunched, as demonstrated in Figure 2-12. By growing AlN films at lower temperatures, a transition from step bunched to bilayer step morphology was observed, signifying a shift in $\alpha^*$ with growth temperature. Further studies showed that decreasing or increasing the growth temperature resulted in increasing or decreasing $\alpha^*$, respectively. Therefore, it was found that if the surface diffusion length of Al was comparable to the step terrace width, bilayer step morphology was obtained; if the diffusion length was sufficiently longer than the step terrace width, step bunched
morphology was obtained. It is important to note that even though $\alpha^*$ can be shifted, there is a limitation due to the transition to 2D nucleation growth. Eventually, by lowering the temperature further the surface will form the macro-sized islands, indicating that there exists a tight window of tolerance for the substrate misorientation angle. Changing the diffusion properties helps to relax this tight window, however, it is clear that precise control of the misorientation angle during the AlN substrate preparation from the boule must be realized for consistent bilayer step films to be achievable. Furthermore, this trend was also found to be independent of the substrate upon which the AlN layer was grown further supporting the claim that this step bunching phenomena is solely dependent on the adatom surface kinetics during the final step flow growth stage.

Figure 2-12: 2x2 µm² AFM images representing AlN homoepitaxial films grown at different temperatures.
2.5 Al-rich AlGaN

2.5.1 Surface Morphology of AlGaN Grown on AlN and Sapphire Substrates

For the 60 to 100% Al-content compositional range studied, there was no significant difference in the types of morphologies for films grown on the native AlN substrates. As already mentioned, Figure 2-4 shows the morphologies for both AlN and Al-rich AlGaN grown on the native AlN substrates. This trend did not hold true, however, for the AlGaN films grown on AlN templates on sapphire. The larger dislocation density present in films grown on sapphire substrates resulted in step pinning and a high degree of spiral growth. This additional spiral growth mechanism resulted in overall rougher surfaces. Figure 2-13 shows the surface of an AlN and Al$_{0.60}$Ga$_{0.40}$N film grown on sapphire. The AlN surface has a much smoother surface relative to the Al$_{0.60}$Ga$_{0.40}$N surface, with over an order of magnitude difference in RMS roughness.
heteroepitaxial films grown on AlN templates on sapphire.

The amount of Ga in the alloy films directly affected the spirals as predicted by the BCF theory. The BCF model states that the terrace width about a dislocation spiral is inversely proportional to the natural logarithm of the vapor supersaturation,

\[ \frac{1}{w} \propto \ln(1 + \sigma) \]  

where \( w \) is the average terrace width. A 2x2 \( \mu m^2 \) AFM image of the growth spirals is given in Figure 2-14. These spirals are formed due to dislocations that have a component of the displacement vector normal to the growth surface, i.e. mixed and screw type dislocations. In particular, the spirals observed in Al-rich AlGaN and AlN are double spirals comprising of two interlocking spiral ramps since each dislocation pins two steps.\textsuperscript{86} By introducing Ga, the supersaturation is reduced since the equilibrium vapor pressure of Ga is much larger than the
equilibrium vapor pressure of Al. Studies on the 60 to 100% Al-content AlGaN films grown on sapphire indicated a direct correlation of increasing terrace width about a spiral with an increase of Ga incorporation. Most importantly, for any further reduction in RMS roughness of AlGaN films using a sapphire substrate, spiral mediated growth must be suppressed.

Figure 2-14: 2x2 µm² AFM image of growth spirals on AlGaN films grown on AlN templates on sapphire.

2.5.2 2D Nucleation to Step Flow Growth Transition

The general trends observed in terms of growth rate, temperature, and substrate misorientation angle for AlGaN on native AlN substrates as compared to homoepitaxial AlN were the same for Al-content greater than 60%. Figure 2-15 demonstrates the transition from the 2D nucleation to step flow growth mode by reducing the growth rate for Al₀.₈₀Ga₀.₂₀N on AlN homoepitaxial films. The misorientation angle and growth temperature were kept constant
at 0.17° and 1100 °C, respectively. A 2D nucleation growth mode was beginning to appear for a growth rate of 1200 nm/hr. The islands are slightly tilted due to the misorientation angle, similar to those shown in Figure 2-8. By reducing the growth rate to 600 nm/hr, a purely step flow growth mode occurred and resulted in an atomically smooth bilayer step morphology. These observations are identical to the ones discussed for AlN. By reducing the growth rate, the surface supersaturation is reduced making it less likely for nucleation to occur.

Figure 2-15: 5x5 µm² AFM images representing Al₈₀Ga₂₀N on AlN homoepitaxial films grown at different growth rates.

2.5.3 Step Bunching

There was no detectable difference in the critical misorientation angle for step bunching for AlN as compared to Al-rich AlGaN. Figure 2-16 indicates the critical point for nominal Al₇₀Ga₃₀N grown with a growth rate and temperature of 600 nm/hr and 1100 °C,
respectively, on homoepitaxial AlN films. The $\alpha^*$ was determined to be around 0.4° for these films, which is in agreement with the results shown in Figure 2-12 whereby a reduction in growth temperature increased the $\alpha^*$ for AlN. The step bunched surface morphologies were characterized in the same manner as indicated for Figure 2-10, in that the entire step bunch was considered for both the step height and width. Below a misorientation angle of around 0.4°, bilayer step morphology was observed with step heights measured to be around 2.5 ± 0.1 Å. The step height deviated as expected by $\lambda_0 = h/tan(\alpha)$. Similar to the case of the AlN, an increase in $\alpha$ resulted in an increase in the step bunch height. The step bunch width remained relatively constant in the range from 0.4 to 0.55° misorientation. Somewhere between 0.55 and 0.65° misorientation, the step bunch width began to decrease which also matches the trends discussed earlier for AlN. Figure 2-16 includes films misoriented toward [1-100], [11-20], and variations in between which shows that the general trends for step height and width were not affected by the misorientation direction. It is expected that these trends are similar to AlN due to the high Al-contents studied here. This is further supported by the fact that the Al-content for these nominally Al$_{0.70}$Ga$_{0.30}$N films is not exactly 70% due to effects of the misorientation angle on the composition, which will be discussed later in more detail.
Figure 2-16: Step height and width as a function of misorientation angle for nominally Al$_{0.70}$Ga$_{0.30}$N on AlN homoepitaxial films. The Al$_{0.70}$Ga$_{0.30}$N was grown with a growth rate and temperature of 600 nm/hr and 1100 °C, respectively.
Figure 2-17 shows the surfaces of 10 and 100 nm thick Al$_{0.70}$Ga$_{0.30}$N films grown on top of AlN homoepitaxial layers. The substrate had a misorientation angle of 0.39° and the AlN homoepitaxial layer was grown with a growth temperature and rate of 1250 °C and 500 nm/hr, respectively, resulting in a step bunched morphology. Al$_{0.70}$Ga$_{0.30}$N was then deposited at a reduced temperature of 1100 °C with a growth rate of 600 nm/hr. The 10 nm film exhibited 2D nuclei on the terraces of large step bunches. These 2D nuclei disappear as the film gets thicker and the step density increases. Nano-pits, with a density of around $10^9$ to $10^{10}$ cm$^{-2}$, are observed in the 10 nm thick film, as seen in Figure 2-17. These nano-pits have been observed in strained AlN homoepitaxial films and are expected to form as a partial strain relaxation mechanism, which will be discussed in Section 2.6.1. It is clear that within 100 nm of deposition, the morphology transitioned from step bunched to an atomically smooth surface with bilayer steps. This indicates that the process of step bunching is reversible. Also, since the total strain increases with an increase of the pseudomorphically grown Al$_{0.70}$Ga$_{0.30}$N film thickness, it is expected that eventually the surface should recover step bunching if this is a sufficient means of strain relaxation. To test this idea, 700 nm of Al$_{0.70}$Ga$_{0.30}$N was deposited in the same manner on an identical step bunched AlN homoepitaxial layer. The Al$_{0.70}$Ga$_{0.30}$N surface looked identical to that of the 100 nm thick film showing no onset of step bunching. HRXRD confirmed that the film was fully strained to the AlN layer and no detectable relaxation had occurred. These results, along with the discussion given earlier on sapphire, indicate that step bunching is not a response to the bulk strain. Furthermore, this result on the 700 nm thick film indicated that the film surface of Al$_{0.70}$Ga$_{0.30}$N had finished evolving to
respond to the change in growth conditions even after 100 nm of growth. The same held true for all Al-contents studied, including pure AlN.

Figure 2-17: 5x5 µm² AFM images representing 10 nm (left) and 100 nm (right) of Al₀.₇₀Ga₀.₃₀N grown on step bunched homoepitaxial AlN.

2.5.4 Composition Dependence on the Surface Morphology

It is clear that for an atomically smooth surface, bilayer stepped AlGaN is desirable. It was determined that the composition was dependent on the misorientation angle for AlGaN films deposited with bilayer stepped morphology. Figure 2-18 shows this dependence for AlGaN films grown with identical growth conditions where all of the surfaces consisted only of bilayer steps. The composition of these films was determined through reciprocal space maps (RSMs). With an increase of the misorientation angle from ~0.05 to 0.40° there was a decrease in the Al-content of more than 10%. This is a significant change in composition and it is
important to realize the origin of this change since such a change in composition amounts to fluctuations in the emission wavelengths of optoelectronic structures.

![Graph](image)

Figure 2-18: The dependence of misorientation angle on the Al-content of AlGaN films with bilayer step morphology.

This effect can be understood by considering the model that was developed in Section 1.5.3. It was determined that the composition could be related to the surface diffusion flux of both the Al and Ga adatoms at the step edge, indicating that there is a dependence of the composition on the surface diffusion properties. For Figure 2-18, the only value that is being changed is $\lambda_0$; therefore, according to kinetic theory, the trend that is observed suggests that $\lambda_{s,Ga} < \lambda_{s,Al}$. Using Equations 20-22 from Chapter 1, this is more easily seen in the specific case of when $\lambda_0 > \lambda_{s,Ga}$ and $\lambda_0 < \lambda_{s,Al}$, which gives that the composition deviates as
\[ x_{Al} = \frac{A}{A + \frac{B}{\lambda_0}} \]  

(8)

where A and B are constants. According to this expression, an increase in \( \lambda_0 \) will cause \( x_{Al} \) to increase, which is observed experimentally. These results indicate that at these high Al-contents and a relatively high temperature of 1100 °C, the desorption rate of Ga must be sufficiently high and that of Al very low. Either way, control of the misorientation angle is crucial for having the ability to control the Al composition of AlGaN.

Aside from the dependence of the absolute Al composition on misorientation angle, Al-rich AlGaN epitaxial films grown with bilayer stepped morphologies always resulted in films with a uniform composition. However, step bunched AlGaN resulted in compositional inhomogeneity. The films shown in Figure 2-19 represent AlGaN films grown at the same time but with two different misorientation angles, one below \( \alpha^* \) and the other above. Low temperature (3K) PL spectra indicated that the bilayer stepped film had a single emission whereas the step bunched film contained two pronounced emissions. Gain measurements reported by Guo et al. indicated that the lower energy peak of step bunched AlGaN can possess significant gain as compared to the higher energy peak.\(^{87}\) This compositional inhomogeneity is also present for quantum well structures grown on step bunched layers, therefore optoelectronic devices demonstrate multiple emissions.
Figure 2-19: 5x5 μm$^2$ AFM images representing AlGaN grown on a low (a) and high (c) misoriented AlN native substrate resulting in bilayer and step bunched morphologies, respectively. Corresponding low temperature PL spectra (b) and (d).

High angle annular dark field (HAADF) STEM imaging was performed using a probe corrected FEI Titan G2 60-300 kV S/TEM equipped at 200 kV for Z-contrast imaging to better
understand the compositional inhomogeneity in the AlGaN films. Ga-rich AlGaN streaks could be seen in Z-contrast STEM when step bunching occurred. However, these streaks were not present when bilayer steps were present, as indicated in Figure 2-20. The streaks were approximately 2-5 nm in width. The angle of the streaks changed as a function of misorientation angle, indicating a correlation between the step fronts and the Ga incorporation. These streaks appear relatively uniformly spaced and can be thought of potentially as quantum sheets. In fact, power dependence measurements on multiple quantum well structures that were step bunched indicated a higher efficiency for the lower energy peak, which correlated to the Ga-rich streaks, as compared to structures with bilayer steps. This observation suggests an additional confinement mechanism such as the quantum sheets.

Figure 2-20: HAADF STEM images along the <1-100> zone axis of bilayer stepped (left) and step bunched (right) AlGaN grown on homoepitaxial AlN.
It is expected that the Ga adatom incorporates differently on the step terrace versus the step bunched edge due primarily to the large differences in step densities. This incorporation difference is believed to cause the compositional inhomogeneity seen in step bunched AlGaN epitaxial films and not in bilayer stepped films. In particular, Ga adatoms seem to prefer to incorporate near the step bunched edge. Figure 2-21 shows the surfaces of step bunched homoepitaxial GaN and homoepitaxial AlN grown under similar conditions. The GaN film was grown on an Ammono GaN substrate with fewer than $10^5$ cm$^{-2}$ dislocations. Both AFM images indicate that 2D nuclei are present on the step bunches. For the GaN surface, the nuclei are on the outer edge of the step bunch whereas in the case of AlN the nuclei reside near the inside of the step bunch. The reason for this is still unclear, however, the results match well with the observations in AlGaN and supports what is observed in Figure 2-20. All of these results indicate the importance of mitigating the formation of step bunching in AlGaN epitaxial layers.
2.6 Surface Defects

Surface defects can form in response to structural defects near the surface or particulates on the surface. Structural defects can include dislocations, stacking faults, or even a strained layer near the surface. Particulates can come from the susceptor, insufficient cleaning of the substrate, or the reactor environment (powder which deposited in the gas line). Surface defects caused by particulates are typically easy to detect since AlN does not grow in a step flow growth mode on these particulates. The highly supersaturated growth atmosphere causes AlN to nucleate on the particulates forming 3D grains. These defects are usually larger than all other surface features and have an irregular shape. In this section, the primary focus will be on surface defects in Al-rich AlGaN and AlN caused by structural defects since removing these
first requires an understanding of their origin whereas removing particulates simply requires establishing appropriate cleaning practices.

2.6.1 Pits

Figure 2-22 shows the triple axis $\omega-2\theta$ scans of the (0002) reflection from two different regions of a 200 nm thick AlN homoepitaxial film grown at 1250 °C. These $\omega-2\theta$ scans probe the top 40 μm of the sample and are very sensitive to any lattice dilations. The first region (red trace) shows an epilayer peak overlapping the substrate peak, indicating an excellent epitaxial relationship, while the second region (blue trace) shows a broadened (0002) peak from the epilayer that is shifted toward larger angles, indicative of a non-uniform tensile strain. A quantitative analysis of the peak displacement revealed that the residual strain in that region amounted to approximately 0.4%. A close examination of the strained region of the AlN homoepitaxial film using differential interference contrast (DIC) and AFM imaging (not shown) revealed micro-cracks, indicative of stress relaxation. Since the wurtzite crystal structure has very few operable slip systems, catastrophic cracking is the predominant stress relaxation mechanism for AlN epitaxial layers. The non-uniformity of strain and strain gradients in this homoepitaxial AlN film made it ideal for the study of possible strain relaxation mechanisms as a function of tensile strain with magnitudes between 0 and 0.4%. Since cracking occurred at the upper boundary of the range, one may be able to identify other, less severe relaxation mechanisms on the same film that exhibited cracking.69
Figure 2-22: HRXRD triple-axis ω-2θ scans of the (0002) reflection acquired from two different regions of a homoepitaxial AlN film deposited at 1250°C: strain free region (red trace), strained region (blue trace).

In order to reveal any changes on the surface of the epilayer, different regions of the film were studied by AFM. Figure 2-23 shows two 5x5 μm² AFM images taken in the unstrained and strained regions of the AlN film. The unstrained region of the film showed a smooth surface with bilayer steps (Figure 2-23 (a)), typical of perfect homoepitaxial growth of AlN, while the strained region showed a surface with numerous hexagonal nano-pits (Figure 2-23 (b)). The pit density varied across the surface and was measured to be as high as $10^{10}$ cm⁻² near the region with micro-cracks where the residual strain was the highest; it decreased gradually toward the unstrained region, where no pits were observed. In fact, after studying more than ten other nano-pitted homoepitaxial AlN films, with both bilayer step and step bunched surface morphologies, the magnitude of the measured residual strain and the pit
density in all cases were found to be correlated. Additionally, in all of the films studied, no visible surface damage or defects were observed by AFM in the substrates before homoepitaxial growth.

Figure 2-23: Two 5x5 µm² AFM images of a homoepitaxial AlN film deposited at 1250 °C. (a) strain-free region without pits (b) strained region with a pit density of ~8 x 10⁸ cm⁻².

A perusal of the AFM images of the pitted surfaces revealed step pinning at the nanopits. This indicated that these pits had formed during film growth and not after as they interfered with the step flow. Since pitting or cracking post growth is usually thought to be a result of thermal effects from cooling that immediately follows deposition, the presence of step pinning at the pits removed thermal effects as a possible cause. Additionally, the non-uniform distribution of pits verified that the pits were not associated with growth-related parameters such as a temperature gradient or a variation in gas flow.
Extensive TEM and AFM studies verified that these pits were distinct from the V-defects, which are a common surface defect found in III-nitride epitaxial layers.  Figure 2-24 shows the characteristics of a V-defect through AFM and TEM imaging. The surface shown contains a macro-sized island surface morphology, however; V-defects were also seen on surfaces with bilayer and step bunched surface morphologies. Studies revealed that V-defects in AlN epitaxial layers have sidewalls inclined ~30° from the surface normal and are centered along threading dislocations. These surface defects have a hexagonal shape and continually grow in size with film thickness reaching diameters of over a micron. V-defects only appeared in films grown at high vapor supersaturations. By reducing $\sigma$, through increasing the growth temperature or reducing the growth rate, the V-defects tended to disappear. The nano-pits shown in Figure 2-23 were also hexagonal in shape, but had a diameter of less than 100 nm
regardless of the film thickness; this was verified by growing AlN films that were up to 2 μm thick.

In order to determine if the nano-pits were a result of dislocations, as are the V-defects, TEM was performed on samples prepared from nano-pitted films. A full TEM tilt series was performed in order to locate any possible dislocations within the pitted film. Figure 2-25 (a) shows a cross-sectional bright field TEM image of a pitted homoepitaxial AlN layer. As can be seen in the figure, no dislocations were observed to correspond to the pits. Supplementary TEM imaging revealed strain contrast near the homoepitaxial/substrate interface of the pitted film. Figure 2-25 (b) and (c) shows two cross sectional bright field TEM images with g=0002 of a pitted and pit-free homoepitaxial AlN film, respectively. The absence of a prominent interface, caused by strain, for the pit-free film indicates once again that strain is directly related to the formation of the nano-pits. Furthermore, it seems that the strain measured in pitted films is initiated somewhere near the film/substrate interface.
Figure 2-25: Cross-sectional bright field TEM images of pitted ((a), (b)) and pit-free (c) homoepitaxial AlN films with g=0002. No dislocations are associated with the pits but strain contrast can be seen near the film/substrate interface.

It is also important to recognize that pits in III-nitrides have been associated with inversion domains within an epitaxial layer. To determine if inversion domains are a possible cause of these nano-pits, selective etching was performed on the pitted surfaces. Selective etching was performed using MF-319 developer at 70 °C for 10 min. Figure 2-26 shows the
resulting etched surface through a 5x5 µm² AFM image. Since N-polar AlN etches more than ten times faster than Al-polar AlN with the etching conditions used, if the pits were related to small inversion domains, one would expect a substantial change in the surface morphology. Selective etching resulted in a negligible change in the surface roughness and pit size. Therefore, the inversion domains are excluded as a possible cause of the observed pitting.

Figure 2-26: 5x5 µm² AFM image of a selectively etched nano-pitted homoepitaxial AlN film.

To understand the influence of pitting on optical properties of AlN, PL studies were performed on different regions of a non-uniformly strained AlN film. By using a relatively small laser spot size of approximately 1 mm in diameter, it was possible to analyze regions on the surface with varying pit densities. Figure 2-27 shows the resulting low temperature (LT) near band edge PL spectra. The PL spectra showed a pronounced change in the intensity and peak width as a function of pit density. The peak intensities decreased by more than a factor of two and the free exciton (FX) peak shifted from the reported relaxed position of 6.041 eV to
lower energies as the pit density increased. In the systematic study, the Si donor bound exciton (DBX) peak was monitored due to its higher intensity as compared to other PL peaks. The FWHM of the Si DBX peak was determined to be below 500 µeV for the area without pits, which is consistent with the LT-PL measurements of strain-free homoepitaxial AlN layers. With an increase in the pit density, the Si DBX peak shifted by 2 meV and broadened from a FWHM of < 0.5 to 3.7 meV. These results confirmed both an increase in the total tensile strain and strain non-uniformity in the pitted areas. Therefore, LT-PL measurements support the trend observed by HRXRD, whereby the amount of pitting scales directly with the amount of tensile strain.

Figure 2-27: Low temperature near band edge PL spectra taken in various regions of a homoepitaxial AlN film deposited at 1250 °C. The DBX peak width increases with pit density. All intensities were normalized to the Si DBX peak.
The formation of pits during growth has been observed previously in other systems.\textsuperscript{58} Even though pitting increases the surface area and associated surface energy, deformation of the surface causes partial strain relaxation, which locally reduces the total energy of the film. Surface roughening has been found to relax strain and is usually reported to occur in the form of islanding.\textsuperscript{54,55,95,96} However, previous studies have revealed that the mechanisms involved in islanding are very similar to those in pitting.\textsuperscript{97} All of the results presented support that pitting is a favorable mechanism of partial strain relaxation in epitaxial AlN films. It is evident that the total elastic strain energy needed to form surface pits is smaller than that needed to form cracks, since cracking only occurred with higher levels of strain. Most importantly, contrary to what has been observed before by Floro et al. in AlGaN/GaN heterostructures, misfit dislocation formation as a means of strain relaxation in (0001) AlN is less favorable than pitting or cracking.\textsuperscript{98} When the strained films grow thicker, the pits are no longer a sufficient means of strain relaxation and the AlN films under tensile stress eventually crack. Therefore, cracking follows pitting as the film grows thicker and acquires a larger amount of total strain energy. The presence of these nano-pits can be used as a direct measure of the quality of AlN epitaxy. Furthermore, the origin of the residual strain causing this pitting was revealed to be non-uniform subsurface polishing damage in the substrate by surface sensitive HRXRD studies by Bobea et al., which matches with the TEM results given in Figure 2-25.\textsuperscript{99}

Another consequence of having these nano-pits is that in AlGaN films, the surface defect causes compositional inhomogeneity. Plan-view HAADF STEM was conducted for Z-contrast imaging on Al\textsubscript{0.90}Ga\textsubscript{0.10}N grown on an AlN homoepitaxial film. This film exhibited nano-pitting with densities up to 10\textsuperscript{10} cm\textsuperscript{-2}, as seen by AFM imaging. Figure 2-28 shows STEM
images which indicate a clear variation in the Al-content near the nano-pits, with brighter areas correlating to more Ga-rich regions. The atomic hexagonal symmetry can be easily seen by the high resolution imaging. Furthermore, the shape of the nano-pits is more clearly discernable in the high resolution plan-view STEM images. The reason for the compositional fluctuation near the nano-pits is expected to be similar to the reason for the inhomogeneity in step bunched films. The difference in step density of the nano-pit defect compared to the rest of the surface causes fluctuations in Al and Ga incorporation for the two different regions according to the surface kinetics described in Section 1.5.3. Nevertheless, homogenous alloy films are desirable for optoelectronic and electronic devices; therefore, controlling the subsurface polishing damage in the substrate is necessary for high quality AlGaN films.

Figure 2-28: Plan-view HAADF STEM images of nano-pits seen in Al$_{0.90}$Ga$_{0.10}$N grown on homoepitaxial AlN.
2.6.2 Hillocks

Large hexagonal shaped defects could be seen on AlN and Al-rich AlGaN epitaxial film surfaces by DIC microscopy. These defects seemed to protrude from the surface and were only present on films grown on the high crystalline quality native AlN substrates, i.e. when the dislocation density of the film was below $10^6$ cm$^{-2}$. The surface of films grown on the AlN templates on sapphire were dominated by dislocation mediated spiral growth due to the high dislocation densities as discussed earlier. DIC microscopy revealed defect densities greater than $10^2$ cm$^{-2}$ for most of the films studied. Due to the large size, at densities of $10^7$ cm$^{-2}$ the entire surface consisted of these surface defects. The size increased with an increase in film thickness and Ga-content. Films grown with the same growth conditions, even simultaneously, on two different substrates often times exhibited vastly different defect densities indicating a dependence on substrate conditions. Even substrates cut from the same crystal boule could produce films with varying defect densities. Two primary categories could be identified through DIC imaging by considering the shape at the top of these defects. One type appeared to have a sharp top ($H_s$ type) and the other type a flat top ($H_f$ type). A majority of the defect density comprised of $H_s$ defects. In fact, $H_f$ defects consistently appeared with a density of less than $10^2$ cm$^{-2}$.

AFM imaging confirmed that the hexagonal features observed by DIC imaging were hexagonal pyramids as opposed to depressions, therefore, these surface defects will hereinafter be referred to as hillocks. Hillocks have been reported for epitaxial films grown on single crystalline GaN substrates, but not for films grown on AlN substrates.$^{100,101}$ In this study, more than 500 hillocks were investigated by AFM on homoepitaxial AlN and Al-rich AlGaN grown
on AlN substrates with Al-contents ranging from 60 to 100% in order to understand the distinguishing characteristics of these surface defects. Furthermore, GaN homoepitaxial films were grown on vicinal (0001) oriented Ammono GaN substrates using similar growth conditions in order to better compare the hillocks reported in literature to the ones seen in AlN and Al-rich AlGaN grown on AlN substrates. Due to the size, density, and variety of the hillocks, DIC imaging was always used to target certain regions of the film surface to image by AFM.
Figure 2-29: AFM amplitude error (grey scaled) and height (color scaled) images of a representative H$_f$ hillock seen on AlN and Al-rich AlGaN surfaces.

Figure 2-29 provides representative AFM amplitude error and height images of a H$_f$ hillock seen in AlN and Al-rich AlGaN. The shape of the hillock is symmetric along the [11-20] direction and asymmetric along the [1-100] direction. The size of H$_f$ hillocks did not
deviate across the film surface as long as the substrate was flat (radius of curvature greater than 100 m). This suggests that all of these particular defects are initiated near the film/substrate interface. Undisturbed bilayer steps are clearly distinguishable around the hillock and are aligned to the misorientation of the substrate. This film had a low enough misorientation angle that 2D nuclei are present along the step edges. The asymmetry of the hillock was found to be directly dependent on the misorientation angle. At higher misorientation angles (greater than 0.6°) the formation of the hillock surface defects could be avoided, at the expense of step bunching. It is expected that in this case the defects within the crystal which cause these hillocks are not removed but are rather inhibited relative to the surface interactions. The top of 

H₃ hillocks always consisted of triangular 2D nuclei which resided within a slight depression, as seen in Figure 2-29 (b). This image demonstrates the result of having anisotropic step edges as discussed in Section 2.3. At the edge of the flat top, the step density increases significantly.

Representative AFM amplitude error and height images of H₃ hillocks seen in AlN and Al-rich AlGaN are shown in Figure 2-30. The sharp top seen by DIC imaging was determined to be comprised of an assortment of different types of micro-scale surface features. These hillocks had polycrystalline grains, pits, and spirals at the top, an example of each is given in Figure 2-30. AFM imaging was difficult due to the sharp surface topography near the top of the hillocks. In fact, tips readily chipped or broke while traversing across the apex. Typical indications of noise from the AFM tip during imaging can be seen in Figure 2-30 (a) at the top of the hillock. These grains and pits were usually greater than 10 nm tall and deep, respectively, for 200 nm thick films and increased with an increase in film thickness, similar to V-defects. The grains usually protruded from within a pit as shown in Figure 2-30 (d). H₃ hillocks with
multiple spirals, pits, and grains at the top exhibited convex and concave hillock edges as indicated in Figure 2-30 (b). $H_s$ hillocks were not uniform in size across the film surface as were the $H_f$ hillocks. Figure 2-30 (f) indicates that $H_s$ hillocks can form at the onset of growth or during growth. Moreover, the hillock density increases with film thickness. Eventually, the hillock density and size becomes so large that they coalesce when the film is grown thick enough. The actual film thickness where this occurs depends on the initial hillock density at the onset of growth and the AlGaN composition.
Figure 2-30: AFM amplitude error (grey scaled) and height (color scaled) images of representative H₃ hillocks seen on AlN and Al-rich AlGaN surfaces.
H₂₇ and Hₛ hillocks were observed in homoepitaxial GaN as well. Representative AFM amplitude error images are given in Figure 2-31. The hillock sizes increased with film thickness that was comparable to the hillocks found in AlN and Al-rich AlGaN. The H₂₇ hillocks had a top that consisted of 2D nuclei consistent with what was shown in Figure 2-29. The H₂₇ hillock size remained constant across the film surface. A distinguishing trait for the hillocks observed in GaN was that the Hₛ hillocks only had spirals at the tops. One or more spirals could be found at the top of all the Hₛ hillocks studied in homoepitaxial GaN. In contrast, out of the over 500 hillocks studied in AlN and Al-rich AlGaN, only one Hₛ hillock was found to have only spirals at the top. Also, the size of all the Hₛ hillocks did not change across the GaN film surface. The total hillock density was fixed at the initiation of growth and did not deviate with an increase in film thickness. As discussed in Section 2.5.1, spiral growth occurs in response to mixed and screw type threading dislocations that terminate at the surface. This spiral growth initiates from a pre-existing dislocation in the GaN substrate. Using this concept, an average lower bound on the dislocation density can be determined for the GaN films studied assuming a single dislocation per pyramid at around 3 x 10⁴ cm⁻². The actual dislocation density will be larger since some of the hillocks presented multiple spirals. All of these results on GaN suggest that the grains and pits formed at the top of AlN and Al-rich AlGaN Hₛ hillocks are a result of something other than dislocations from the AlN substrate. This is further supported by the fact that these AlN substrates have dislocation densities less than 10³ cm⁻² yet hillock densities of 10⁵ to 10⁷ cm⁻² were commonly observed.
Figure 2-31: AFM amplitude error images of representative $H_f$ (left) and $H_s$ (right) hillocks seen on homoepitaxial GaN.

Compositional inhomogeneity can exist in AlGaN that exhibits step bunching and nano-pitting as discussed in Sections 2.5.3 and 2.6.1, respectively. PL indicated that when AlGaN films contained a high density of hillocks or the hillocks were relatively large in size,
two dominant band edge emissions existed suggesting another mechanism for compositional inhomogeneity in AlGaN. It is important to note that these films did not have step bunched or nano-pitted surfaces. Figure 2-32 provides room temperature PL spectra for two AlGaN films grown at the same time on two substrates from different boules. The resulting films had what is considered average and small hillock densities of $\approx 5 \times 10^5$ cm$^{-2}$ and $\approx 2 \times 10^3$ cm$^{-2}$, respectively. Both PL spectra contain two peaks. The film with the larger hillock density had two prominent emissions at around 5.02 and 5.30 eV whereas the other film had emissions around 5.02 and 5.18 eV. The higher energy peak was not the same between the two samples due to misorientation angle dissimilarities, which can be understood through the discussion in Section 2.5.4. The intensity of the lower energy peak increased/decreased with an increase/decrease in the total hillock area hinting that this peak was directly related to the surface defects.

Figure 2-32: Room temperature PL of two AlGaN films grown at the same time on two different substrates which exhibited different hillock densities.
Room temperature micro-CL mapping was performed on an AlGaN film with hillocks to further confirm this idea. CL indicated that the hillocks emit at a lower energy than the rest of the AlGaN layer, as shown in Figure 2-33. In this case, the lower energy is shifted too far below the higher energy to be accounted for by strain alone. This lower energy is directly correlated to more Ga incorporation in the hillock region, which shows yet again the importance of achieving atomically smooth and surface defect free AlGaN films. The hillocks in this CL map are H₅ hillocks with grains and pits at the top, the most prevalent type on these surfaces. The Ga-rich regions exist everywhere that the hillock disrupts the step density from being the fixed density due to the substrate misorientation surrounding the hillock. The step density is higher in these regions therefore it is thought that more Ga is incorporated here for the same reasons that a higher misorientation angle tended to incorporate more Ga in the bulk of AlGaN (see Section 2.5.4). The CL intensity was greater in the hillock region which matches the results from PL where the lower energy peak became more intense than the higher energy peak at the higher hillock densities even though the total absorption area was still larger for the regions around the hillocks. A sharp decrease in the CL intensity could be seen at the top of the H₅ hillocks suggesting an increase in non-radiative recombination, occurring due to the presence of dislocations.
Figure 2-33: Room temperature CL maps of the dominant emission peak of AlGaN epitaxy with hillock surface defects.
The presence of these hillocks greatly hinders the performance of optoelectronic and electronic devices because of the compositional inhomogeneity. Multiple emissions are typically not desirable for optoelectronic applications. Since dopant ionization energies increase with an increase in Al-content, as will be discussed in detail in Chapter 4, regions near the hillocks could potentially be more conductive than the bulk of the film making it difficult to provide high break down Schottky contacts. Additionally, LEDs were fabricated from these films and it was determined that the hillocks provide electrical leakage paths through the device, as evidenced by higher forward and reverse current for devices with hillocks. For all of these reasons, removal of these hillocks is necessary.

Sharp and flat top triangular shaped hillocks have been seen in homoepitaxial [111] Si films. Takakuwa et al. claimed that hillocks with grains at the top were a result of contaminants on the substrate surface, such as oxides, Si particles, or SiC precipitates.\textsuperscript{102} Polycrystalline Si was thought to grow on these contaminants and initiate the hillock formation due to the newly introduced extended defects, i.e. dislocations and stacking faults. Takakuwa et al. demonstrated that by properly cleaning the substrate surface via the use of photoexcited hydrogen, the density of hillocks with grains could be reduced by as much as 75\%.\textsuperscript{102}

In many cases, the hillocks found on AlGaN and AlN films were aligned and appeared as if they were emerging from a scratch. These scratches were traced back to the substrate. By chemically etching an AlN substrate with KOH, precipitates observed by DIC imaging were decorated by a trailing scratch indicating a potential source of the scratches. Scratches were also visible in areas where no precipitates were discernable by DIC imaging prior to etching. Often times, before etching, the scratches would not be visible which indicates that subsurface
polishing damage could be present in these substrates. Another way to reveal the subsurface polishing damage was through reactive ion etching whereby pillars were formed upon etching. These pillars are likely formed due to a masking effect. The density of these pillars were directly correlated with the density of hillocks after epitaxial film growth.

Energy-dispersive spectroscopy studies on one AlGaN cross-section TEM sample with hillocks revealed Ta related material at the bottom of a hillock near the growth interface. It is possible that Ta deposits from the PVT growth process are embedded in the substrate and during polishing, the deposits which are near the surface move around causing subsurface polishing damage. Furthermore, this would explain the scratch-like features which become more visible on substrates upon both dry and wet etching. The subsurface polishing damage could cause the formation of dislocations. Considering the idea of subsurface polishing damage caused by deposits/contaminants and the results presented by Takakuwa et al. on Si, a series of studies were conducted to attempt a cleaning and potential recovery of the AlN substrate surface through H₂ annealing.¹⁰²

Prior to epitaxial growth, AlN substrates were annealed at high temperatures in a H₂ atmosphere at 20 Torr total pressure for 10 minutes. Annealing temperatures between 1100 and 1550 °C were investigated. AlGaN epitaxial films were then deposited on these annealed substrates in order to produce films with relatively large hillocks that could be easily seen by DIC imaging for density counting. It was determined that an optimal temperature range of 1400 to 1500 °C existed where a significant reduction of hillocks consistently occurred. Table 2-1 gives the results for a series of AlGaN films grown on surfaces that were prepared with and without H₂ annealing at 1400 °C. A single substrate was quartered and three quarters were
grown on at the same time. By using a single substrate, the role of slight variations in wafer processing from the boule was negated. The control, Sample A, underwent the standard cleaning procedure with acid cleaning as discussed in Section 2.2. Samples B and C were H$_2$ annealed, with the acid cleaning step being omitted for Sample B. Using the standard cleaning procedure produced a film with a hillock density of more than $10^5$ cm$^{-2}$. By using the additional H$_2$ annealing step, the hillock density was reduced to less than $10^3$ cm$^{-2}$. Furthermore, besides the fact that the hillock densities were nearly identical between Samples B and C, no significant differences could be found by AFM, PL, or HRXRD studies indicating that substrates annealed in H$_2$ do not require the acid cleaning step. A consistent reduction of over one order of magnitude was observed for all films grown on substrates with the H$_2$ annealing step. It is important to note that similar to the results from Takakuwa et al., only H$_s$ hillocks with grains and pits could be detectably reduced using this procedure.102

Table 2-1: Hillock density for AlGaN films grown on AlN substrates prepared as indicated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acid Cleaning</th>
<th>H$_2$ Annealing</th>
<th>Hillock density (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (control)</td>
<td>yes</td>
<td>no</td>
<td>$&gt; 10^5$</td>
</tr>
<tr>
<td>B</td>
<td>no</td>
<td>yes</td>
<td>$&lt; 10^3$</td>
</tr>
<tr>
<td>C</td>
<td>yes</td>
<td>yes</td>
<td>$&lt; 10^3$</td>
</tr>
</tbody>
</table>

To better understand the origin of this hillock reduction, the AlN substrate surface was studied after various H$_2$ annealing conditions. A substrate was quartered and each quarter was
studied before and after H$_2$ annealing. AFM images are given in Figure 2-34 showing the transformation of the surface. Before annealing, all four quarters exhibited similar morphologies with a bilayer step structure being clearly visible. No pits or scratches could be found by AFM imaging. Small protrusions, 1 to 2 nm tall, could be seen on the polished surface by AFM and is attributed to surface hydroxides. These are removed after the nitridation step of the standard cleaning procedure. Here, it is clear that H$_2$ annealing also removes these small protrusions. The misorientation angle was determined to be approximately 0.18 ± 0.01° for all of the quarters.

The AFM images in Figure 2-34 indicate that with an increase in H$_2$ annealing temperature from 1400 to 1550 °C at a total time of 10 minutes, the surface steadily roughened. The RMS roughness for the 5x5 µm$^2$ AFM images increased from 100 to 360 pm with the 150 °C increase in annealing temperature. The terrace width increased and step bunching began to occur. At these H$_2$ annealing conditions, Al adatoms are expected to detach from the step edges, diffuse, and reattach at other step edges or desorb. The surface continued to change with an increase in annealing time and became even rougher. H$_2$ annealing at 1500 °C at a total time of 30 minutes produced a surface RMS roughness of more than 2.7 nm for a 5x5 µm$^2$ AFM scan area. At this stage, subsurface polishing damage was detectable through macro sized surface features. The surface mass transport due to the H$_2$ annealing procedure seemed to decorate the areas with damage. Needless to say, atomically smooth epitaxial films with reduced hillock densities could only be realized on the substrates that contained bilayer steps upon H$_2$ annealing. Therefore, a mild H$_2$ annealing step should be considered as a way to reduce the hillock density in Al-rich AlGaN and AlN epitaxial films grown on AlN substrates.
Figure 2-34: AFM images of AlN substrates before and after H₂ annealing at various conditions.
2.7 Summary

In this chapter, a surface kinetic model was developed by using already established BCF theory to better understand how to control the growth of polar (0001) Al-rich AlGaN and AlN deposited by MOCVD. The dependence of the misorientation angle and vapor supersaturation on the surface supersaturation was determined with the theory. By adjusting the surface supersaturation, the expected changes in surface morphology were observed experimentally, as predicted by the model. By properly controlling the surface supersaturation, transitions between surfaces dominated by 2D nucleation, bilayer step flow, and step bunching were realized. For each transition, it was shown that the critical supersaturation could be realized by changing either the growth conditions or the substrate terrace width, i.e. the vapor supersaturation or misorientation angle, respectively. These observations, which were only possible through the use of the native AlN substrates, made calculating the surface energy of (0001) AlN achievable for the first time.

The role of dislocations on the morphology were also discussed. By studying films grown on AlN and sapphire substrates, the surface kinetic model was demonstrated to be universal in that it can be applied to any AlGaN or AlN material. A low dislocation density was necessary to achieve the smoothest morphologies, where the RMS roughness was less than 50 pm for a 5x5 μm² AFM scan area.

Studies presented in this chapter showed that the composition of AlGaN is sensitive to the morphology. Step bunching resulted in compositional inhomogeneity. This was explained by the dependence of the Ga incorporation on the terrace width of the growth surface. Once the Ga surface diffusion length becomes smaller than the terrace width, its incorporation
depends on the step density. This theory was supported by observing an increase in the Ga-content with an increase in misorientation angle for bilayer stepped AlGaN grown with the same growth conditions.

Surface defects in the form of pits and hillocks were studied as well. Nano-pitting and cracking were found to be the main partial strain relaxation mechanisms in epitaxial Al-rich AlGaN and AlN thin films as opposed to misfit dislocation formation. Hillocks on the surfaces of Al-rich AlGaN and AlN were investigated and it was found that by properly cleaning the substrate, the density of hillocks could be reduced by more than one order of magnitude. In addition, all of the surface defects studied in this chapter resulted in compositional inhomogeneity in AlGaN films.

The surface kinetic framework provided in this chapter designates a control scheme for achieving atomically smooth bilayer stepped surfaces for Al-rich AlGaN and AlN epitaxial thin films. This methodology, along with the demonstration of high quality epitaxy on AlN substrates, will help to improve electronic and optoelectronic devices based on AlGaN.
CHAPTER 3: Non-polar Growth

3.1 Motivation

There has been increasing interest in the growth and characterization of non-polar and semi-polar AlN as it is expected to overcome limitations encountered in polar AlN. Current research on AlN is mainly directed at materials grown in the polar c-plane orientation.\textsuperscript{22, 23, 69} It is thought that deep UV LEDs and LDs using high Al-content AlGaN alloys based on c-plane AlN are negatively affected by large internal electric fields due to the characteristic spontaneous and piezoelectric polarizations in strained nitride device structures.\textsuperscript{3, 7} These polarizations cause a spatial separation between the holes and electrons in quantum confinement structures, therefore limiting radiative recombination efficiencies.\textsuperscript{12, 13, 103} A potential way of eliminating these effects of the polarization fields is through growth of films in directions perpendicular to the polar axis.

Non-polar growth has mostly been reported for GaN and AlN heteroepitaxy. These heteroepitaxial films grown on foreign, non-polar substrates suffer from large densities of threading dislocations and stacking faults, which can be detrimental to subsequent device structures grown on such films.\textsuperscript{104-106} Such extended defects are expected to act as nonradiative recombination centers and consequently lower quantum efficiencies within quantum confined structures.

It has not yet been made clear which non-polar surface, (1-100) m-plane or (11-20) a-plane is preferred for the growth of high quality III-nitride epitaxial films. It is clear, however, that native substrates will reduce the density of threading dislocations. Although, growth of devices on native non-polar bulk substrates has not been studied in AlN, it promises a
significant reduction in the density of extended defects as well as improvement in device properties.\textsuperscript{107} Thus, an extensive study of the growth on non-polar bulk substrates and an investigation of the achievable surface and crystal quality are needed to clarify the fundamental materials properties of high quality non-polar Al-rich AlGaN and AlN in order to pave the way for their future application.

3.2 Non-polar AlN Substrate Characteristics

3.2.1 Substrate Misorientation

The AlN substrates used in this study were processed from AlN boules grown by physical vapor transport in the [000-1] direction and have been shown to possess very high crystalline quality with dislocation densities lower than $10^3 \text{ cm}^{-2}$.\textsuperscript{1,77} M-plane substrates were then obtained by slicing these boules parallel to the m-plane by a diamond wire saw. All of the substrates are then mechanically polished and next subjected to CMP in a proprietary alkaline slurry of nanometer-size abrasives.

Substrates that are nominally (0001) can have misorientation directions between <1-100> and <11-20>. The effects of the different misorientation directions as well as magnitudes on the surface morphology of epitaxial films grown on such substrates was discussed extensively in Chapter 2. For nominally (1-100) substrates there are other directions which must be considered. Because of the non-centrosymmetric nature of the wurtzite crystal structure, a misorientation direction of [0001] is different than [000-1], when it comes to the surface energetics. This anisotropy is one of the main reasons behind the difficulty being faced for non-polar growth. Misorientation directions can be anywhere between [0001], [000-1], and
±<11-20>. From this point forward, ±<11-20> will be denoted as [11-20] and [-1-120] without loss of generality. It has been shown in GaN, that the surface morphology of epitaxial films can be quite different depending on the misorientation direction relative to these four directions.\textsuperscript{100}

Prior to any epitaxial growth, the surface morphology and misorientation of all nominally (1-100) AlN substrates were studied using AFM and HRXRD. AFM imaging of all substrates prior to growth determined that they were all free of surface defects such as polishing scratches or pits, indicating the successful removal through polishing of the plastic damage caused by the boule slicing.\textsuperscript{23} Clear steps, as shown in Figure 3-1, were present on all surfaces with a measured step-height of 2.7 ± 0.1 Å, which matches nicely the theoretical height of one m-plane monolayer (\(\sqrt{3}/2 \ a \approx 2.69 \ \text{Å}\)). The RMS roughness of the substrates was consistently below 100 pm for 5x5 μm\(^2\) scan areas.
Figure 3-1: 5x5 μm² AFM image of a typical m-plane AlN substrate with an RMS roughness of less than 100 pm. Parallel monolayer steps could be observed on all m-plane AlN substrates studied.

The step-to-terrace ratio and step orientation relative to the c-plane crystallographic facets of the substrate could be directly measured by AFM to quantify the misorientation angle relative to [1-100] and the direction relative to [0001]. HRXRD techniques were used to further confirm the misorientation of all the substrates and were found to be in agreement. This agreement is mainly attributed to the large radius of surface curvature of the substrates at over 100 m.

3.2.2 Substrate Preparation for Growth

Due to the high affinity of Al for oxygen, oxygen is a common impurity in AlN and particularly on its surface. A number of studies on powder, thin film, and bulk AlN have shown
that AlN forms an aluminum hydroxide layer when exposed to air or water; this is in the form of aluminum oxide-hydroxide [AlOOH] or a mixture of AlOOH and aluminum trihydroxide [Al(OH)₃]. For AlN substrates, the nature of the aluminum oxide-hydroxide layer depends on the process history of the substrates, especially the polishing process. A basic requirement for optimal homoepitaxial thin film growth on polished substrates is surface preparation, including removal of particulates, metallic contaminants, adsorbed species, and native oxides. Furthermore, a suitable surface recovery technique has not yet been reported on for m-plane AlN substrates.

Rice et al. developed a procedure for preparing nominally (0001) c-plane AlN substrates for epitaxial growth. The following presents a study on implementing this same procedure to determine if it is also suitable for m-plane AlN substrates and has already been published. The procedure included ultrasonically cleaning the as-polished substrates sequentially in acetone, methanol, and then deionized water. Following the cleaning, the substrates were wet etched in a 3:1 mixture of sulfuric and phosphoric acid for 10 minutes at 90 °C. Wet etched substrates were then rinsed in deionized water for 10 minutes, dried with flowing nitrogen, and transferred into the MOCVD reactor. The reactor was then pumped down to high vacuum (less than 10⁻⁶ Torr) and back-filled with ammonia. The substrates were annealed in flowing ammonia at 60 Torr for 15 minutes at 1100 °C.

AlN substrate surfaces were characterized in the as-polished condition, following the wet etching, and after ammonia annealing by x-ray photoelectron spectroscopy (XPS). The peak areas of Al 2p, N 1s, and O 1s core level spectra were used to determine the surface molar ratios of elements. As-polished substrates were typically stored in ambient air for several
weeks prior to characterization or processing. Substrate exposure to ambient air following wet etching or ammonia annealing was limited to a few minutes prior to loading substrates into the XPS ultra high vacuum (UHV) analysis chamber.

A survey scan was realized to identify the elements present and to assess the chemical makeup of the surface. Figure 3-2 shows a typical spectrum of the CMP m-plane AlN substrates. Intense photoelectron peaks representing core levels of AlN: Al 2s, Al 2p, and N 1s, were clearly observed. The spectrum also contained peaks from other surface species represented by the C 1s, F 1s, and O 1s. In addition to the photoelectron peaks, Auger KLL peaks from both nitrogen and oxygen were observed. The presence of fluorine was attributed to residue from the Fluoraware storage container, thus further consideration was not necessary. The presence of adventitious carbon was always observed, as it was in c-plane AlN substrates studied previously and is known to be adsorbed while the substrates are exposed to air. Therefore, neither fluorine nor carbon are considered in the surface chemistry analysis presented here.
Figure 3-2: XPS survey scan of a CMP m-plane AlN substrate; oxygen, fluorine, and carbon are the primary surface contaminants.

XPS analysis of the CMP m-plane substrates indicated that the amount of surface contamination by oxygen in m-plane substrates was nearly the same as that of c-plane substrates. The Al:N:O surface molar fractions, for the CMP m-plane substrates were found to be about 4:4:1 compared to 5:4:1 reported for c-plane substrates. Figure 3-3 shows a summary of molar ratios for an m-plane AlN substrate surface in the CMP condition as well as following wet etching and ammonia annealing. Assuming a 1:1 stoichiometry between the Al and N in the AlN bulk, the excess Al over the 1:1 ratio arose due to replacement of nitrogen for oxygen during the formation of the oxide-hydroxide layer. The Al to N ratio remained above 1 after all surface treatments indicating that there was still some oxide-hydroxide on the surface. O/N and O/Al surface molar ratios were used for comparison of the amount of oxygen on the surface. Both ratios clearly decreased with processing, which was an indication of the
reduction in oxide-hydroxide. These measured amounts of oxygen are known to be equal or slightly higher than the true amount representative of each processing step, since the surfaces were briefly exposed to air during transfers to the XPS chamber.

![Graph showing surface molar ratios](image)

**Figure 3-3:** Surface molar ratios of m-plane substrates following each preparation process.

A representative high resolution O 1s core level peak for an m-plane CMP surface is shown in Figure 3-4. The broad peak was deconvoluted into three components with binding energies of 530.4, 531.5, and 532.7 eV, corresponding to O$^{2-}$, OH$^-$, and H$_2$O, respectively.\(^{113}\) The molar ratios of O$^{2-}$:OH$^-$:H$_2$O were found to be about 2:6:2 for m-plane, while they were reported to be around 4:5:1 for c-plane substrates; interestingly, the more stable oxide component was significantly lower on the m-plane substrates.\(^{23}\) A summary of the O 1s core level component molar ratios following the various surface preparation steps can be seen in Figure 3-4 as well. The ratios suggest a native oxide composed of a mixed aluminum hydroxide and aluminum oxide-hydroxide. In the CMP condition, the distribution of the amount of each
component differed between the c- and m-plane substrates, however the oxide-hydroxide layer in both was dominated by the OH\(^-\) component.

Figure 3-4: Deconvoluted O 1s core level peak of a CMP m-plane substrate surface (left) and O 1s core level peak component molar ratios for each surface preparation process (right).

Wet etching of as-polished substrates resulted in a reduction in oxygen surface contamination. The Al:N:O surface molar ratios were found to be about 5:4:1 for wet etched m-plane substrates. Additionally, the wet etching modified the molar ratios of O\(^2-\):OH\(^-\):H\(_2\)O to 3:6:1. The overall reduction in total oxygen during wet etching of m-plane wafers was 73%; this compared favorably to a 50% overall reduction reported for c-plane AlN.\(^{23}\)

Following the ex-situ surface preparation steps, ammonia annealing was performed in the MOCVD reactor. The purpose of this step was to convert the substrate hydroxide layer to AlN.\(^{23\,115}\) The success of this nitridation step depended on the stability of the surface oxide: a more hydrated oxide was more energetically favorable for the transformation to AlN using
NH$_3$. In general, Al hydroxides are less stable compounds than the oxides and are a desired form of AlN surface passivation.$^{116}$ Rice et al. developed and implemented a thermodynamic model for the nitridation of aluminum oxide in order to find suitable processing conditions within the parameter space of a typical nitride MOCVD system.$^{23}$ The nitridation of the aluminum oxide-hydroxides on m- and c-plane AlN substrate surfaces were expected to proceed more readily than nitridation of aluminum oxide. The reactor conditions for the experiments in this work were found to meet the necessary requirements for nitridation according to the thermodynamic model.

The Al:N:O surface molar ratio following ammonia annealing was found to be about 5:4:0 for the m-plane substrates. The measured total oxygen on the surface was reduced by 82% from CMP to ammonia annealing for the m-plane AlN. The molar ratio of O$^{2-}$:OH$^{-}$:H$_2$O for m-plane substrates after nitridation was found to be about 3:6:1. It is likely that the surface hydroxide is completely removed during this nitridation, and the inevitable exposure to moist air before loading for XPS measurements causes slight oxidation of the surface. It is thought that this amount and composition of surface hydroxide is indicative of the initial oxidation of a pristine AlN surface upon exposure to moist air, as it is with the c-plane AlN.$^{23}$ This is also consistent with studies on freshly deposited AlN films (not presented here), which showed similar amounts of oxygen upon transfer from the MOCVD reactor to the UHV XPS system through air.

The composition of the oxide-hydroxide on the surface of the m-plane substrates was dominated by the OH$^{-}$ component for all three stages of processing. In contrast, for the c-plane, the O$^{2-}$ and OH$^{-}$ were approximately equal throughout processing. It is predicted by the
thermodynamic stability of hydrated alumina species that Al(OH)$_3$ should be more energetically favorable at ambient conditions.$^{116}$ However, a perfect hydroxide was observed neither on m- nor c-plane surfaces; both are mixed oxide-hydroxides, which are favorable for an effective nitridation and surface recovery prior to the epitaxial growth.

3.3 AlN Homoepitaxy

3.3.1 Surface Morphology

The growth of homoepitaxial films on bulk m-plane substrates has been proved to be strongly dependent on the substrate surface preparation. Therefore, before MOCVD homoepitaxial deposition, all polished substrates were treated following the substrate treatment procedure described in detail in Section 3.2.2.$^{25}$ AlN homoepitaxial films were grown by MOCVD under 20 Torr total pressure using trimethylaluminum and ammonia as the aluminum and nitrogen precursors, respectively. The V/III ratio was maintained at 1000, unless otherwise noted, and hydrogen was used as the diluent gas for all the homoepitaxial films that will be discussed in this section.

3.3.1.1 Dependence on the Growth Temperature

In order to understand the effect of growth temperature on the homoepitaxial film characteristics, growth at temperatures between 1250 and 1550 °C was performed on a set of substrates with identical misorientation angles of 0.45° off [1-100] toward [0001].$^{73}$ This selection ensured comparability of the results by reducing the possible influence of the misorientation angle on growth mode and consequently surface morphology. All films were
grown to a total thickness of 1.2 μm and appeared smooth and featureless without cracking through optical DIC microscopy imaging.

AFM images of the resulting surfaces for films grown at different temperatures can be seen in Figure 3-5. Relatively rough films with preferential faceting along the ±[0001] direction was visible for films grown at and below 1350 °C. The RMS roughness ranged between 8 to 13 nm from 5x5 μm² AFM images of the films grown at the lower temperatures. This type of striped morphology, known as “slate” morphology, is commonly seen in m-plane GaN and AlN epitaxial films.106, 107, 117, 118 Above a growth temperature of 1350 °C, atomically smooth surfaces were obtained with no preferential faceting along the ±[0001] direction. At the highest growth temperature of 1550 °C, RMS roughness values of less than 0.4 nm from 5x5 μm² AFM images were measured. At the higher growth temperatures, monolayer steps were resolved with step-heights identical to those seen on the AlN substrates prior to growth. A small degree of macro-stepping (two to four monolayers) was still present for these samples and is attributed to the misorientation magnitude and direction.100, 119 Moreover, as seen in Figure 3-5, all monolayer steps did not follow the direction of the misorientation.

There was no observable growth rate difference with a change in growth temperature from 1250 to 1550 °C. This was expected, however, since the same held true for growth on (0001) c-plane AlN substrates, discussed in Chapter 2. The thickness of the layers was determined from the spacing in the Pendellösung fringes observed in the symmetric (10-10) 2θ-ω line scans from HRXRD using the following equation

\[ t = \frac{\lambda}{2\Delta\theta\cos(\theta)} \] (1)

116
where $t$ is the film thickness, $\lambda$ is the x-ray wavelength, $\Delta \theta$ is the spacing between the fringes, and $\theta$ is the Bragg angle. Therefore, a change in growth rate or film thickness cannot be used to explain the differences in step morphology, as seen in Figure 3-5. It should be mentioned that for thicker films, the average width of the large stripe features in the lower growth temperature films increased (not shown). Also, the average width of the stripes increased with growth temperature for films which had the same thickness. At the higher growth temperatures, the height of the macro-steps did not change with film thickness but did decrease with an increase in growth temperature. These trends at the higher temperatures are a direct consequence of a change in the diffusion length of the surface adatoms during growth.
Figure 3-5: 5x5 μm² AFM images of 1.2 μm thick (1-100) homoepitaxial AlN films grown at four different temperatures. A large improvement in surface roughness could be obtained at higher growth temperatures.

To identify if these differences in surface morphology with growth temperature were caused by the initial stages of growth, a two layer homoepitaxial film was grown with 600 nm
grown at 1450 °C followed by 600 nm grown at 1350 °C on a substrate with an identical misorientation angle to the substrates used for the samples shown in Figure 3-5 of 0.45° off [1-100] toward [0001]. Figure 3-6 (a) illustrates the sample structure and Figure 3-6 (b) shows an AFM image of the surface of the two layer film. Even though the initial 600 nm of AlN was grown at the higher temperature of 1450°C and had an atomically smooth morphology as shown in Figure 3-5, the final surface had the large stripe morphology seen in the films grown at the lower temperature of 1350 °C. This suggests that the observed changes in morphology with growth temperature are purely dependent on the surface energetics and diffusion length of the adatoms during growth and not a growth initiation driven effect. Therefore, it seems that the growth temperature is critical for the faceting and step behavior of homoepitaxial (1-100) AlN.
Figure 3-6: (a) Schematic drawing and (b) 5x5 μm² AFM image of a two layer 1.2 μm thick (1-100) homoepitaxial AlN film with 600 nm grown at 1450 °C followed by 600 nm grown at 1350 °C.

These observations were followed by a study on the early stages of lower temperature growth at 1250 °C in order to better understand the origin of the preferential faceting along the ±[0001] direction. Figure 3-7 shows AFM images of the surface evolution during the initial stages of growth. The substrate used for the study shown in Figure 3-7 had a misorientation angle of 0.10° off [1-100] and direction of 30° off [000-1] toward [-1-120]. AFM images of the CMP surface indicates clear parallel monolayer steps similar to those shown in Figure 3-1, flowing along the misorientation direction. After the nitridation step, it is much more difficult to make out the monolayer steps and it almost appears as if a new step structure is generated along the ±[0001] direction. Furthermore, the overall RMS roughness of the surface has increased at this point from 100 to 300 pm. Etching is not expected to occur under these
nitridation conditions, therefore any reconstruction of the surface should occur because of surface adatom migration.

This potential reorientation of the step structure became more apparent once AlN was deposited. Figure 3-7 (c)-(e) show the surface after 4, 8, and 200 nm of homoepitaxial growth at 1250 °C. The striped morphology becomes clear even after only 4 nm of deposition. With further growth, the stripes become larger. After 8 nm of growth, (000-1) facets are becoming stable on the surface. The surface RMS roughness increases up to 8 nm once 200 nm has been grown. With further growth, the stripes become wider and taller as shown in Figure 3-5. These results indicate that the (1-100) surface is unstable at these temperatures and wants to reconstruct itself to facet along the ±[0001] direction. Growth does not initiate through the typical step-flow growth mode as presented on in Chapter 2 for these lower growth temperatures. Instead, adatom migration occurs to reduce the total surface energy by forming the (000-1) facets.
Figure 3-7: Evolution of a (1-100) AlN surface morphology which showed a re-alignment of initial step features with the [000-1] direction. (a) CMP, (b) nitried at 1200 °C, (c) 4 nm of growth, (d) 8 nm of growth, and 200 nm of growth, all at 1250 °C.

3.3.1.2 Dependence on the Substrate Misorientation

The dependence of substrate misorientation angle on surface morphology was also studied for m-plane since a strong dependence of substrate misorientation on film surface morphology for polar c-plane growth was observed as discussed throughout Chapter 2. AlN homoepitaxial layers were grown at 1250 °C with a thickness of 1 µm on AlN substrates with a misorientation angle of about 0.35° off [1-100] and misorientation directions toward [11-20], [-1-120], [0001], [000-1], and directional variations between. AFM imaging revealed that
preferential faceting along the ±[0001] direction occurred for all films grown at this temperature independent of the misorientation direction. The misorientation angle off [1-100] was also considered since the step density directly controls the Al adatom surface kinetics. A substrate misorientation angle range from 0.10 to 0.64° off [1-100] was investigated with AlN deposition at the same conditions just mentioned. This range of angles did not seem to drastically change the overall type of surface morphology. In all cases, a rough striped surface was present. The overall RMS roughness deviated anywhere between 7 and 46 nm in 5x5 μm² AFM images. There was no clear trends on the stripe heights or widths with a deviation in misorientation angle within the studied range. The misorientation magnitude did seem to have an effect on the stripe size, however, with misorientations toward [11-20] or [-1-120] the stripe widths and heights were much larger than when the misorientation was towards [000-1] or [0001]. Figure 3-8 shows a 1 µm thick AlN homoepitaxial film grown at 1250 °C on a substrate with a misorientation angle of 0.43° off [1-100] and direction of 52° off [0001] toward [11-20]. Even though the misorientation angle was similar to the films shown in Figure 3-5, there is a clear difference in the size of the stripes due to the misorientation direction difference. Furthermore, at this lower growth temperature, changing the growth rate by a factor of two, from 500 to 1000 nm/hr had no effect on the surface morphology even though by changing this growth parameter the surface supersaturation was increased.
Figure 3-8: 5x5 μm² AFM image of a 1 μm thick (1-100) homoepitaxial AlN film grown at 1250 °C with an RMS roughness of 43 nm.

A similar study to the one discussed in the previous paragraph was carried out for films grown with a film thickness of 1 μm at a higher growth temperature of 1450 °C. Misorientation angles between 0.27 and 0.55° were studied with directions between [11-20], [-1-120], [0001], and [000-1]. In all of these films, the surface consisted of relatively smooth surfaces free of the characteristic faceting seen for the lower growth temperatures. Varying degrees of macro-stepping, i.e. step bunching, was observed by AFM. Within this range of misorientation angles, there was no clear trend with surface roughness similar to the results at the lower temperature. A change in the misorientation direction seemed to have the largest effect on the degree of step bunching. Figure 3-9 (a) shows a AlN homoepitaxial film grown at 1450 °C on a substrate with a misorientation angle of 0.41° and direction of 34° off [000-1] toward [11-20]. The misorientation angle was similar to the film shown in Figure 3-5, however, there is a clear
difference in the degree of step bunching due to the misorientation direction difference. Moreover, monolayer steps were always visible on the step bunched surfaces for films grown at the higher growth temperatures, as shown in Figure 3-9 (b).

Figure 3-9: (a) 5x5 μm² and (b) 1x1 μm² AFM images of 1 μm thick (1-100) homoepitaxial AlN films grown at 1450 °C with RMS roughnesses of 0.6 and < 0.05 nm, respectively.

3.3.1.3 Hillocks

Hillocks were observed on some of the m-plane AlN homoepitaxial layers, equivalent to those presented on in Section 2.6.2. At the lower growth temperatures, i.e. when the striped morphology existed, no hillocks could be seen using optical DIC microscopy imaging or AFM. This could potentially be attributed to the growth mode or the initial stages of growth at these lower growth temperatures. At the higher growth temperatures, when step-flow growth was observed, large rectangular based hillocks were seen on the surface. Similar hillocks have been
observed in GaN grown by MOCVD on native (1-100) GaN substrates, where one face of the hillock is inclined toward the [0001] direction, one face is inclined toward the [000-1] direction, and two faces are symmetrically inclined toward the ±[11-20] direction. There were three distinct types of hillocks detected which are directly analogous to the ones that were seen in (0001) polar AlN and AlGaN growth on native AlN substrates. One type consisted of a sharp top with a misoriented crystal at the center. These crystals seemed to originate from a pit, as discussed in Section 2.6.2. This type of hillock made up a majority of the hillock density and was nearly impossible to image by AFM due to the sharp features of the grain at the top of the hillock. The other two types had either a sharp pointed, H_s, or flat top, H_f. Figure 3-10 shows AFM amplitude error images of these two of the three types of hillocks observed. The flat-topped hillocks were always observed at a density of less than 10 cm\(^{-2}\) whereas the sharp hillocks were observed at a density of low \(10^4\) cm\(^{-2}\). By annealing the substrate under a H\(_2\) atmosphere before growth, the densities of these two types of hillocks were never measurably reduced. Only the hillocks with grains could be removed in significant quantities by modifying the substrate surface prior to growth.
Figure 3-10: 5x10 μm² AFM amplitude error images of two types of hillocks seen on a 1.2 μm thick (1-100) homoepitaxial AlN film grown at 1550 °C.

3.3.2 Crystalline Quality

The growth temperature series of homoepitaxial films, described in the previous sections, was characterized by HRXRD through rocking curves, triple axis 2θ-ω line scans, and RSMs in order to better understand the crystalline quality of the films and see if it was related to the observed changes in surface morphology. The FWHMs of the symmetric (10-10)
rocking curves along [0001] ranged from 12-25 arcsec for all the films grown with the proper substrate surface preparation, which is near the resolution limit of ~12 arcsec for the HRXRD system. Figure 3-11 gives representative rocking curves for the low and high temperature growth regimes.

![Rocking Curve Image](image)

Figure 3-11: HRXRD symmetric (10-10) rocking curves of 1.2 μm thick (1-100) homoepitaxial films grown at two different temperatures.

These FWHM values are comparable to that of the substrates themselves demonstrating that the epitaxial layers are of at least the same quality as the substrates and that the bulk crystalline quality did not degrade with a roughening of the surface seen by AFM. Most importantly, this demonstrates one of the main advantages of using these high quality native AlN substrates.

Resulting (10-10) 2θ-ω spectra of the growth temperature series are displayed in Figure 3-12. Pendellösung fringes were present in the 2θ-ω line scans, which is indicative of an abrupt
difference in electron density somewhere between the substrate and epitaxial layer since the spacing between the fringes correlates to the thickness of the epitaxial film as given by Equation 1. Furthermore, the presence of symmetric 2θ-ω peaks indicated the absence of strained homoepitaxial layers.

![HRXRD triple axis (10-10) 2θ-ω curves of 1.2 μm thick (1-100) homoepitaxial AlN films grown at four different temperatures.](image)

For a more complete depiction of these observations, full RSMs were acquired for the (10-10) reciprocal lattice points. Figure 3-13 gives (10-10) RSMs representative of the low and high temperature growth regimes. There are distinct differences seen in the extension of the crystal truncation rod (CTR). The CTR was more intense and extended much further for the films grown at a higher temperature, indicating a more uniformly abrupt truncation or termination of the crystal lattice at the surface. Furthermore, the pole diffuse scatter was
much reduced for the films grown at a higher temperature. Since the bulk properties were similar between these two samples, these differences in diffuse scatter can be attributed to surface roughness effects.\textsuperscript{121} These results compare well with the AFM data which showed that the surface roughness was reduced from an RMS roughness of 18 to less than 0.4 nm from 5x5 μm$^2$ AFM images for the low and high temperature growths, respectively.

Figure 3-13: (10-10) RSMs for 1.2 μm thick (1-100) homoepitaxial layers grown at two different temperatures.
To further confirm that the homoepitaxial layers were strain free, absolute lattice parameters were acquired using a HRXRD method that was initially developed by Fewster et al. and since has been adapted for the case of AlN here.\textsuperscript{122} This technique will be briefly described in the following. The procedure for calculating the lattice parameters and error associated with them involved analyzing 2θ-ω line scans taken from various diffraction conditions. The 2θ Bragg angles were extracted from the experimentally measured line scans. The measured error in the 2θ value was found to primarily consist of the error in determining the peak position through a Pseudo-Voigt peak fitting; therefore, the error was taken to be the FWHM of the peaks. The \( d \) lattice spacing associated with each 2θ value was calculated using the basic Bragg’s law.

\[
d = \frac{\lambda}{2\sin(\theta)} \tag{2}
\]

There were two independent variables, \( \lambda \) and \( \theta \); therefore the associated measured error, \( \delta \lambda \) and \( \delta \theta \), was considered. After use of standard error propagation, the error associated with \( d \) is given by:

\[
\delta d = \sqrt{\frac{1}{4\sin^2 \theta} \delta \lambda^2 + \frac{\lambda^2}{4} \cot^2 \theta \csc^2 \theta \delta \theta^2} \tag{3}
\]

To extract the \( a \) and \( c \) lattice parameters from \( d \), the \( d \) lattice spacing equation for a hexagonal crystal system was used.

\[
\frac{1}{d^2} = \frac{4}{3} \frac{h^2+k^2+hk}{a^2} + \frac{t^2}{c^2} \tag{4}
\]

where here \( h, k, \) and \( l \) are the associated crystallographic positions for the diffraction conditions within reciprocal space. Equation 4 was then fitted by weighted least squares fitting to the
calculated $d$ values extracted from the line scans. The weighting was introduced by using the following weights:

$$w_i = \frac{1}{(\delta d_i)^2}$$

(5)

where $\delta d_i$ is the calculated error for each calculated $d$ value.\(^{123}\) The error for each of the fitted $a$ and $c$ values was taken to be the root mean square error. This is a common practice when dealing with random error, which we have here as opposed to a systematic error. The general equation for root mean square error is given by:

$$error = \sqrt{\frac{1}{N} \sum (x_i - x_c)^2}$$

(6)

where $N$ is the number of measured diffraction conditions, $x_i$ is the experimental value and $x_c$ is the calculated value using the fitted values.

Using this method, the $a$ and $c$ lattice parameters were realized along with the associated error for an as-received (1-100) AlN substrate and homoepitaxial films from the growth temperature series using a set of nine skew-symmetric reflections under the same zone axis.\(^{124}\) These values are given in Table 3-1 and demonstrate that there was no significant difference between the lattice parameters for the films as compared to the substrates further confirming that these films were nearly strain free. This was important to realize since polishing induced damage within the substrate has been known to introduce strain in homoepitaxial AlN thin films, as discussed in Section 2.6.1.\(^{69}\)
Table 3-1: Lattice parameters for a (1-100) as-received AlN substrate and three 1.2 µm thick (1-100) homoepitaxial layers grown at different temperatures.

<table>
<thead>
<tr>
<th>Material Description</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1-100) AlN Substrate</td>
<td>$3.11163 \pm 0.00007$</td>
<td>$4.98182 \pm 0.00038$</td>
</tr>
<tr>
<td>(1-100) AlN Film T=1150°C</td>
<td>$3.11172 \pm 0.00005$</td>
<td>$4.98129 \pm 0.00041$</td>
</tr>
<tr>
<td>(1-100) AlN Film T=1350°C</td>
<td>$3.11165 \pm 0.00007$</td>
<td>$4.98169 \pm 0.00037$</td>
</tr>
<tr>
<td>(1-100) AlN Film T=1550°C</td>
<td>$3.11184 \pm 0.00008$</td>
<td>$4.98176 \pm 0.00059$</td>
</tr>
</tbody>
</table>

Figure 3-12 demonstrated the presence of Pendellösung fringes, as mentioned previously. The abrupt change in electron density causing these interference patterns could be a result of differences in the impurities or native point defects in the substrate as compared to the film. It could also be due to an interfacial layer of different electron density between the film and substrate. Cross-section HAADF STEM imaging along with elemental analysis by energy-dispersive spectroscopy (EDS) was performed to study the substrate/film interface. A ~5 nm thin interfacial layer was visible at the substrate/film interface in Z-contrast STEM imaging along the <0001> zone axis, as indicated in Figure 3-14. Nice atomic resolution STEM imaging was realized and clearly indicated the hexagonal symmetry along the <0001> direction. Furthermore, EDS showed that this interfacial layer was rich with silicon. The source of silicon could be the polishing media used for substrate preparation. This region which is rich with silicon is thought to be the cause for the displayed interference fringes in XRD.
Moreover, even with this interfacial layer, the homoepitaxial films are highly crystalline and strain free.

![Z-Contrast](image)

Figure 3-14: Z-contrast STEM images and elemental EDS analysis of a (1-100) homoepitaxial layer grown at 1250 °C.

3.3.3 Point Defect Incorporation and Identification

3.3.3.1 Optical Properties

Figure 3-15 shows a typical low temperature (T = 3 K) PL near band-edge spectrum of the homoepitaxial films in order to demonstrate the optical quality of the homoepitaxial films and determine the defect incorporation. For all homoepitaxial films, the excitonic peaks near
the band edge were very intense. The presence of well-defined DBX and FX transitions demonstrates the high quality of the homoepitaxial films. The dominant DBX at 6.012 eV has been identified as the Si°X, indicating the presence of Si in the film and had a FWHM of 550 μeV, which is comparable to state of the art high quality (0001) homoepitaxial films. These narrow widths allow for an unambiguous identification of these exciton peaks. Additional peaks in Figure 3-15 are labeled according to the assignments discussed by Bryan et al. who also identified the peak at 6.006 eV as the O°X due to the unintentional incorporation of O in (1-100) homoepitaxial films. The Γ₁ and Γ₅ FX’s having energy values of 6.032 and 6.040 eV indicate that the film was free of strain, which is consistent with HRXRD results discussed in the previous section. Other peaks are observed at 6.010 and 6.003 eV. They have not yet been identified and are not typically observed in (0001) homoepitaxial films.
Figure 3-15: Low temperature near band-edge PL spectrum of a 1.2 μm thick (1-100) homoepitaxial AlN film grown at 1450 °C.

Because of the high optical quality of these films, an in-depth analysis of the anisotropic optical properties of (1-100) AlN was performed by comparing emission and spectroscopic ellipsometry (SE) data. The (1-100) surface allows for full access to the anisotropic optical response in the hexagonal AlN crystal by probing with the electric field polarization perpendicular (E \perp c) and parallel (E \parallel c) to the optical c-axis. By doing this, elements of the dielectric tensor can be extracted as described in detail elsewhere. Feneberg et al. utilized SE to accurately determine the ordinary \varepsilon_\perp and the extraordinary \varepsilon_\parallel complex dielectric functions (DFs) of AlN corresponding to E \perp c and E \parallel c, respectively. He did this by measuring a single crystalline bulk AlN boule grown by PVT which was large enough to access
a sufficient area of the (1-100) plane. Here we will discuss SE analysis on the high quality (1-100) homoepitaxial films reported on in the previous sections. Generalized SE was recorded using a commercially variable-angle spectroscopic ellipsometer V-VASE (Woollam) at room temperature. At low temperature \((T = 20 \text{ K})\), a synchrotron-based home-built ellipsometer was employed.\(^{127}\)

In AlN, the valence band ordering at the \(\Gamma\) point is directly linked to the exciton fine structure. There are three valence bands with the uppermost designated as \(\Gamma_{7+,v}\) and two lower ones as \(\Gamma_{9,v}\) and \(\Gamma_{7-,v}\). Exciton optical transitions from the conduction band, \(\Gamma_{7,c}\), to the \(\Gamma_{7+,v}\), \(\Gamma_{9,v}\), and \(\Gamma_{7-,v}\) are commonly labeled as the \(A (\Gamma_{7+})\), \(B (\Gamma_{9})\), and \(C (\Gamma_{7})\) excitons, respectively. AlN exhibits a negative crystal field energy of \(\Delta_{cf} = -221\) meV, which is approximately the energy difference between \(\Gamma_{7+,v}\) and the lower \(\Gamma_{9,v}\) and \(\Gamma_{7-,v}\). The lower two are split by the spin-orbit interaction energy of \(\Delta_{so} = 13\) meV. These three exciton groups can be further split when accounting for the short range spin-exchange interaction. Of particular interest for (1-100) AlN is splitting of the \(\Gamma_{7+}\) exciton into a \(\Gamma_{5}\) and \(\Gamma_{1}\), both seen in Figure 3-15, by taking into account symmetry and the measured spin-exchange interaction constant of \(j = -4\) meV.\(^{128}\)

Furthermore, transition probabilities deviate between the \(\Gamma_{7+}\), \(\Gamma_{9}\), and \(\Gamma_{7}\) excitons depending on the polarization of the excitation source relative to the optical c-axis. The transition probability for \(\Gamma_{7+}\) is the highest for \(E \parallel c\), whereas for \(\Gamma_{9}\) and \(\Gamma_{7}\) it is the highest for \(E \perp c\).

The dielectric functions \((\varepsilon_x = \varepsilon_{1,x} + i \varepsilon_{2,x} , x = \perp, \parallel)\) are comprised of real and imaginary parts. Here, for simplicity only \(\varepsilon_2\) will be discussed since this is directly related to the absorption and more importantly \(\varepsilon_1\) can easily be understood through the Kramer-Kronig relation using \(\varepsilon_2\). Figure 3-16 gives the resulting \(\varepsilon_{2,\perp}\) and \(\varepsilon_{2,\parallel}\) at low and room temperature for
a (1-100) AlN homoepitaxial film grown at 1450 °C. The curves have been decomposed using a model presented by Elliot, modified for the existence of electron-phonon complexes (EPCs) and the known band structure of AlN.\textsuperscript{126,129} The sum of all the model contributions from the EPCs, the excited states of FXs, and the exciton continuum or band-to-band absorption is shown as a continuous solid curve plotted over the experimental data.
Figure 3-16: Imaginary parts of the dielectric functions for the electric field vector oriented parallel (E∥c, blue) and perpendicular (E⊥c, red) to the optical axis of a (1-100) AlN film.

For E⊥c, contributions from the two valence bands Γ₉ and Γ₇ were considered, however for E∥c, only the highest valence band Γ₇⁺ was considered. Comparing the SE data at the Γ₇⁺ excitonic resonance for E∥c at low temperature to the PL data from Figure 3-15, it
must be noted that only the $\Gamma_1$ contribution was predominately visible in SE whereas both the $\Gamma_1$ and $\Gamma_5$ were clearly distinguishable in PL for the $\Gamma_{7+}$ band. This is explained by the higher density of states for the $\Gamma_1$ as compared to the $\Gamma_5$ with the considered experimental geometry. Both $n = 1$ and $n = 2$ excited states were clearly distinguishable in the $\varepsilon_{2,\perp}$ and $\varepsilon_{2,\parallel}$ curves. Furthermore, an increase in temperature from low to room temperature resulted in the expected broadening and damping due to phonons. The phonons cause a reduction of exciton lifetime due to the introduced scattering events. Even with this broadening the excitonic excited states, EPCs, and the exciton continuum were clearly resolvable indicating the high material quality. The blueshift observed from the high to low temperature measurements matched nicely the shift observed in emission by Bryan et al.$^{15}$ The difference in the onsets of the $\varepsilon_{2,\perp}$ and $\varepsilon_{2,\parallel}$ curves are a little more than 200 meV, which matches closely with the reported $\Delta_{c,f} = -221$ meV as well.$^{128}$

A full list of characteristic energy values obtained from the SE data is given in Table 3-2. The energy position of the $\Gamma_1$ exciton from SE is in agreement with reported PL data here and elsewhere at 6.032 eV at low temperature.$^{73,128}$ This reveals that no Stokes shift is observed between the emission and absorption of related features, as expected for such high-quality material and spectra. These characteristic energy values are in near perfect agreement with data obtained by Feneberg et al. on the bulk AlN, yielding more evidence for the homoepitaxial film maintaining high structural quality during growth.$^{126}$
Table 3-2: Characteristics energy values (in eV) of the free excitons comprised of holes from different valence bands ($\Gamma_{7+}$, $\Gamma_{9}$, and $\Gamma_{7}$), exciton binding energies ($E_B^X$) and longitudinal-optical phonon energies ($\Delta E_{ph}$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$T = 298$ K</th>
<th>$T = 20$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E \parallel c$</td>
<td>FX ($\Gamma_{7+}$)</td>
<td>5.952</td>
</tr>
<tr>
<td></td>
<td>$E_B^X$</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_{ph}$</td>
<td>0.111</td>
</tr>
<tr>
<td>$E \perp c$</td>
<td>FX ($\Gamma_{9}$)</td>
<td>6.171</td>
</tr>
<tr>
<td></td>
<td>FX ($\Gamma_{7}$)</td>
<td>6.181</td>
</tr>
<tr>
<td></td>
<td>$E_B^X$</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_{ph}$</td>
<td>0.110</td>
</tr>
</tbody>
</table>

SE measurements were also conducted on a (1-100) homoepitaxial film grown at 1250 °C and compared to a film grown at 1450 °C similar to that which was just discussed. The comparison is presented in Figure 3-17. SE measurements are sensitive to the surface roughness. Due to the higher surface roughness present in the lower temperature film, extracting the dielectric function was hindered by the lack of physically meaningful modeling. In contrast, at the higher growth temperature when the surface was smooth a low experimental error was realized evidenced by the close agreement in characteristic energy values with those reported in literature. From Figure 3-17, there is a clear difference in the absolute value of $\varepsilon_2$ below the absorption onset for the film grown at a lower temperature. This is attributed to the
surface roughness as discussed by Aspnes et al.\textsuperscript{130} All in all, the significantly smoother surface attained from high temperature growth allowed for state of the art SE measurements to be achievable for the first time on a (1-100) AlN thin film.

![Figure 3-17: Imaginary parts of the dielectric functions at 298 K for samples grown at 1250 °C and 1450 °C.](image)

3.3.3.2 Oxygen Incorporation

The surface roughness was not the only variable which had an effect on the optical properties of the (1-100) homoepitaxial films. Bryan et al. determined that the O°X peak intensity seemed to correlate to the growth temperature in these films indicating a potential
change in the incorporation of point defects. In fact, with an increase in growth temperature, the Si\textsuperscript{0}X became dominant over the O\textsuperscript{0}X peak. The unintentionally incorporated impurities of these films were analyzed by calibrated SIMS depth profiling in order to quantitatively determine the concentration of O, Si, and C impurities and see how this related to the growth temperature. Figure 3-18 gives the SIMS depth profile for the structure presented in Figure 3-6 which is a two layer 1.2 μm thick (1-100) homoepitaxial AlN film with 600 nm grown at 1450 °C followed by 600 nm grown at 1350 °C. All of the impurity levels were found to be above the detection limit of the SIMS system. The SIMS depth profile indicates that the growth temperature directly affected the O incorporation within the film. A reduction in O atomic concentration of over one order of magnitude was observed with an increase in growth temperature of 100 °C. Furthermore, the C and Si were reduced in the thin film as compared to the substrate. Si and O levels spiked up to mid-$10^{19}$ and $10^{20}$ cm$^{-3}$, respectively, at the interface of the substrate and homoepitaxial layer. It is expected that the source of these impurities is the polishing medium for the AlN substrate. Furthermore, this seems to correlate well with the EDS results presented in Figure 3-14.
Figure 3-18: Calibrated SIMS depth profile for O, Si, and C in a two layer 1.2 μm thick (1-100) homoepitaxial AlN film with 600 nm grown at 1450 °C followed by 600 nm grown at 1350 °C.

Additionally, 200 nm thick (1-100) and (0001) films were grown at identical growth conditions with a growth temperature of 1250 °C and analyzed by calibrated SIMS in order to potentially explain the rather large incorporation of O in these (1-100) films. The Si and C concentrations were comparable to the levels shown in Figure 3-18; however, the O concentrations differed significantly. O concentrations of ~4 x 10^{20} and ~3 x 10^{17} cm^{-3} were present in the (1-100) and (0001) epitaxial films, respectively. The surface morphology of the (0001) film consisted of a smooth bilayer step structure as compared to the heavily faceted (1-100) film, seen in Figure 3-5. The presence of the (1-100) vertical growth surface and (000-1)
facets on the (1-100) film is expected to cause a significant difference in the O concentration as compared to the (0001) surface since the (1-100) and (000-1) planes preferentially incorporate O, as is seen in both GaN and AlN.\textsuperscript{131, 132} Therefore, it is clear from this SIMS analysis that (1-100) AlN homoepitaxial growth at higher temperatures as compared to (0001) growth is necessary for high purity epitaxial films, as the impurity incorporation depends on surface morphology.

These differences in impurity concentrations was also evident by obvious differences in the room temperature deep defect PL for each of the 1.2 μm thick films grown at temperatures between 1250 and 1550 °C, as seen in Figure 3-19. It is important to note that these are relative measurements. With an increase in growth temperature it is clear that the deep defect luminescence reduced in intensity. These broad peaks are comprised of a minimum of three distinct peaks with energies at around 3.2, 3.6, and 3.8 eV. Based on SIMS data, the C and Si incorporation remained unchanged with a change in growth temperature at around 3 x 10\textsuperscript{17} and 2 x 10\textsuperscript{18} cm\textsuperscript{-3}, respectively. The O concentration changed significantly and could be directly related to the point defects causing these emissions. This is in agreement with the observations made by Youngman and Harris who attributed these emissions to O in their sintered AlN ceramics.\textsuperscript{133} An in-depth discussion on the identification of these point defects will be presented in Section 4.2.2.
3.3.4 Stacking Faults

SFs are the most common type of extended defect discussed for non-polar epitaxial III-nitrides. These extended defects are one of the primary detriments for non-polar III-nitride materials and their device applications. First-principle calculations by Stampfl and Van de Walle have determined that the formation energies of SFs increase going from GaN to InN to AlN meaning that the formation of such defects should be less probable in AlN compared to the other III-nitrides, however, still high densities are present in all non-polar AlN reported on prior to the work presented now in this dissertation. Moreover, these theoretical studies showed that intrinsic $I_1$ type stacking faults always have the lowest formation energy over intrinsic $I_2$,.
intrinsic I₃, and extrinsic SFs. Of the observed SFs in non-polar III-nitrides, BSFs tend to prevail with Frank partial dislocations terminating the SFs. These extended defects are more difficult to get rid of once they are formed as compared to threading dislocations (TDs). The density of BSFs in non-polar films do not strongly reduce with an increase in film thickness. Therefore, it is critical that the cause of their formation is well understood in order to produce low BSF density films.

Most reports of SFs in wurtzite III-nitrides are based on non-polar GaN, consequently most of the understanding behind the epitaxial growth and microstructure of non-polar III-nitrides come from GaN studies. To reduce the density of SFs in (1-100) GaN, typical lateral epitaxial overgrowth (LEO) has been considered and the use of buffer layers has also been investigated for heteroepitaxial films. Even with these techniques, the defect densities for heteroepitaxial films are relatively high and remain problematic for device applications. Nearly SF and TD-free (1-100) GaN have been realized through homoepitaxial growth on low defect density free standing GaN with TD and SF densities below the resolution of TEM imaging, i.e. lower than 5 x 10⁶ cm⁻² and 1 x 10³ cm⁻¹, respectively. Here a study on the extended defects in the (1-100) AlN homoepitaxial films will be discussed.

In order to investigate the extended defects in (1-100) AlN, a TEM study was conducted on the two layer film shown in Figure 3-6. Two TEM samples were prepared from the structure in order to access the appropriate diffraction conditions for studying BSFs and TDs, one oriented parallel and the other perpendicular to the [11-20] direction as indicated in Figure 3-20. Cross-sectional TEM images taken with g=11-20, g=1-100, and g=0002 diffraction conditions are also given in Figure 3-20 with white arrows being used to indicate the interfaces
for the two layers grown at different temperatures and the substrate. Imaging with g=0002 revealed that no TDs were visible with ±[0001] components. TEM imaging with g=1-100 and g=11-20 also revealed a film free of contrast due to dislocations further indicating that no new TDs were generated in the epitaxial film. It is expected that these films have even fewer dislocations than those seen in the substrate (< 10³ cm⁻²), since these substrates are processed from boules grown by PVT in the [000-1] direction. Only dislocations that are near the substrate surface have an opportunity to propagate through the epitaxial film. This further supports all of the observations made by HRXRD and SE whereby the quality of the film was indistinguishable from that of the substrate.
TEM imaging with $g=100$ and $g=110$ are used to observe BSFs. A full tilt series was considered and no faults could be observed either in the low or high temperature film. The only observable contrast seen in TEM imaging was due to sample thickness deviations and preparation artifacts. These results indicate that the BSF density is lower than $5 \times 10^3$ cm$^{-1}$, the
TEM imaging resolution shown here. Typical BSF densities for (1-100) AlN epitaxial films are between $5 \times 10^5$ and $5 \times 10^6$ cm$^{-1}$.\textsuperscript{137} It is clear now the importance of having a high quality native AlN substrate for the realization of such low extended defect density epitaxial films.

The surface morphology of epitaxial films is governed by the surface supersaturation which is directly related to the substrate misorientation, surface diffusion length, and growth conditions, i.e. vapor supersaturation, as discussed in detail throughout Chapters 1 and 2. Typically, the presence of high densities of dislocations will dominate the characteristics of the surface morphology. TDs are known to pin steps, initiate V-defect formation, and even cause the well-known spiral growth discussed thoroughly by BCF theory.\textsuperscript{41} In the same way, a connection between the slate-like morphology seen in non-polar III-nitrides has been made with BSFs.\textsuperscript{104, 117}

BSFs in non-polar III-nitrides grown heteroepitaxially have been shown to initiate at the onset of growth. The reason is that the large lattice mismatch between the film and substrate makes it necessary for the initiation of growth to proceed by three-dimensional island nucleation.\textsuperscript{138} These islands will nucleate with $\ldots$AaBbAa$\ldots$ and $\ldots$CcBbCc$\ldots$ stacking sequences along the [0001] direction on different terraces. When the islands eventually coalesce, an intrinsic $I_1$ type BSF is formed at the boundary on the c-plane sidewalls.\textsuperscript{56} These BSFs then make it favorable for the surface to facet along the fault line. This has been confirmed through a direct correlation between the stacking fault orientation and density with the stripe orientation and density for slate-like surface morphology.

A LEO study of GaN by Hirai et al. even suggested that SFs are necessary for the slate-like morphology.\textsuperscript{139} In that study, it was determined that growth conditions could be found
which resulted in a smooth surface morphology even with high BSF densities. The BSF density could only be reduced through the lateral growth of the wing region over the LEO mask. However, under growth conditions that promoted the slate-like morphology, the only way to reduce the density of stripes was to reduce the density of BSFs in the wing regions of the LEO, therefore making it seem necessary for the BSF to be present for the characteristic stripe along the ±[0001] to form. The conclusion was that if a slate-like morphology is present then SFs should be as well. These claims are slightly contrary to the results shown in Figure 3-20, which indicates that the slate-like morphology, present in the lower growth temperature layer, is not necessarily related to BSFs. It could be that BSFs simply promote the formation of the (000-1) facets and that through appropriate growth conditions, similar surface features can become energetically favorable. All of the results presented in this section indicate that further investigations are needed to establish a better understanding of the surface kinetics and energetics involved in the formation of the slate-like morphology seen in non-polar III-nitrides from literature and here in the (1-100) homoepitaxial AlN films grown at the lower growth temperatures, since such strong claims have been made to correlate this morphology to BSFs in the literature.

3.4 Al-rich AlGaN

3.4.1 Surface Morphology

Finally, once high quality, atomically smooth homoepitaxy was realized, AlGaN epitaxial films were investigated since nearly all optoelectronic and electronic device designs require the high quality ternary alloy in combination with the high quality AlN layers. All of
the preliminary studies shown here were performed on 600 nm thick AlGaN films which were
deposited on 600 nm of smooth AlN homoepitaxy grown at 1450 °C. The growth conditions
were chosen to mimic that of state of the art AlGaN growth on c-plane AlN, which was
discussed by Dalmau et al. and here in Section 2.5.22 The Ga input partial pressure was kept
constant and the growth temperature varied from 1000 to 1350 °C under 20 Torr total pressure
with H2 as the diluent gas. Due to the desorption rate of Ga at these growth temperatures, the
increase of growth temperature resulted in an increase in Al-content from 60 to 97%,
respectively, allowing for a study on both the effect of temperature and Al-content. All of the
substrates had a misorientation angle of around 0.45 ± 0.05° off [1-100] and directions
spanning between 44° off [-1-120] toward [0001] and purely [0001]. Figure 3-21 shows AFM
images of the surfaces for the resulting films.
Figure 3-21: 5x5 μm² AFM images of 600 nm thick (1-100) AlGaN films grown at four different temperatures.

All films exhibited heavy degrees of step bunching and faceting. The roughest AlGaN film was grown at the lowest temperature of 1000°C with a RMS roughness of 13 nm. The morphology did not follow a trend with temperature or composition as has been seen with
AlGaN grown on c-plane AlN, discussed in Section 2.5, however, the morphologies were smoother overall compared to the homoepitaxial (1-100) AlN films grown at the same temperatures. Furthermore, adding Ga in the films seemed to remove the preferential faceting along the ±[0001] direction seen in the homoepitaxy, however, faceting still existed. The cause of these morphology differences is nearly impossible to determine without further studies. For the AlN epitaxial films, a high growth temperature was required to overcome the energetics causing the faceting. In the case of AlGaN, the upper limit of usable growth temperature is determined by the Ga species, where at these relatively high temperatures the desorption rate is so great that very little Ga is incorporated in the film. Further studies indicated that Ga incorporation was not detectable at temperatures above 1350 °C, even with an increase of the Ga partial pressure by more than 10x. It is important to note that these studies were done in an atmosphere of H₂, by using N₂ instead, the vapor supersaturation of the Ga species can be increased and potentially provide a higher usable growth temperature for AlGaN. If the transition seen in AlN was due to an increase in the Al diffusion length at the higher temperatures, then it will be very difficult to achieve atomically smooth AlGaN since the growth conditions needed for the higher Al diffusion length results in a subsequent significant reduction in the Ga diffusion length. Either way, all of these results indicate that the surface energetics are very different for (1-100) as compared to (0001) AlGaN and that much work is needed before smooth interfaces can be achieved for heterostructures, in particular, for quantum wells.
3.4.2 Composition Inhomogeneity

All of the (1-100) AlGaN epitaxial films were studied by HRXRD in order to determine the compositional uniformity. Symmetric triple axis (10-10) 2θ-ω curves suggested that the films were not compositionally uniform. Figure 3-22 shows that more than one dominant Bragg peak was present for the AlGaN layer indicating that either there were different relaxation states across the samples or that there were different Al-contents within the same film, with the later being the more likely based on the results discussed on in Section 2.5.3 for (0001) AlGaN. The studies on (0001) AlGaN indicated that when step bunching existed on AlGaN surfaces, there was always an ensuing inhomogeneity in the composition due to the differences in step densities across the step bunches. These compositional gradients appeared sharp through Z-contrast STEM imaging and behaved similar to quantum sheets.

The optical quality of these films were investigated through room temperature PL which is also given in Figure 3-22. The near band edge spectra exhibited broad emission peaks compared to the AlN which is typical of AlGaN and caused by alloy scattering. Furthermore, the spectra contained multiple free exciton emissions confirming the compositional inhomogeneity seen in HRXRD. Lastly, these luminescence spectra indicate the detriment of having rough AlGaN for devices. Before the benefit of removing the polarization effects through the use of non-polar (1-100) AlGaN can be realized and correctly investigated, a more complete understanding of the surface kinetics must be gathered. At this point, there are no reports in the literature which indicates that smooth AlGaN is achievable through the use of typical AlGaN growth conditions, therefore, new techniques may be required to overcome this issue of faceting and step bunching in (1-100) AlGaN.
Figure 3-22: Symmetric triple axis (10-10) 2θ-ω curves by HRXRD (top) and room temperature photoluminescence (bottom) of 600 nm thick (1-100) AlGaN films grown at four different temperatures.
3.5 Summary

In this chapter, (1-100) m-plane AlN single crystal substrates were used to grow high quality AlN and Al-rich AlGaN by MOCVD. In order to achieve smooth AlN surface morphologies, growth temperatures greater than 1350 °C were necessary. Below 1350 °C, the AlN surface consisted of macrosteps oriented along the ±[0001] directions. High-resolution XRD symmetric rocking curves had FWHM values of 12-25 arcsec, which matched that of the high quality substrate. PL spectra revealed several sharp and intense DBX peaks with a FWHM as narrow as 550 µeV, demonstrating the highest quality films ever reported. The DBX transition at 6.006 eV was identified as originating from the neutral-oxygen-donor (O°X) in AlN. This point defect identification was made possible by the unintentional incorporation of oxygen and its dependence on growth temperature and orientation. High-resolution XRD and TEM studies were performed to investigate strain and dislocation behavior in the non-polar epitaxial films. Both studies indicated that no basal plane stacking faults were present, which was in contrast to results on non-native substrates. All of the results presented in this chapter bring about new insight on m-plane Al-rich AlGaN and AlN epitaxial growth, which is crucial to the development of AlN based non-polar devices.
CHAPTER 4: Doping in AlN and Al-rich AlGaN

4.1 Motivation

There exists no miscibility gap for AlN and GaN, therefore AlGaN alloys through the entire compositional range have been realized and studied. It is common for Al-rich AlGaN to be grown using foreign substrates, such as sapphire. These films exhibit high dislocation densities due to the large lattice mismatch between the substrate and film. The high dislocation densities hinder the overall conductivity of the doped films, making it desirable to reduce them. Recently, the development and availability of AlN single crystal substrates with low dislocation densities (< 10^3 cm^-2) has made it possible to grow Al-rich AlGaN with low densities of extended defects. These high quality films have demonstrated high optical gain and conductivity making an electrically injected laser diode very feasible in the near future.

Achieving control of electrical conductivity in Al-rich AlGaN has proven to be very difficult. In order to achieve n-type conductivity in Al-rich AlGaN, Si is commonly used since it incorporates readily as a substitutional impurity on the cation site, therefore acting as a donor. Si has been shown to act as an effective n-type dopant through the entire alloy range from GaN to AlN. Above 80% Al-content, the activation energy increases non-linearly with Al-content up to 255 meV for AlN. Consequently, at room temperature only a fraction of the dopant atoms are activated. To account for this high activation energy, high doping levels are needed with low levels of compensation to achieve high conductivity in Al-rich AlGaN.

For p-type conductivity in AlGaN, Mg is the most commonly used dopant. Mg readily incorporates on a cation site as an acceptor. Only a few studies of conductivity have been
reported on Mg-doped p-type AlGaN and most of these studies investigated films with low Al-content (x < 0.3). This is because of the deep nature of Mg acceptors. The activation energy of Mg increases with Al-content and is even higher than the activation energy of Si. In fact, the Mg acceptor activation energy is expected to reach between 510-630 meV for AlN. Mg-doped Al-rich AlGaN films are of great importance in realizing nitride based devices, consequently investigations that could provide a better understanding and potential realization of p-type Al-rich AlGaN is desired.

Besides dislocation density reduction, identification and elimination of compensating defects are necessary to obtain highly conductive n- or p-type Al-rich AlGaN alloys. Indication of compensation effects for Si-doped Al-rich AlGaN has been demonstrated; however nothing has been reported for Mg doping. The cause of the compensation in Si-doped AlGaN has been under debate for many years. Many propose that the electrons are compensated by cation vacancies and their complexes with oxygen or silicon; however little has been done to definitively prove these claims by properly identifying the specific defects responsible for the compensation.

4.2 Si Doping

In the following studies, Si-doped AlGaN films covering the entire compositional range from GaN to AlN were grown by MOCVD on sapphire substrates. Additionally, Si-doped Al\textsubscript{x}Ga\textsubscript{1-x}N thin films with high Al mole fractions (0.55 ≤ x ≤ 1) were grown on (0001)-oriented single crystalline AlN substrates. Details on the growth of these films are given in Section 2.2, with the exception of the Ga-rich AlGaN and GaN films. These films were grown on GaN
layers grown on sapphire as described by Mita et al. and Rice et al.\textsuperscript{78, 157} For all of the films, SiH\textsubscript{4} was used as the Si dopant source. The Al-content of the AlGaN films was determined using an XRD technique described by Tweedie et al.\textsuperscript{158}

4.2.1 Contacts

The formation of low-resistance Ohmic contacts on Al-rich AlGaN and AlN is not well understood, yet these contacts are crucial for the performance and reliability of electronic and optoelectronic devices. Furthermore, before the electrical properties of conductive AlGaN films can be properly studied, appropriate contacts have to be realized. In particular, Ohmic contacts are desirable to perform Hall effect measurements. By using the Van der Pauw method in conjunction with Hall effect measurements, the resistivity, free carrier mobility, and free carrier concentration for all of the conductive films can be determined. A figure of merit for characterizing the quality of an Ohmic contact is the specific contact resistivity, $\rho_c$. This is an intensive quantity, as it is independent of contact area and shape and is a convenient parameter when comparing contacts of various sizes.

The transfer length method (TLM) was used to measure the specific contact resistivity of contacts based first on the metal stack composed of 30 nm Ti, 100 nm Al, 70 nm Ni, and 70 nm Au, hereinafter referred to as Ti-based contacts, by measuring the resistance between metal contacts across gaps of varying sizes. Figure 4-1 shows a representative optical image of the linear TLM structures used for all the studies to follow. Patterning and fabrication of the TLM structures was accomplished via photolithography, electron beam evaporation and lift off. Mesa isolation etching was conducted by reactive ion etching to minimize current flow in areas
not directly between the rectangular contact pads. Lastly, all TLM structures were rapid thermal annealed in a N₂ atmosphere at various temperatures for 1 min. to reduce the contact resistivity and ultimately determine an optimal annealing temperature. To minimize the error in the calculated $\rho_c$, for each thin film studied, all of the necessary linear dimensions were measured individually using an optical microscope with a calibration slide.

Figure 4-1: Optical image of an array of TLM structures used to extract the contact resistivity and sheet resistance of conductive thin films.
4.2.1.1 Ti-based Contacts on GaN

Si-doped GaN was initially studied since Ohmic contacts on GaN is a well-established and developed technology.\textsuperscript{159, 160} Furthermore, most Ohmic contacts for semiconductors rely on high free carrier concentrations near the contact junction in order to allow for tunneling through any barriers present at the metal-semiconductor interface. In the case of GaN, high free carrier concentrations are easily achievable. For these reasons, GaN should be well-behaved and act as a reliable reference for contacts on Al-rich AlGaN and AlN.

All of the Ti-based contacts tested on Si-doped GaN exhibited linear current-voltage (IV) curves as long as the free carrier concentration was greater than around $3 \times 10^{16}$ cm$^{-3}$. Below this concentration, slight deviations from linearity at low voltages ($< 1.5$ V) could be seen indicating insufficient tunneling through the contact barrier. The TLM method was used to study the Ti-based contacts on GaN with a free carrier concentration of $3 \times 10^{17}$ cm$^{-3}$. Figure 4-2 (a) shows a representative set of IV curves taken from the TLM structures fabricated on the conductive GaN film. As expected, with a decrease in the gap spacing there was a decrease in the total series resistance mainly being attributed to the sheet resistance. Using the TLM method, $\rho_c$ was determined for a range of annealing temperatures and are given in Figure 4-2 (b). A contact resistivity dependence on annealing temperature was observed. An optimum annealing temperature was found for GaN to exist around 800 °C, where a minimum specific contact resistivity of $1.2 \pm 1.0 \times 10^{-6}$ Ω cm$^2$ was obtained. This provides evidence that during annealing, diffusion of metal species and potential vacancies in the semiconductor modifies the barrier at the contact junction. Further XPS studies determined that during annealing, the Al species in the contact plays an important role in decreasing the barrier height. Also, a new
nitride phase with Ti was detectable through XPS when Ti contacts were annealed indicating another potential reason for the decrease in contact resistance.
Figure 4-2: A typical set of IV curves as a function of contact gap spacing (a) acquired from a TLM structure like that shown in Figure 4-1. The specific contact resistivity for the Ti-based contacts on Si-doped GaN as a function of annealing temperature (b).
4.2.1.2 Ti-based Contacts on AlN and Al-rich AlGaN

It is expected that with an increase in the Al-content of n-type AlGaN, the barrier height will increase for Ti-based contacts, meaning that the contact resistance should be greater for AlGaN as compared to GaN. Furthermore, achieving high free carrier concentrations in Si-doped AlGaN and AlN is more difficult and should also hinder the Ohmic contact performance. Keeping this in mind, Ti-based contacts were studied on Al-rich Al$_x$Ga$_{1-x}$N (0.6 ≤ $x$ ≤ 1). Figure 4-3 shows representative IV curves for Si-doped AlN films grown on both native AlN and foreign sapphire substrates. Ti-based large area contacts (> 2x2 mm$^2$) spaced more than 10 mm apart and annealed at 850 °C were used for the IV measurements presented. Similar to the results from GaN, when the free carrier and doping concentrations were relatively low, nonlinear IV curves were obtained. Increasing the doping concentration provided more free carriers for tunneling and the IV curves became linear. For a specific doping range, unique to each Al composition, increasing the doping concentration resulted in a subsequent decrease in the total series resistance. However, at a critical doping level, any further increase in the doping concentration caused an increase in the sheet resistance and nonlinear IV curves appeared. This indicates an onset of compensation effects which will be discussed further in Section 4.2.2.
Figure 4-3: IV curves of Si-doped AlN thin films deposited on both native AlN and foreign sapphire substrates with annealed Ti-based contacts and different Si concentrations.

Additionally, Al-rich AlGaN and AlN films that were grown on sapphire tended to be more than one order of magnitude less conductive than films grown on AlN substrates. In fact, many times IV curves appeared Ohmic for films on sapphire and not Ohmic for films on AlN substrates. The cause of this is expected to be from higher amounts of tunneling which was modeled by Brian et al. as defect-assisted Frenkel-Poole emission. Even though the contact resistance should increase with fewer available free carriers, it appears to decrease due to an increase in electrically active defect states near the metal-semiconductor interface for the case of films on sapphire. This can be clearly seen in Figure 4-3 where Ti-based contacts on Si-doped AlN films grown with the same growth conditions appear Ohmic on sapphire and not Ohmic on an AlN substrate. These results suggest that for effective Ohmic contacts to
homoepitaxial AlN over a wider range of Si concentrations, either an enhancement in the
defect-assisted tunneling, like that seen in films on sapphire, must occur or metals other than
Ti should be considered. It should be noted that all of these general trends were observed for
the entire Al-rich composition range studied.

Even though Ohmic behavior was observed for large area contacts (> 2x2 mm²) on
films with certain doping concentrations, a majority of these Ti-based contacts were not purely
Ohmic. Since \( \rho_c \) is the ratio of the voltage drop to the current density, a nonlinear IV
characteristic will require that \( \rho_c \) is dependent on the voltage. To study these nonlinear Ti-
based contacts to Si-doped Al-rich AlGaN and AlN, a generalized TLM method for nonlinear
contacts discussed by Piotrzkowski et al. was considered.\(^{162}\) For this method, \( \rho_c \) is more
precisely rewritten as:

\[
\rho_c = \frac{w_c R_c R_{c^*}}{\rho} \tag{1}
\]

where \( w_c \), \( R_c \), \( R_{c^*} \), and \( \rho \) are the contact width, common contact resistance (\( R_c = \frac{V}{I_c} \)),
differential contact resistance (\( R_{c^*} = \frac{dV}{dI_c} \)), and specific resistivity of the semiconductor,
respectively. \( I_c \) and \( V \) are meant to represent the total current flowing from the contact to the
semiconductor layer and the applied voltage, respectively. By substituting \( R_c \) for \( R_{c^*} \) in
Equation 1, the most commonly used and original expression for \( \rho_c \) associated with linear TLM
is arrived upon.\(^{163}\) As one can see, this makes no difference for linear IV curves. For that
reason, the original approach was used for the Si-doped GaN films that were discussed earlier
without loss in generality.
Figure 4-4: Specific contact resistivity as a function of current density (a) and the applied voltage (b) for Ti-based contacts on Si-doped Al-rich AlGaN and AlN.
Figure 4-4 gives $\rho_c$ as a function of current density, $j_c$, and the applied voltage for Ti-based contacts annealed at 850 °C on Si-doped AlGaN with a range of Al-contents from 60 to 100%. The data points represent averages of over more than 10 TLM structures on each film. The doping concentration and measured voltage range were fixed at $2 \times 10^{19}$ cm$^{-3}$ and -20 to 20 V, respectively. Only the voltage range from 0 to 20 V is given since the contacts tended to provide symmetric IV curves. Furthermore, the measurement system had a compliance level of 100 mA for this voltage range, providing an upper limit for the total current density. This is the reason for the data stopping at different voltages for each of the different Al-contents. Finally, at low enough voltages changes in $R_c^*$ were very abrupt due to the contact barriers, making it difficult to accurately calculate $\rho_c$; therefore this data was omitted for the higher Al-contents.

For all of the Al-contents, the contact resistance decreased with an increase in the applied voltage as is expected for back-to-back semi-rectifying contacts. The contact resistivity increased with an increase in Al-content. Additionally, the semiconductor resistivity increased with an increase in Al-content which will be discussed further later in this Chapter. For these reasons, all of the data does not span the same current density range. The plot showing the dependence on the applied voltage is of practical relevance since devices based on these films should be operated within a reasonable voltage range. After all, these contacts need to supply the necessary current through the active region of the device with a voltage drop across the contact that is small compared to the voltage drop across the active region.

A summary of $\rho_c$ for a constant applied voltage of 10 V is given in Figure 4-5, including the optimal value achieved for GaN. The specific contact resistivity increased exponentially
from $3.1 \times 10^{-5}$ to $67 \ \Omega \ cm^2$ for an increase in Al-content from 60 to 100%. These values at the high Al-contents are relatively high for Ohmic contacts; therefore, the contact resistance needs to be further reduced. In particular, for most deep UV optoelectronic devices, 70 to 90% Al-content layers are required for cladding and/or waveguide regions. These layers are contacted for current injection into the active region and need to provide a low contact resistance along with a low sheet resistance.

Figure 4-5: Specific contact resistivity at an applied voltage of 10 V as a function of composition for the entire compositional range from GaN to AlN.

4.2.1.3 Improving the Contact Resistance

To improve the contact resistance, surface pretreatment and the metal contact composition were both considered. For surface pretreatment, a standard solvent cleaning was
conducted immediately before loading the samples into the UHV system for metal deposition. After contact annealing, IV curves indicated no noticeable differences compared to the control surface, which did not see the surface pretreatment. Other pretreatments were considered including a hydrofluoric acid clean, a hydrochloric acid clean, a 1:1 hydrofluoric:hydrochloric acid mixture clean, and simple water rinsing. All four of these pretreatments also showed very little if any discernable changes in the contact resistance. It should be noted that AFM imaging was performed on surfaces that were exposed to such types of pretreatments and no signs of significant etching, through the presence of roughening, were observed. Bilayer steps were clearly visible before and after the pretreatments. At this point in the contact studies, only annealing the contacts significantly reduced the contact resistance as discussed earlier.

Due to their work functions and favorability to form a metal-nitride upon annealing, zirconium and vanadium-based contacts were studied. The metal stacks were identical to the Ti-based stacks except for the replacement of the first layer; V-based comprised of 30 nm V, 100 nm Al, 70 nm Ni, and 70 nm Au and Zr-based comprised of 30 nm Zr, 100 nm Al, 70 nm Ni, and 70 nm Au. Figure 4-6 shows $\rho_c$ as a function of current density for Al$_{0.65}$Ga$_{0.35}$N doped with $2 \times 10^{19}$ cm$^{-3}$ of Si. All of these contacts were annealed at 850 °C. The data points represent averages over more than 10 TLM structures. The contact resistance decreased by using the Zr-based and V-based contacts as compared to the Ti-based contacts. The V-based contacts gave the lowest $\rho_c$ of around $1 \times 10^{-6}$ Ω cm$^2$. France et al. achieved a similar $\rho_c$ for V-based contacts on n-type Al$_{0.70}$Ga$_{0.30}$N and attributed the low value to the formation of vanadium nitride upon annealing.$^{164}$ Song et al. demonstrated that after annealing V on GaN at temperatures greater than 650 °C that different phases of vanadium nitride were formed.$^{165}$
It is known that VN has a lower work function than V.\textsuperscript{166} XPS studies on the AlGaN films presented here confirmed the formation of vanadium nitride after contact annealing. Furthermore, it is thought that the formation of these metal-nitrides during annealing introduces nitrogen vacancies, which act as donors, near the metal-semiconductor interface further reducing the contact resistance.

![Graph showing specific contact resistivity as a function of metal contact for n-type Al\textsubscript{0.65}Ga\textsubscript{0.35}N.](image)

Figure 4-6: Specific contact resistivity as a function of metal contact for n-type Al\textsubscript{0.65}Ga\textsubscript{0.35}N.

4.2.1.4 Contact Performance Inconsistencies

LEDs fabricated with these contacts on n-type Al-rich AlGaN grown on the native AlN substrates indicated a variability in the on-resistance between devices located in different areas of the wafer. Therefore, the lateral uniformity of the contact performance across a wafer was tested. Figure 4-7 gives the specific contact resistivity calculated using TLM on n-type
$\text{Al}_{0.80}\text{Ga}_{0.20}\text{N}$ with a Si concentration of $2 \times 10^{19}$ cm$^{-3}$. The contacts were Ti-based and annealed at 850 °C. This wafer was nearly 24 mm in diameter and TLM structures were fabricated on a section cleaved from the wafer that spanned the entire length of the wafer. The contact properties were extracted from all of the TLM structures, which were not damaged during the fabrication process. Each data point represents an average of the $\rho_c$ values taken from an entire array of TLM structures like that shown in Figure 4-1. Figure 4-7 (b) gives $\rho_c$ values at the constant current density of 100 A/cm$^2$ denoted by the dashed line in Figure 4-7 (a). The contact resistance clearly deviated across the sample surface. These contacts were tested over a fixed voltage range which implies that the total series resistance increased from one end of the sample to the other. In particular, more current density existed for any given applied voltage at location -9 mm as compared to location 9 mm from the center.
Figure 4-7: Specific contact resistivity for Ti-based contacts on Si-doped Al$_{0.80}$Ga$_{0.20}$N as a function of the position on a wafer.
Both $\rho_c$ and the sheet resistance increased together. The sheet resistance calculated from TLM as a function of position on the wafer is given in Figure 4-8, with 0 representing the center of the wafer. This increase in sheet resistance was directly correlated to the misorientation angle of the thin film. AFM imaging revealed that the surface had bilayer steps only and that the misorientation angle decreased from the location at -6 mm to the location at 6 mm. Section 2.5.4 explains that the Al-content increases with a decrease in the misorientation angle, which supports these electrical results. An increase in the Al-content causes an increase in the semiconductor resistivity. With fewer free carriers available near the contact barrier, the contact resistance increases. Large area Ti-based contacts (> 2x2 mm$^2$) annealed at 850 °C were fabricated in a Van der Pauw geometry on this film to measure the sheet resistance before the sample was cleaved. The sheet resistance value using this method is given in Figure 4-8 and indicates a close agreement with the TLM method. This macro-scale approach does not resolve the differences in resistance across the film. These results provide a potential reason for the variability in LED performance across a wafer and further indicate the importance of having flat and appropriately misoriented AlN substrates, a topic which was already discussed throughout Chapter 2. Nevertheless, these large area contacts are good enough to properly study the electrical properties of the n-type AlGaN films and reliably obtain the free carrier concentration and mobility, which will be provided throughout the rest of this Chapter.
4.2.2 Point Defects and Compensation

The conductivity of Si-doped Al-rich AlGaN has been under investigation for decades, yet reports still give widely varying values for films which should exhibit very similar properties such as doping concentration and crystalline quality.\cite{2,152,153} Therefore, structural defects, i.e. dislocations and stacking faults, must not be the only defects which significantly affect the conductivity in these materials. The following studies will provide evidence for both extended and point defect contributions to the electrical properties of Si-doped Al-rich AlGaN by studying films grown on both native AlN and foreign sapphire substrates.

Figure 4-8: Sheet resistance for Si-doped Al$_{0.80}$Ga$_{0.20}$N as a function of the position on a wafer.
4.2.2.1 Conductivity Dependence on Al-content

The resistivity of Si-doped AlGaN increases with an increase in the Al-content as mentioned in the previous sections. Figure 4-9 shows the room temperature resistivity, free carrier concentration and mobility for AlGaN films deposited on native AlN substrates using a SiH$_4$ flow of 200 µmol/min, which is expected to be equivalent to a doping concentration of about 8 x 10$^{18}$ cm$^{-3}$ by using Vegard’s law and calibrated SIMS measurements on Si-doped GaN and AlN. Both the free carrier concentration and mobility decrease with an increase in the Al-content. In particular, the free carrier concentration decreased from around 7.8 x 10$^{18}$ cm$^{-3}$ for Al$_{0.65}$Ga$_{0.35}$N to 1.0 x 10$^{15}$ cm$^{-3}$ for AlN using the same doping concentration indicating that the change in resistivity is primarily determined by the change in free carrier concentration. This decrease can be from either an increase in the activation energy of the Si donor, an increase in compensation effects, or both. The mobility decreased from 58 to 18 cm$^2$/Vs for the same composition range and is expected to be due to the lowering of the free carrier concentration. A reduction in the free carrier concentration will increase the Debye length; therefore, reducing point defect field screening.
Figure 4-9: Room temperature resistivity, n-type carrier concentration, and carrier mobility for Al-rich AlGaN deposited on native AlN substrates with a constant doping concentration of around $8 \times 10^{18}$ cm$^{-3}$. 
4.2.2.2 Si Donor Activation Energy

To better understand the decrease in free carrier concentration as a function of Al-content, temperature dependent measurements were conducted to initially study the Si donor activation energy. Later, the compensation effects will be discussed using the same measurements. Equation 6 from Chapter 1 describes the free carrier concentration as a function of temperature and can be rewritten by solving for $n$ as follows:

$$n = \frac{1}{2} \left[ -\left( N_A + \frac{1}{g} N_C e^{\frac{-E_a}{k_B T}} \right) + \sqrt{\left( N_A + \frac{1}{g} N_C e^{\frac{-E_a}{k_B T}} \right)^2 + 4 \frac{1}{g} N_C (N_D - N_A) e^{\frac{-E_a}{k_B T}}} \right]$$  \hspace{1cm} (2)

By fitting this expression to the temperature dependence of the free carrier concentration, $E_a$ can be extracted. Figure 4-10 shows the temperature dependence of $n$ for a Si-doped AlN homoepitaxial film. Upon fitting the data, $E_a$ was determined to be $244 \pm 6$ meV, which is nearly 10 times the amount of thermal energy available at room temperature.
A similar analysis was conducted on the entire composition range from GaN to AlN. The activation energy for the Si donor is given in Figure 4-11 for a nominal Si concentration of around $8 \times 10^{18}$ cm$^{-3}$. Also included in the figure are the activation energies given by Collazo et al. as a comparison since these films were grown using the same MOCVD system and similar growth conditions.\textsuperscript{2} The activation energy increased significantly around 80\% Al-content. Below 80\%, the activation energy was less than 25 meV and essentially remained constant, meaning that nearly all of the donors are thermally activated at room temperature. Collazo et al. attributed these low activation energies to electron screening of the impurity potential due to the high free carrier concentrations which eventually leads to a Mott transition.\textsuperscript{2} Above 80\%
Al-content only a fraction of the donors are activated at room temperature, which helps explain the results shown in Figure 4-9.

![Graph showing Donor activation energy of Si for the entire composition range from GaN to AlN. Values reported by Collazo et al. are also given.](image)

Figure 4-11: Donor activation energy of Si for the entire composition range from GaN to AlN. Values reported by Collazo et al. are also given.²

The activation energies determined in the present work are similar to those presented by Collazo et al.² The small deviations around 80 to 90% Al-content could be due to the conditions that were assumed for this particular composition range. If \( n \ll N_A \) and \( n \ll N_D - N_A \) then Equation 6 from Chapter 1 can be rearranged into a linear approximation of the following form.

\[
\ln \left( 2ngT^{-\frac{3}{2}} \right) \approx \ln \left( \frac{N_D - N_A}{N_A} \frac{2N_C}{T^2} \right) - \frac{E_a}{k_B T}
\]  

(3)
Assuming that these above mentioned conditions are met, $E_a$ in Al$_{0.85}$Ga$_{0.15}$N would be $9 \pm 1$ meV as compared to $54 \pm 2$ meV determined by using Equation 2. Furthermore, the compensation ratio, $N_A/N_D$, would be $0.64 \pm 0.05$ for the approximation compared to $0.11 \pm 0.01$ without the approximation. In this composition range, the assumptions are not valid since $n$ is on the same order as $N_A$ and $N_D-N_A$.

Figure 4-12: Temperature dependence of the free carrier concentration for Si-doped Al$_{0.85}$Ga$_{0.15}$N grown on a native AlN substrate.

Figure 4-12 shows the temperature dependence of the free carrier concentration for Al$_{0.85}$Ga$_{0.15}$N. The red trace is the fit determined by using Equation 2. The blue trace represents the approximation method using Equation 3 with the parameters determined by Equation 2. These results potentially explain the differences seen between the present work and what has been reported previously.
4.2.2.3 Self-compensation in Al$_{0.65}$Ga$_{0.35}$N

Compensation effects could also contribute to the sharp decrease in free carrier concentration seen in Figure 4-9. Multiple doping levels on films grown on both native AlN and foreign sapphire substrates were realized to differentiate potential compensation arising from the presence of dislocations from those related to the intrinsic formation of point defects; either native defects or unintentional impurities in Al-rich AlGaN. Figure 4-13 shows the n-type free carrier concentration and carrier mobility at room temperature for Al$_{0.65}$Ga$_{0.35}$N films deposited on AlN substrates and sapphire substrates as a function of SiH$_4$ flow. It was observed that up to a critical Si concentration, the free carrier concentration was nearly proportional to the SiH$_4$ flow. Any further increase in SiH$_4$ flow beyond the critical Si concentration led to a reduction of the carrier concentration. This trend provides a strong indication of self-compensation for donor incorporation larger than a critical concentration. It is clear from Figure 4-13 that the degree of self-compensation is significant at the high Si doping levels. A maximum free carrier concentration of $1.4 \times 10^{19}$ and $2.2 \times 10^{18}$ cm$^{-3}$ could be achieved on the AlN and sapphire substrates, respectively. This indicates that more than $10^{19}$ cm$^{-3}$ compensating defects could have been incorporated at the higher doping levels. In fact, samples that were grown with 1800 μmol/min SiH$_4$ flow were insulating.
Figure 4-13: N-type carrier concentration (a) and carrier mobility (b) at room temperature for Al\textsubscript{0.65}Ga\textsubscript{0.35}N films deposited on AlN substrates and sapphire substrates as a function of SiH\textsubscript{4} flow.
There was at least an order of magnitude difference in the carrier concentrations obtained for Al$_{0.65}$Ga$_{0.35}$N films grown on AlN and those on sapphire at all doping levels. This suggests that the films on sapphire incorporate more compensating defects, which could be due to the locally induced strain fields around the dislocations that can alter the formation energy of such point defects.\textsuperscript{167} The overall mobility was much greater for the films grown on AlN as well, which can be explained by the differences in dislocation density and point defect concentrations. The large dislocation density of the films on sapphire and the increased incorporation of compensating point defects result in additional scattering events not present in the films on AlN. Therefore, it is necessary to grow AlGaN thin films with low dislocation densities to reduce these mentioned effects.

The incorporation of native compensating defects was correlated with a change in the room temperature PL spectra. The PL spectra of the Al$_{0.65}$Ga$_{0.35}$N films deposited on AlN substrates and sapphire substrates as a function of SiH$_4$ flow are shown in Figure 4-14. The same broad defect related peaks could be seen around 2.4 and 3.0 eV for both the films grown on AlN and on sapphire substrates. Fringes were present in the spectra of films grown on sapphire due to interference caused by the contrast in indices of refraction at the interface between the sapphire and AlN. The overall intensity of the defect luminescence for the films on sapphire was more than 8 times larger than that for the films on AlN substrates. This increase cannot be accounted for by reflection at the sapphire interface and indicates that potentially more compensating defects are incorporated in these films on sapphire, which correlates well with the previous observations from electrical measurements. For both substrates, as the Si doping level increases, the 2.4 eV emission becomes the most prominent
emission indicating that more defects related to this emission have been incorporated with the addition of Si. This transition is a direct consequence of the onset of over compensation of the Si donor by the introduction of a new compensator.
Figure 4-14: Room temperature photoluminescence spectra of Al$_{0.65}$Ga$_{0.35}$N films deposited on AlN substrates (top) and sapphire substrates (bottom) with varying SiH$_4$ flows. With an increase of SiH$_4$ flow, an emission at 2.4 eV becomes dominant over an emission at 3.0 eV.
4.2.2.4 Point Defect Identification in Al$_{0.65}$Ga$_{0.35}$N

Formation energies of defects were calculated using density functional theory in the plane wave expansion as implemented in VASP 5.3. The hybrid exchange-correlation functional of Heyd, Scuseria, and Ernzerhof (HSE) was used to better capture the band gap of AlGaN. These hybrid functionals include a fraction of short-range exact Hartree-Fock exchange and have been used to predict the defect formation energies and concentrations of point defects and complexes in InN, GaN, and AlN. Formation energies were calculated using the standard approach. To approximate a random solid solution, five separate 96-atom Al$_{0.65}$Ga$_{0.35}$N supercells were used, in which 31 Al and 17 Ga atoms were pseudorandomly distributed on the cation sublattice, each with a 2 x 2 x 2 mesh of k-points and a kinetic energy cutoff of 500 eV. Multiple configurations were run for each defect and the formation energies were averaged over all configurations. Because of the high Al-content of the alloys studied here, the fraction of exact exchange was chosen to be the same as the fraction chosen for AlN, 0.32, which was selected to best fit the band gap of AlN. Further details on the procedure used for generating the pseudorandom AlGaN alloys will be published elsewhere.

It is well known that cation vacancies readily incorporate in AlGaN with the presence of Si through studies by monoenergetic positron beams. Therefore, it is expected that these lower midgap PL signatures are related to cation vacancies that are either isolated or bound in a complex. Isolated defects and defect complexes related to carbon, silicon, oxygen, and vacancies were investigated. In the III-nitrides, each atom has four nearest neighbors with one along the c-axis, c-type bond, and three that are 108° off the c-axis, a-type bonds. This non-
centrosymmetric crystal structure character in the III-nitrides results in different bond lengths along the c-axis as compared to the a-axis. Therefore, for these DFT calculations, configurations of complexes that involve both bond directions were considered. After considering the formation energies of these defects and their binding energies, it was determined that the most probable defects to form in the Si-doped Al\textsubscript{0.65}Ga\textsubscript{0.35}N films are isolated C\textsubscript{N} and cation vacancies in a complex with oxygen. In particular, for n-type Al\textsubscript{0.65}Ga\textsubscript{0.35}N isolated cation vacancies, anion vacancies and anion vacancy complexes are not energetically favorable to form. Table 4-1 gives an overview of the predicted thermodynamic and optical signatures from the hybrid DFT calculations for Al\textsubscript{0.65}Ga\textsubscript{0.35}N including the transition charge state of interest, zero phonon line (ZPL), absorption, emission, and Stokes shift. The isolated vacancies are given here for later discussion in Sections 4.3 and 4.4. All of the predicted absorption energies are higher than the emission energies due to the Frank-Condon shift. These emissions are minimum predicted values for the case where complete relaxation of the lattice has occurred. The actual emission could be slightly higher as seen for the transition involving C\textsubscript{N} in AlN by Collazo et al.\textsuperscript{26} Differences in the absorption and emission energies predicted by DFT for other point defects in the nitrides have been confirmed experimentally in previous studies, further supporting these predictions.\textsuperscript{26, 169, 170}
Table 4-1: Thermodynamic and optical transitions of defects in Al$_{0.65}$Ga$_{0.35}$N.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Transition</th>
<th>ZPL (eV)</th>
<th>Absorption (eV)</th>
<th>Emission (eV)</th>
<th>Stokes (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{N}^{-1}$</td>
<td>-1</td>
<td>0</td>
<td>3.5</td>
<td>3.9</td>
<td>2.9</td>
</tr>
<tr>
<td>V$_{III}^{-3}$</td>
<td>-3</td>
<td>-2</td>
<td>2.0</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>V$_{N}^{+}$</td>
<td>1</td>
<td>2</td>
<td>3.7</td>
<td>5.1</td>
<td>3.6</td>
</tr>
<tr>
<td>(V$<em>{III}$+1O$</em>{N}$-a)$_{-2}$</td>
<td>-2</td>
<td>-1</td>
<td>2.5</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>(V$<em>{III}$+1O$</em>{N}$-c)$_{-2}$</td>
<td>-2</td>
<td>-1</td>
<td>2.6</td>
<td>3.1</td>
<td>2.0</td>
</tr>
<tr>
<td>(V$<em>{III}$+2O$</em>{N}$-a)$_{-1}$</td>
<td>-1</td>
<td>0</td>
<td>2.9</td>
<td>3.4</td>
<td>2.3</td>
</tr>
<tr>
<td>(V$<em>{III}$+2O$</em>{N}$-c)$_{-1}$</td>
<td>-1</td>
<td>0</td>
<td>2.8</td>
<td>3.3</td>
<td>2.2</td>
</tr>
<tr>
<td>(V$<em>{III}$+3O$</em>{N}$-a)$_{0}$</td>
<td>0</td>
<td>1</td>
<td>3.7</td>
<td>4.3</td>
<td>3.0</td>
</tr>
<tr>
<td>(V$<em>{III}$+3O$</em>{N}$-c)$_{0}$</td>
<td>0</td>
<td>1</td>
<td>3.4</td>
<td>4.1</td>
<td>2.8</td>
</tr>
</tbody>
</table>

It was found that transitions from the conduction band to C$_{N}$, V$_{III}$+3O$_{N}$, and V$_{III}$+2O$_{N}$ acceptor states are predicted to provide minimum emissions around 2.9 eV, 3.0 eV, and 2.3 eV, respectively, as shown in Table 4-1. Figure 4-15 shows Gaussian peak fitting for the PL spectra of two Si-doped Al$_{0.65}$Ga$_{0.35}$N films which represent films with a Si concentration below and above the critical Si concentration where the onset of over compensation was observed electrically. It tended to get more difficult to separate the higher energy peak into two peaks as the lower energy peak became dominant. It is clear from the fits and DFT calculations
that the C\textsubscript{N}, V\textsubscript{III}+3O\textsubscript{N}, and V\textsubscript{III}+2O\textsubscript{N} are likely responsible for the emissions that are observed in these Si-doped films.
Figure 4-15: Room temperature photoluminescence spectra with peak fitting for Si-doped Al$_{0.65}$Ga$_{0.35}$N films which electrically fall below (top) and above (bottom) the onset of over compensation.
Figure 4-16 provides the formation energy as a function of Fermi level for these defects in Al$_{0.65}$Ga$_{0.35}$N. As this is a ternary system, the constraints on the chemical potentials are defined by the equation for bulk stability, $0.65\Delta\mu_{Al} + 0.35\Delta\mu_{Ga} + \Delta\mu_{N} = \Delta H_{f}^{\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}}$. $\Delta\mu_X$ is the difference between the chemical potential of component X (Al, Ga, or N) in the alloy and its reference value, the chemical potential of the pure substance (Al or Ga metal, or N$_2$ gas) at 0 K. $\Delta H_{f}^{\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}}$ is the enthalpy of formation of the alloy and is determined here to be -2.66 eV for Al$_{0.65}$Ga$_{0.35}$N. Unlike pure AlN or GaN where chemical potentials are constrained along a line between cation rich to nitrogen rich conditions, the alloy stability criteria can be met by a range of points on a plane in chemical space. This plane is also plotted in Figure 4-16. The thermodynamic transition levels for defects containing Al or Ga vacancies were found to be insensitive to the type of cation. For plotting convenience, the formation energies in Figure 4-16 are plotted in Ga-rich conditions at a point in chemical space where the formation energies for Ga and Al vacancies are equal. This point is indicated in Figure 4-16 as an open circle on the Ga-rich boundary ($\Delta\mu_{Ga} = 0$) and corresponds to when $\Delta\mu_{Al}$ equals -2.05 eV. The equality of the formation energies of V$_{Al}$ and V$_{Ga}$ holds across the dashed line in the figure. For any other point off the dashed line in the chemical plane, the formation energies for V$_{Al}$ and V$_{Ga}$ would no longer be equivalent. This plot indicates that as the Si content is increased in these films, i.e. the Fermi level moves nearer to the conduction band, the formation energy of the V$_{III}$$+2$O$_N$ complex decreases while the formation energy of the V$_{III}$$+3$O$_N$ stays the same. Therefore, the V$_{III}$$+2$O$_N$ concentration is expected to increase with higher Si content, while the V$_{III}$$+3$O$_N$ concentration is not expected to change. All of these
theoretical predictions for Al$_{0.65}$Ga$_{0.35}$N agree with the experimental results already shown since an increase in the concentration of $V_{\text{III}+2\text{O}_N}$ complexes, which act as acceptors, would cause an increase in compensation.
Figure 4-16: (top) Formation energy as a function of Fermi level for $C_N$, $O_N$, and cation vacancies ($V_{III}$) as well as first nearest neighbor complexes between cation vacancies and oxygen atoms. (bottom) The plane defining the constraints on the elemental chemical potentials in $Al_{0.65}Ga_{0.35}N$. The open circle point on the plane in Ga-rich conditions indicates where in chemical space the formation energies are plotted.
4.2.2.5 Self-compensation in Al$_{0.85}$Ga$_{0.15}$N

This onset of self-compensation was observed for Al-rich compositions with Al mole fractions between 0.55 and 1. Room temperature electrical and optical measurements for Si-doped Al$_{0.85}$Ga$_{0.15}$N films deposited on AlN substrates are shown in Figure 4-17. Al$_{0.85}$Ga$_{0.15}$N films were also deposited on sapphire substrates, however, these films were all highly resistive, i.e. heavily compensated, which further supports that films grown on sapphire substrates tended to incorporate much higher amounts of the compensating defects as compared to films grown on AlN substrates. It should be noted that the Si incorporation is expected to be about the same between the films represented in Figure 4-13 and those in Figure 4-17, since Si is mass transport limited under the growth conditions used. Therefore, any significant changes observed in the free carrier concentrations are due to either an increase in donor activation energy or an increase in the density of compensating point defects. From Figure 4-17, it is clear that there is an onset of over compensation, which shows up by the decrease in free carriers and with the increase in intensity of the emission at around 2.9 eV as the SiH$_4$ flow is increased.
Figure 4-17: Room temperature carrier concentration and mobility (a) and room temperature photoluminescence spectra (b) as a function of SiH$_4$ flow for Al$_{0.85}$Ga$_{0.15}$N films deposited on AlN substrates.
The significant decrease in overall carrier concentration for the $\text{Al}_{0.85}\text{Ga}_{0.15}\text{N}$ films as compared to the $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ films was further investigated by temperature dependent Hall effect measurements to separate the effect of donor activation energy from compensating point defects. $N_A/N_D$ and $E_a$ were quantified for the $\text{Al}_{0.85}\text{Ga}_{0.15}\text{N}$ films utilizing Equation 2. $E_a$ was determined to remain unchanged over the doping range investigated at a value of $53 \pm 2$ meV. Consequently, at 85% Al-content, around 12% of the donor atoms are activated at room temperature due to this large activation energy. The compensation ratio steadily increased, from $0.11 \pm 0.01$ to $0.66 \pm 0.02$, with an increase in the Si concentration indicating that at the highest doping level more than half of the donor atoms were compensated. Both of these results demonstrate why it is so challenging to achieve high conductivity Al-rich AlGaN.

Furthermore, the increase in intensity of the emission at 2.9 eV over the emission at 3.5 eV correlates with this increase in $N_A/N_D$. These peaks are expected to be caused by the same defects discussed for $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ since the difference in defect energies between the two compositions match the change in bandgap.

4.2.2.6 Point Defect Identification in AlN

Midgap luminescence was also present in Si-doped homoepitaxial AlN films as indicated in Figure 4-18. The intensity of the luminescence increased with an increase in the Si doping concentration. This emission was comprised of at least three different peaks. Three Gaussian curves were fit to the broad luminescence profile with resulting peak positions at 3.2, 3.6, and 3.8 eV. With an increase in Si doping concentration, the intensities of the lower energy
peaks increased significantly compared to the higher energy peak intensity, similar to the cases described earlier for Al-rich AlGaN films.
Figure 4-18: Room temperature photoluminescence spectra with peak fitting for Si-doped homoepitaxial AlN films which electrically fall below (top) and above (bottom) the onset of over compensation.
This broad defect related luminescence was not only found in Si-doped films, but also seen in films with significant amounts of oxygen as discussed in Section 3.3.3. Figure 4-19 shows room temperature PL spectra for undoped, O-doped, and Si-doped AlN films. The luminescence for the O- and Si-doped films look nearly identical. The O-doped film was unintentionally doped with O and had O and Si concentrations of $3 \times 10^{19}$ and $1 \times 10^{18}$ cm$^{-3}$, respectively. The intentionally Si-doped film had O and Si concentrations of $4 \times 10^{17}$ and $1 \times 10^{19}$ cm$^{-3}$, respectively. All three films had a constant C concentration of around $1$ to $3 \times 10^{17}$ cm$^{-3}$. Si-doped films with similar Si concentrations found in the O-doped film exhibited luminescence at a higher energy (3.6-3.8 eV) as indicated in Figure 4-18, therefore the presence of the high concentration of O in this film must be the reason for the lower energy emission. Similarly, the lower energy peak did not appear as the dominant emission peak until Si-doped films were doped with high concentrations of Si. All of these results can be explained through the Fermi level effect. At growth temperature, having high concentrations of either O, Si, or both push the Fermi level closer to the conduction band making it more energetically favorable to form the point defects causing this midgap luminescence.
Figure 4-19: Room temperature photoluminescence spectra of undoped, O-doped, and Si-doped homoepitaxial AlN films.
Si-doped HVPE grown AlN on these native AlN substrates were studied as well. HVPE films with similar Si concentrations as the MOCVD grown films shown here contained the same emissions but with higher intensities. The near band edge emissions were much broader as well, indicating a higher incorporation of the point defects responsible for these midgap emissions. It is hard to directly compare the HVPE and MOCVD grown films due to the differences in growth conditions. The formation energies of point defects directly depends on both the Fermi level position and the chemical potentials of the Al and N species. It is expected that MOCVD growth lies closer to Al-rich conditions, i.e. when $\mu_{\text{Al}}$ is high, however it is unknown where HVPE growth conditions fit in the spectrum from N-rich to Al-rich conditions. Also, the HVPE grown films tended to have higher O concentrations between 2 and $5 \times 10^{18}$ cm$^{-3}$. Nevertheless, it is now known that HVPE grown films incorporate many more of the compensating point defects causing this midgap luminescence around 3.2 to 3.8 eV due to these PL studies. This was further supported by capacitance-voltage (CV) measurements performed on nickel Schottky contacts to a Si-doped HVPE grown AlN film with Si, O, and C concentrations of $2.8 \times 10^{18}$, $2.5 \times 10^{18}$, and $1 \times 10^{17}$ cm$^{-3}$, respectively, determined by SIMS. CV analysis indicated strong compensation with a compensation ratio, $N_A/N_D$, of approximately 0.96.

Hybrid DFT was used to study point defects which could be present in Si-doped AlN. Isolated defects and defect complexes were considered as was done in the case of Al$_{0.65}$Ga$_{0.35}$N discussed earlier. Details on the approach used for the hybrid DFT calculations conducted here can be found in previous publications.$^{26, 169, 170}$ The predicted thermodynamic and optical transitions for isolated vacancies ($V_{\text{Al}}$ and $V_N$) and complexes ($V_{\text{Al}}+n\text{O}_N$; $n=1-4$) are given in
Table 4-2. Similar to the results for Al$_{0.65}$Ga$_{0.35}$N, the absorption and emission do not match due to the relatively large Stokes shifts. The emissions reported here are predicted minimum emissions. The actual emission may be higher if the system does not fully relax before the excited electron releases energy in the form of a photon. The a- and c-type configurations give similar yet different predicted optical signatures and helps to explain the broadness of the midgap luminescence. Most importantly, the predicted emissions of the vacancy-oxygen complexes seem to match with the luminescence seen in Si-doped AlN.

Table 4-2: Thermodynamic and optical transitions of defects in AlN.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Transition</th>
<th>ZPL (eV)</th>
<th>Absorption (eV)</th>
<th>Emission (eV)</th>
<th>Stokes (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_{Al}^{-3}$</td>
<td>-3</td>
<td>-2</td>
<td>3.0</td>
<td>3.3</td>
<td>2.3</td>
</tr>
<tr>
<td>V$_{N}^{+}$</td>
<td>1</td>
<td>2</td>
<td>4.9</td>
<td>5.9</td>
<td>4.1</td>
</tr>
<tr>
<td>(V$<em>{Al}$+1O$</em>{N}^{-a}$)$^{-2}$</td>
<td>-2</td>
<td>-1</td>
<td>3.6</td>
<td>4.0</td>
<td>2.9</td>
</tr>
<tr>
<td>(V$<em>{Al}$+1O$</em>{N}^{-c}$)$^{-2}$</td>
<td>-2</td>
<td>-1</td>
<td>3.5</td>
<td>3.8</td>
<td>3.0</td>
</tr>
<tr>
<td>(V$<em>{Al}$+2O$</em>{N}^{-a}$)$^{-1}$</td>
<td>-1</td>
<td>0</td>
<td>3.9</td>
<td>4.4</td>
<td>3.2</td>
</tr>
<tr>
<td>(V$<em>{Al}$+2O$</em>{N}^{-c}$)$^{-1}$</td>
<td>-1</td>
<td>0</td>
<td>3.9</td>
<td>4.4</td>
<td>3.2</td>
</tr>
<tr>
<td>(V$<em>{Al}$+3O$</em>{N}^{-a}$)$^{0}$</td>
<td>0</td>
<td>1</td>
<td>4.4</td>
<td>5.1</td>
<td>3.8</td>
</tr>
<tr>
<td>(V$<em>{Al}$+3O$</em>{N}^{-c}$)$^{0}$</td>
<td>0</td>
<td>1</td>
<td>4.3</td>
<td>5.0</td>
<td>3.6</td>
</tr>
<tr>
<td>(V$<em>{Al}$+4O$</em>{N}^{-c}$)$^{1}$</td>
<td>none</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The binding energy of the $V_{Al}+1O_N$ complex with respect to dissociation into $V_{Al}$ and $O_N$ is predicted by these hybrid DFT calculations to be greater than 1 eV. Therefore, if oxygen is present in AlN, there exists a strong driving force for the complex to form. When the Fermi level is near the conduction band, as is the case for Si-doped AlN, the $V_{Al}+1O_N$ and $V_{Al}+2O_N$ behave as acceptors. With an increase in the Si concentration, the concentration of these complexes should increase explaining the increase in the lower energy peak intensities of the midgap luminescence. For these reasons, the 3.2, 3.6, and 3.8 eV emission are assigned to transitions involving the $V_{Al}+1O_N$, $V_{Al}+2O_N$, and $V_{Al}+3O_N$, respectively.

To further support these assignments, a multilayered homoepitaxial AlN film was grown with each layer consisting of different Si concentrations. The SIMS depth profile is given in Figure 4-20. The solid black lines indicate where the SiH$_4$ flow was increased or decreased. The C concentration remained relatively constant throughout the film at around $1 \times 10^{17}$ cm$^{-3}$. The Si concentration matched the intended doping concentrations. The O concentration tended to increase with the Si concentration even though the only intentional change in growth conditions between the layers was the SiH$_4$ flow. It was verified that this change in O concentration was not related to the SiH$_4$ source. Instead, this shows that O is more readily incorporated when the formation of the vacancy-oxygen complexes is favorable at the higher Si doping concentrations. There is no other reason for O to incorporate in the film since it is a donor like Si, unless it incorporates in some type of complex which behaves as an acceptor. Even though the vacancies cannot be detected by SIMS, Uedono et al. have detected vacancy-oxygen complexes in AlN films studied by positron annihilation.\textsuperscript{155}
Figure 4-20: Calibrated SIMS depth profile for O, Si, and C in a homoepitaxial AlN film with layers intentionally doped with different Si concentrations.

PL of PVT grown AlN substrates, with high C concentrations (> $1 \times 10^{19}$ cm$^{-3}$) exhibit dominant emissions around 3.9 and 2.8 eV. These emissions have been directly correlated to the isolated C$_N$ and a donor-acceptor pair (DAP) recombination between the C$_N$ and V$_N$, respectively. Additionaly, the well-known UV absorption band around 4.7 eV was shown to be caused by the C$_N$ point defects making the AlN substrates nontransparent in the optical range of interest for many optoelectronic applications. Gaddy et al. determined that if PVT grown AlN was intentionally co-doped with Si then the absorption at 4.7 eV along with the subsequent emissions around 3.9 and 2.8 eV could be suppressed. By co-doping, the AlN substrates became UV semi-transparent (absorption coefficient < 100 cm$^{-1}$ at 4.7 eV). Si formed a complex with C, i.e. C$_N$+Si$_{Al}$ complex, which resulted in a new absorption and
emission around 5.5 and 4.3 eV, respectively. The emissions around 3.2 to 3.8 eV also appeared in the semi-transparent AlN because of the large concentrations of Si. Photoluminescence excitation (PLE) measurements were realized on a semi-transparent PVT grown AlN substrate and are given in Figure 4-21. PLE indicated an excitation channel of 5.0 eV for a broad emission around 3.5 eV, which is in close agreement with the DFT predictions for the vacancy-oxygen complexes.

![Figure 4-21](image)

Figure 4-21: Room temperature PLE measurements on a semi-transparent PVT AlN substrate.

4.2.2.7 Point Defects and Compensation Overview in Si doped Material

All of the results presented for Al-rich AlGaN and AlN provide evidence that point defects involving carbon, silicon, oxygen, and vacancies play a crucial role in determining the optical and electrical properties of these wide bandgap semiconductors. As mentioned
previously, self-compensation was observed at high Si doping concentrations for all of the Al-rich compositions studied. Figure 4-22 (a) shows the room temperature free carrier concentration as a function of SiH₄ flow for Al-contents from 65 to 100%. To make a fair comparison between the compositions, the growth rate differences were accounted for by adjusting the SiH₄ flow. Therefore, the Si incorporation is the same here for all compositions shown for each given SiH₄ flow. Figure 4-22 (a) indicates the onset of self-compensation by the reduction in carrier concentration at high doping levels. Additionally, with an increase in Al-content, the onset of over compensation seems to be present at lower Si concentrations. DFT calculations indicate that this is due to a reduction in the formation energy of the compensating defects as the Al-content is increased.
Figure 4-22: Room temperature carrier concentration as a function of SiH\textsubscript{4} flow for Al-rich AlGaN and AlN (a). Maximum measured carrier concentration as a function of Al-content, along with the calculated carrier concentration assuming an absence of compensation (b).
The maximum achieved free carrier concentration at room temperature is plotted in Figure 4-22 (b) as a function of Al-content. Also included is the theoretical free carrier concentration assuming no compensation effects and the donor activation energy given in Figure 4-11. This result clearly indicates the degree of compensation providing evidence that further work is needed to improve the conductivity in Al-rich AlGaN. The increase in compensation at high Si doping levels, along with the exponential increase in donor activation energy with Al-content greatly hinders the overall conductivity for n-type Al-rich AlGaN.

Figure 4-23 gives a summary of all the deep defect-related energy positions of Si-doped GaN, AlGaN, and AlN investigated in this study. For Al\(_{0.65}\)Ga\(_{0.35}\)N, the low energy peak at 2.4 eV is assigned to V\(_{\text{III}+2}\)O\(_N\) and the high energy peak around 2.8-3.0 eV to V\(_{\text{III}+3}\)O\(_N\) or C\(_N\). It is difficult to definitively distinguish the two possible defects for the higher energy peak due to the broadness of the observed peak. The energy levels associated with these defects were also observed to increase with Al-content, where the energy increase was similar to the increase in bandgap. This strongly suggests that the compensation in Al-rich AlGaN was caused by the same native defects. In AlN, the peaks around 3.2, 3.6, and 3.8 eV are now assigned to V\(_{\text{III}+1}\)O\(_N\), V\(_{\text{III}+2}\)O\(_N\), and V\(_{\text{III}+3}\)O\(_N\), respectively. C\(_N\) is known to be responsible for the emission at around 3.9 eV in AlN, which also fits well with the current assignments given in Figure 4-23.\(^{26}\) Furthermore, in GaN the yellow luminescence around 2 eV is widely debated and expected to be related to C\(_N\) and/or Ga vacancies in a complex form with oxygen, which is consistent with these assignments.\(^{168,175}\)
Figure 4-23: Energy values of deep defect-related peaks seen in room temperature PL spectra for Si-doped AlGaN films spanning the entire composition range from GaN to AlN.

Even though these newly identified defects are expected to exist in Si-doped films, it is understood that they may not be the only defects present since over compensation requires that more than $10^{19}$ cm$^{-3}$ acceptors are incorporated during growth. Chichibu et al. suggested that $V_{\text{III}}$+$Si_{\text{III}}$ complexes could be a major culprit for the compensation in Al$_{0.6}$Ga$_{0.4}$N films grown by MOCVD. With further DFT calculations, currently being performed, it may be possible to provide support for or against this suggestion. At this time, it has been proven through the discussion given in this section that compensation from carbon and vacancy-oxygen complexes occurs in Si-doped Al-rich AlGaN and AlN.
4.2.2.8 Point Defect Reduction

Bryan et al. demonstrated a technique for reducing the concentration of these compensating point defects in Al-rich AlGaN through controlling the Fermi level during growth.\textsuperscript{176-178} By illuminating the film with above bandgap light during growth, a non-equilibrium steady state population of minority carriers were generated. This increase in minority carriers shifted the quasi-Fermi levels and increased the formation energy of the compensating defects; therefore the incorporation of the compensating defects was reduced. This reduction in compensation was evident through both a reduction in the electrical resistivity and midgap defect luminescence for films grown with UV illumination. In particular, the free carrier mobility increased by up to 3 times and the free carrier concentration increased by up to one order of magnitude.

The following study presents another method for reducing the incorporation of compensating point defects in Al-rich AlGaN. Mita et al. showed that in Si-doped GaN, the C concentration was inversely proportional to the Ga vapor supersaturation, $\sigma_{Ga}$.\textsuperscript{78} It was demonstrated through modifying growth process conditions such as the V/III ratio and the diluent gas that a larger $\sigma_{Ga}$ resulted in a smaller concentration of C and a subsequent reduction in electrical resistivity of the GaN films. Using this concept, a series of Al$_{0.70}$Ga$_{0.30}$N films were grown on sapphire with the same Si doping concentration but different V/III ratios. The V/III ratio was adjusted by only changing the NH$_3$ flow. A SiH$_4$ flow was chosen such that the film fell on the left side of the compensation curve since in this range the dominant compensator is expected to be carbon. Figure 4-24 (a) gives the room temperature free carrier concentration and mobility as a function of V/III ratio. By increasing the V/III ratio from 550
to 1800, the free carrier concentration increased over one order of magnitude and the mobility increased from 10 to 46 cm$^2$/Vs. The mobility at the highest V/III ratio was comparable to values found in Al$_{0.70}$Ga$_{0.30}$N films grown on native AlN substrates with similar Si doping concentrations; consequently, indicating the significant role of charged compensating point defects on the mobility in these Al-rich AlGaN films. Even though the dislocation density was over 6 orders of magnitude greater in the films grown on sapphire, the large amounts of point defects dominate the electrical properties of both the Si-doped AlGaN films grown on native AlN and sapphire substrates. This reduction in resistivity was correlated with a reduction in defect luminescence shown in Figure 4-24 (b). The emission at around 3.2 eV, which is expected to be from either C$_N$, V$_{III}$+3O$_N$ or both, reduced in intensity with an increase in V/III ratio. At the highest V/III ratio, the defect luminescence was barely distinguishable from the background level. All of these results strongly suggest that the carbon concentration decreased by increasing the V/III ratio during growth which supports the concept presented by Mita et al.$^{78}$
Figure 4-24: Room temperature free carrier concentration and mobility (a) of Al$_{0.70}$Ga$_{0.30}$N films grown with a fixed Si doping concentration on sapphire with different V/III ratios. Corresponding room temperature PL spectra (b).
The dependencies on growth temperature were studied in order to see if the vacancy-oxygen complexes concentrations could be reduced. Armstrong et al. indicated that by decreasing the growth temperature for Si-doped Al$_{0.70}$Ga$_{0.30}$N films, compensation by vacancies was greatly reduced. At typical Al-rich AlGaN growth temperatures (1000 to 1100 °C), the composition is highly sensitive to changes in the temperature due to the sensitivity in Ga incorporation. Therefore, a series of Si-doped homoepitaxial AlN films were grown with two Si concentrations (1 x 10$^{19}$ and 3 x 10$^{19}$ cm$^{-3}$) and two growth temperatures (1100 and 1250 °C). Figure 4-25 shows the low temperature (T = 3 K) PL spectra of the four Si-doped homoepitaxial AlN films. Midgap luminescence around 3.2 to 3.8 eV caused by the vacancy-oxygen complexes was visible in all four films. The intensity and position of these peaks did not significantly deviate with growth temperature, which implies that the reductions observed by Armstrong et al. could be related to the Ga species. It must be pointed out, however, that emission around 4.3 eV was present in the films grown at the lower temperature and not in the films grown at the higher temperature. The intensity of this peak increased with an increase in the Si concentration. As mentioned earlier, this emission at 4.3 eV is observed in semi-transparent co-doped PVT grown AlN substrates and was identified by Gaddy et al. to be related to a C$_N$+Si$_{Al}$ complex.
4.3 Mg Doping

In the following studies, Mg-doped AlGaN films covering the entire compositional range from GaN to AlN were grown by MOCVD. Mg-doped Al-rich AlGaN and AlN were grown on native AlN substrates and sapphire substrates whereas Mg-doped GaN was grown on native GaN substrates (from Ammono) and sapphire substrates. Cp₂Mg was used as the Mg dopant source. Details on the growth of the Al-rich AlGaN and AlN films are given in Section 2.2. Bryan et al. provides information on the Mg-doped GaN growth. A XRD technique
described by Tweedie et al. was implemented to determine the composition of all the AlGaN films.\textsuperscript{158}

4.3.1 Point Defects

4.3.1.1 Mg-doped GaN

Achieving p-type conductivity in the III-nitrides has proven to be even more difficult than realizing n-type conductivity. In particular for Al-rich AlGaN and AlN, there are no reports indicating unambiguous proof of p-type conductivity at room temperature. The reason for this is the lack of a p-type dopant with a low activation energy. Mg is the most commonly used p-type dopant for GaN, AlGaN, and AlN. The activation energy for Mg is the lowest in GaN with reported values between 125 and 215 meV.\textsuperscript{180} This provides an activation ratio $(\exp(-E_a/k_BT))$ of $8 \times 10^{-3}$ and $2 \times 10^{-4}$ at room temperature, respectively, indicating that high doping concentrations are necessary to achieve reasonable free carrier concentrations like those achieved in n-type films, reported on in the previous sections.

Mg doping is further complicated by passivation and compensation effects. It has been reported for GaN that Mg is passivated by H during growth through the formation of a neutral Mg\textsubscript{Ga}+H\textsubscript{i} complex.\textsuperscript{181} Therefore, p-type GaN was not readily realized until discovering that this complex could be dissociated through low-energy electron-beam irradiation (LEEBI) or thermal annealing.\textsuperscript{182-184} Nakamura et al. demonstrated that thermal annealing of Mg-doped GaN made the film conductive providing the nitride community with the first consistent process for creating p-type material.\textsuperscript{184} This thermal annealing process requires temperatures that are great enough for complex dissolution and H diffusion but low enough such that no
vacancies are introduced into the material. More specifically, $V_N$ have a low formation energy and are thermodynamically favorable to form at equilibrium for p-type GaN.\textsuperscript{150}

Similar to the case of Si-doped AlGaN, discussed in Section 4.2.2, signs of over compensation exist at high Mg doping concentrations in GaN.\textsuperscript{180, 185} It is thought that as the Mg concentration is increased, more triply ionized $V_N$ donors incorporate to heavily compensate the material. This is evident by a reduction in conductivity for Mg doping concentrations above $2 - 3 \times 10^{19}$ cm$^{-3}$. Figure 4-26 shows room temperature and low temperature ($T = 3$ K) PL spectra of a series of Mg-doped GaN films grown on sapphire with doping concentrations determined through calibrated SIMS measurements. Fringes were present due to the optical interference between the sapphire and thin film caused by contrast in the indices of refraction. With an increase in doping concentration, a broad emission around 2.8 eV emerged correlating directly to the decrease in electrical resistivity.\textsuperscript{186} Luminescence around this energy value is expected to be related to the deep $V_N$ donor.\textsuperscript{187-189} Peak fitting revealed that this emission is comprised of at least two peaks at 2.8 and 2.85 eV.
Figure 4-26: PL spectra of Mg-doped GaN with different Mg doping concentrations.
Emission at 2.85 eV is also present in undoped GaN and n-type GaN that is doped with small amounts of Si and Ge, not shown here. With an increase in the n-type dopant the emission disappears at 2.85 eV, which is consistent with the identification of a transition from the \( V_N \) to the valence band. The emission at 2.8 eV is only present in Mg-doped films making it seem probable that this emission is from a DAP transition between the \( V_N \) and \( \text{Mg}_{\text{Ga}} \). Furthermore, this emission is commonly accepted as being related to such a DAP transition.\(^{188}\) This association is further verified by studies by Reschikov et al. which showed thermal quenching of this emission at high temperatures with an activation energy around 0.3 to 0.4 eV indicating a deep donor state associated with the DAP transition.\(^{189}\)

Furthermore, the yellow luminescence around 2 eV is expected to be related to \( C_N \) and/or Ga vacancies in a complex form with oxygen discussed in Section 4.2.2. There was no clear changes in the intensity of this emission with an increase in Mg doping concentration. The broad emission around 3.2 eV at low temperature, which is comprised of two peaks at 3.20 and 3.23 eV, have been reported previously as being associated with DAP transitions between \( O_N \) and \( \text{Mg}_{\text{Ga}} \).\(^{177,190}\) These peaks are not found in undoped or n-type GaN films and the intensity increased slightly with increasing Mg concentration but not as much as the broad emission around 2.8 eV. All of these results on Mg-doped GaN indicate the importance of understanding the incorporation of point defects for the electrical and optical characteristics of these wide bandgap III-nitrides and provide a base of knowledge for interpreting the results to follow on AlN and Al-rich AlGaN.
4.3.1.2 Mg-doped AlN

Mg-doping of homoepitaxial AlN has not been reported on thus far, nevertheless the high crystalline quality promises great potential for higher free carrier mobilities and reduced compensation effects. In order to study the incorporation of Mg in AlN, calibrated SIMS depth profiling was performed on a multilayered structure with undoped and Mg-doped layers. The growth rate was fixed throughout the entire growth and only Mg was intentionally introduced using different \( \text{Cp}_2\text{Mg} \) flow rates in the doped layers. Figure 4-27 gives the SIMS depth profile and indicates the Mg, H, O, Si, and C concentrations. Mg was measured using an O beam whereas all other impurities were measured at a different spot using a Cs beam; therefore there could be slight deviations in the absolute depth position between the impurity profiles. The C and Si concentrations stayed constant at the detection limit of the SIMS system. It is important to note that this SIMS system was not the same as the one used for Figures 4-20 and 3-18 and had different detection limits. The Mg, H, and O concentrations did not stay constant. The O concentration increased slightly above the detection limit in the Mg-doped layers. The Mg concentration changed linearly with the \( \text{Cp}_2\text{Mg} \) flow rate providing a means for determining the Mg concentration in all AlN films discussed in the studies to follow. Additionally, the H concentration appeared to follow the Mg concentration in a nearly 1:1 manner. This is only noticeable when the H concentration is above the detection limit of \( 7 \times 10^{18} \text{ cm}^{-3} \). A similar behavior between the Mg and H concentrations was observed in Mg-doped GaN and suggests the idea of Mg incorporating as a \( \text{Mg}^{III}+\text{H}^I \) complex.\(^{191} \)
Figure 4-27: Calibrated SIMS depth profile for Mg, H, O, Si, and C in a homoepitaxial AlN film with layers intentionally undoped and doped with different Mg concentrations.

With the Mg concentration dependence on $C_{p_2Mg}$ flow rate known, a series of Mg-doped homoepitaxial AlN films of around 500 nm thick were grown. The low temperature ($T = 3$ K) PL near band-edge spectra are given in Figure 4-28 (a) for four films with doping concentrations between $5 \times 10^{18}$ and $3 \times 10^{19}$ cm$^{-3}$. Above a Mg concentration of $3 \times 10^{19}$ cm$^{-3}$, the exciton peaks broadened and it became harder to unambiguously discern peaks due to increased impurity scattering. Many narrow and intense excitonic peaks were visible in the films with FWHMs of less than 500 μeV, which is the current state of the art. The well-defined exciton transitions reveal the high optical quality of the homoepitaxial films. HRXRD measurements determined that the films were indistinguishable from the substrate showing that the crystalline quality is high and similar to that of the substrates. The $\Gamma_5$ FX was at 6.040
eV and indicates that all four films were free of strain, which was consistent with HRXRD results as well.

Two emissions at 6.003 and 6.013 eV, that have not yet been identified, showed a dependence on the Mg concentration as demonstrated in Figure 4-28 (b). Temperature dependent PL measurements proved that both emissions were bound excitons. One of these temperature dependent measurements is provided in Figures 4-28 (c) and (d). All of the bound excitons dissociate at a temperature below room temperature. Excitation power dependent PL studies revealed that these transitions were not associated with biexcitons. The emission at 6.003 eV is seen in undoped homoepitaxial AlN, which indicates that this peak cannot be the Mg acceptor bound exciton. Additionally, due to the positions of the peaks relative to the FX, it is expected that both peaks are DBX transitions.
Figure 4-28: Low temperature (T = 3 K) PL spectra of Mg-doped homoepitaxial AlN (a). The bound to free exciton intensity ratio as a function of Mg concentration for two unidentified bound excitons (b). Temperature dependent PL measurements (c) and (d).

The Mg-doped homoepitaxial AlN films exhibited dominant point defect related luminescence within the bandgap around 4.8, 5.2, and 5.5 eV as shown in Figure 4-29. For Mg-doped films on sapphire, the emission around 4.8 eV was present even at lower doping concentrations (< 3 x 10^{19} cm^{-3}) whereas this emission only became visible at high doping
levels in the films grown on AlN substrates. The intensity of all of these emissions increased relative to the band edge emissions with an increase in Mg concentration. The emissions are shifted for films grown on sapphire due to the large amounts of strain. Furthermore, the overall intensity of the emission around 4.8 eV was many times greater for the films grown on sapphire as compared to films grown on the native AlN substrate, which is consistent with the observations discussed in Section 4.2.2 on Si-doped films.

The 5.2 and 5.5 eV peaks are only seen in Mg-doped AlN films whereas the 4.8 eV peak was also seen in nontransparent PVT grown AlN, N-polar AlN on sapphire, and undoped AlN on sapphire. In nontransparent PVT grown AlN, it is known that the material contains high concentrations of C_N and V_N, where the thermodynamic and optical transitions have been determined for these point defects by Collazo et al. and Gaddy et al. With an increase in the n-type Si dopant concentration the emission disappears at 4.8 eV, which is similar to the observation for the 2.85 eV emission in GaN.
Figure 4-29: Room temperature PL spectra of Mg-doped AlN as a function of Mg concentration (top) and substrate type (bottom) indicating the dominant defect luminescence along with Gaussian peak fits.
Nakarmi et al. suggested that the emission around 5.5 eV is caused by a transition between the conduction band and the Mg acceptor which would be consistent with these current results.\textsuperscript{192} This would place the Mg acceptor energy level somewhere around 500 meV above the valence band maximum. Additionally, Lyons et al. used hybrid DFT calculations to discuss the probability of the formation of a Mg\textsubscript{Al}+H\textsubscript{i} complex in AlN.\textsuperscript{181} Similar to the case of GaN, it is thought that such a complex is likely to exist in AlN. The complex is predicted to be electrically neutral except for when the Fermi level is below 0.43 eV where it will behave as a donor. The complex should be optically active and Lyons et al. calculated a minimum emission of 5.13 eV which matches with the 5.2 eV emission seen in Figure 4-29.\textsuperscript{181}

Thermal annealing was conducted on Mg-doped AlN films in both N\textsubscript{2} and O\textsubscript{2} atmospheres for 20 minutes. Multiple annealing temperatures were studied between 700 and 900 °C. These are the common activation annealing conditions used for Mg-doped GaN. If as-grown Mg-doped GaN was passivated, then after annealing with these conditions clear changes in the PL spectra could be observed with an increase in the acceptor bound exciton (ABX) emissions. This is thought to represent the dissolution of Mg\textsubscript{Ga}+H\textsubscript{i} complexes. However, no significant deviations occurred in the near band-edge or deep defect related PL spectra for Mg-doped AlN after annealing indicating that potentially higher annealing temperatures are needed or that the concentration of Mg\textsubscript{Al}+H\textsubscript{i} complexes is low.

Similar to the case of GaN, the V\textsubscript{N} is expected to be thermodynamically favorable in Mg-doped AlN due to the predicted low formation energy.\textsuperscript{150} Hybrid DFT calculations were performed in the same way as discussed in Section 4.2.2 to determine the formation energy of the isolated vacancies, V\textsubscript{Al} and V\textsubscript{N}, along with V\textsubscript{Al}+nV\textsubscript{N} (n=1-4) complexes. Figure 4-30 gives
the formation energy as a function of the Fermi level position for these point defects under N- and Al-rich conditions. For the complexes, a solid line is used in Figure 4-30 when the binding energy is favorable and the complex may form whereas a dashed line is used when the complex is unstable compared to the isolated defects from which it is comprised. Both N- and Al-rich conditions represent the extremes for the chemical potentials, nevertheless, when the Fermi level is near the valence band, i.e. p-type material, the isolated $V_N$ has the lowest formation energy out of any of the other defects. Additionally, the $V_N$ is calculated to have an even lower formation energy in AlN than in GaN.\textsuperscript{150} These results indicate that compensation in Mg-doped AlN by $V_N$ is highly probable and is expected in the same way that it is in Mg-doped GaN.

![Graph](image)

**Figure 4-30:** Formation energy plotted as a function of Fermi level for point defects in AlN.
The predicted thermodynamic and optical transitions for the VN is given in Table 4-2 and suggests that the emission around 4.8 eV is related to an impurity-to-band transition involving the VN. Even though it is not possible to directly detect a VN with positron annihilation, Uedono et al. has discussed the detection of complexes containing cation and anion vacancies by positron annihilation studies in AlN requiring the existence of the isolated VN as well when considering an energetics argument with the formation energies given in Figure 4-30.\textsuperscript{155} Others have suggested that an emission around 4.7 eV in Mg-doped AlN grown on sapphire is related to a DAP transition between a VN and Mg\textsubscript{Al}.\textsuperscript{188, 192, 193} It is thought that this emission is the same as what is seen in the Mg-doped AlN films on sapphire shown in this study. The shift of about 0.1 eV or less can potentially be accounted for by strain that is evident by the band edge position for the films reported by others.\textsuperscript{188, 192, 193} As mentioned before, the emission present at around 4.8 eV in Mg-doped films on sapphire seen in Figure 4-29 was also seen in AlN free of Mg impurities, which clearly shows that this emission cannot be the DAP suggested and further supports the current identification proposed here.

4.3.1.3 Mg-doped Al\textsubscript{0.75}Ga\textsubscript{0.25}N

Figure 4-31 (a) shows room temperature PL of Mg-doped nominally Al\textsubscript{0.75}Ga\textsubscript{0.25}N films grown on AlN substrates with two different NH\textsubscript{3} flows and two different Cp\textsubscript{2}Mg flow rates. Intense and broad defect peaks could be seen at 4.6 and 4.9 eV, as determined by peak fitting (see Figure 4-31 (b)), seeming to correlate to the emissions seen in AlN at 5.2 and 5.5 eV. These peaks are not present in Si-doped or undoped Al\textsubscript{0.75}Ga\textsubscript{0.25}N. Both defect peaks increased in intensity relative to the band-to-band emission with an increase in Mg
concentration, indicating an increase in the incorporation of point defects. The 4.6 and 4.9 eV peaks are thought to be related to the $\text{Mg}_{\text{III}}+\text{H}_i$ complex and $\text{Mg}_{\text{III}}$ defects, respectively, since the changes in energy relative to the AlN emissions are nearly equal to the change in bandgap. Furthermore, by increasing the ammonia flow, i.e. increasing the V/III ratio, the defect luminescence at 4.6 eV decreased in intensity significantly suggesting a reduction in the point defects. Thermal annealing was conducted on the Mg-doped $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ films using the same range of conditions mentioned earlier for AlN. No significant changes were observed in the PL spectra before and after annealing at the various conditions, similar to the results for Mg-doped AlN.
Figure 4-31: Room temperature PL spectra of Mg-doped Al$_{0.75}$Ga$_{0.25}$N as a function of Mg concentration and NH$_3$ flow indicating the dominant defect luminescence (a). Gaussian peak fitting of the dominant defect luminescence (b).
There was no lower energy peak around 4.2 eV, which is expected to be related to the $V_N$, in the Mg-doped Al$_{0.75}$Ga$_{0.25}$N films grown on AlN substrates. Nakarmi et al. suggested this emission to be a DAP transition between $V_N$ and Mg$^{III}$ as mentioned above for the 4.8 eV emission in AlN. However, this emission was also seen in undoped Al$_{0.75}$Ga$_{0.25}$N films. This discrepancy can be easily understood since Nakarmi et al. took an over simplified flat band approach for identifying peaks observed in Mg-doped AlGaN without considering the large Stokes shifts which are known to exist in these wide bandgap semiconductors.

4.3.1.4 Point Defects Overview in Mg doped Material

A summary of all the energy positions at room temperature associated with band-to-impurity and impurity-to-band transitions for Mg-doped GaN, AlGaN, and AlN films grown on native and foreign substrates observed in these studies are given in Figure 4-32. As expected, the peak positions associated with these defects increased with an increase in Al-content, where the energy increase was similar to the increase in bandgap. The $V_N$ causes luminescence at 2.85 and 4.8 eV in GaN and AlN, respectively. Hybrid DFT calculations for Al$_{0.65}$Ga$_{0.35}$N predicted a minimum emission at 3.6 eV, as indicated in Table 4-1, which matches nicely with the PL emission observed at 3.8 eV. This defect-related emission is most readily observed in Mg-doped and undoped films grown on sapphire as opposed to native substrates. The higher energy emissions are shown here to be related to the Mg$^{III}$+H$_i$ complex and Mg$^{III}$ defects based on the discussions by Lyons et al. and Nakarmi et al., respectively.
Figure 4-32: Energy values of deep defect-related peaks seen in room temperature PL spectra for Mg-doped AlGaN films spanning the entire composition range from GaN to AlN.

4.3.2 Electrical Properties

4.3.2.1 Current Voltage Characteristics

Large area Ni/Au contacts (> 2x2 mm²) annealed at 600 °C in air were fabricated in a Van der Pauw geometry for all the electrical measurements on Mg-doped films. Annealing was required for the contacts to show Ohmic IV characteristics on p-type films. Similar to the case for Si-doped films, the degree of Ohmic character was found to be dependent on the doping concentration for the entire studied composition range from GaN to AlN. Figure 4-33 shows two representative IV curves at room temperature for Al$_{0.75}$Ga$_{0.25}$N films with Mg concentrations of 1 and 4 x 10$^{19}$ cm$^{-3}$. With more free holes, sufficient tunneling could occur
through the contact barrier and the IV curve became more linear. At the high Mg concentration, pure Ohmic behavior was observed even at room temperature. These IV curves indicate that the Mg-doped Al$_{0.75}$Ga$_{0.25}$N films are conductive but more resistive than Si-doped Al$_{0.75}$Ga$_{0.25}$N with an equivalent doping concentration. More importantly, these contacts are good enough for reliable resistivity measurements using the Van der Pauw geometry and Hall effect measurements.

![IV curves for Al$_{0.75}$Ga$_{0.25}$N films](image)

Figure 4-33: Room temperature IV curves for Al$_{0.75}$Ga$_{0.25}$N films grown on AlN substrates with different Mg doping concentrations.

4.3.2.2 Self-compensation

For all of the Mg-doped films discussed in this dissertation, the hot-point probe method was implemented to verify p-type conductivity. The sign of the Hall coefficient was also used
to further support the claim of p-type conduction. The PL spectra shown in Figure 4-26 for a series of Mg-doped GaN films grown on sapphire indicated an onset of self-compensation around a Mg concentration of $2 - 3 \times 10^{19}$ cm$^{-3}$ by the introduction of an emission around 2.85 eV. Figure 4-34 gives the room temperature free carrier concentration for Mg-doped GaN films grown on sapphire as well with a range of doping concentrations from $2 - 4 \times 10^{19}$ cm$^{-3}$ indicating a critical Mg concentration whereby further increasing the concentration led to a reduction in the conductivity. Therefore, Hall effect measurements confirm the self-compensation by nitrogen vacancies. A maximum hole concentration of about $6 \times 10^{17}$ cm$^{-3}$ was achieved at room temperature. Further details on the growth conditions for this Mg doping series are reported by Bryan et al.$^{186}$
Figure 4-34: Room temperature free carrier concentration as a function of Mg concentration for GaN on sapphire. Measurements were conducted on as-grown films as well as films annealed at 700 and 900 °C.

Figure 4-34 includes Mg-doped films measured before thermal annealing (as-grown) and after thermal annealing at two different temperatures for 20 minutes in a N₂ atmosphere. Each of the data points represents three different 1 x 1 cm² square samples that underwent the same post growth processing. Two films were grown with a Mg concentration of 3 x 10¹⁹ and produced similar electrical properties as shown in Figure 4-34. These results indicate that these Mg-doped GaN films were already activated upon leaving the MOCVD reactor. Annealing did not significantly change the electrical properties. It is thought that the MgGa⁺Hᵢ complex concentration is sufficiently low in these films due to the growth conditions used.
Self-compensation at high Mg concentrations was also observed in Al-rich AlGaN and AlN. Figure 4-35 gives the resistivity at 100 °C for GaN, Al$_{0.75}$Ga$_{0.25}$N, and AlN doped with different amounts of Mg. The GaN films were grown on sapphire substrates and the Al-rich AlGaN and AlN were grown on AlN substrates. Mg-doped AlGaN and AlN films were also grown on sapphire substrates, however, these films were too resistive to measure even at high temperatures suggesting a higher degree of compensation in these films compared to those grown on AlN substrates. A temperature of 100 °C was used to get sufficient current for reliable measurements on the highly resistive homoepitaxial AlN films.

![Graph](image)

Figure 4-35: Resistivity at 100 °C for Mg-doped films spanning the entire composition range from GaN to AlN.
The lines in Figure 4-35 are included to guide the eye. Increasing the Mg concentration past around $2 \times 10^{19}$ cm$^{-3}$ does not reduce the resistivity further as it should for all of the compositions studied. This is the most apparent for AlN where the resistivity increases significantly at Mg concentrations greater than $2 \times 10^{19}$ cm$^{-3}$. This is not as apparent for the Al$_{0.75}$Ga$_{0.25}$N series, however, there are still indications of an increase in the compensation level since the resistivity did not reduce 1:1 with the Mg concentration above $2 \times 10^{19}$ cm$^{-3}$. Even with the limited number of samples that were studied, it is clear that there is significant compensation at the high Mg levels. It also seems that this onset of over compensation occurs at lower Mg concentrations with an increase in Al-content which is similar to the results for Si doping discussed in Section 4.2.2. These films were measured with and without thermal annealing using the same conditions given earlier for GaN and there was no distinguishable difference found in the electrical properties. All of these results are consistent with the observations discussed previously with the PL spectra, where no changes were visible between an as-grown and thermally annealed film.

4.3.2.3 Mg Acceptor Activation Energy

The Mg acceptor activation energy was studied by performing temperature dependent electrical measurements to better understand the large increase in resistivity with Al-content. Figure 4-36 shows the temperature dependence of the resistivity and $p$ for homoepitaxial AlN, which was calculated using the resistivity and assuming a constant mobility of $1$ cm$^2$/V$s$. The use of this specific mobility value will be supported through later discussion. A significant
amount of free holes were generated with an increase in temperature due to the large activation energy.
Figure 4-36: Temperature dependence of the p-type resistivity (top) and calculated free carrier concentration (bottom) for Mg-doped AlN.
The free electron concentration is very small in p-type semiconductors and the concentration of ionized donors must equal the concentration of donors. Therefore, an expression analogous to Equation 6 from Chapter 1 for n-type semiconductors can be derived for p-type semiconductors.\(^{180}\)

\[
\frac{p(p+N_D)}{N_A-N_D-p} = \frac{N_V}{g} e^{-\frac{E_a}{k_BT}}
\]

Equation 4

In this case, \(E_a\) is now the acceptor activation energy which is equal to the difference between the acceptor energy state and the valence band maximum. \(N_V\) is the density of states for the valence band. Solving for \(p\) gives the temperature dependence of the free holes as follows.

\[
p = \frac{1}{2} \left[ -\left( N_D + \frac{1}{g} N_V e^{-\frac{E_a}{k_BT}} \right) + \sqrt{\left( N_D + \frac{1}{g} N_V e^{-\frac{E_a}{k_BT}} \right)^2 - 4 \frac{1}{g} N_V (N_D - N_A) e^{-\frac{E_a}{k_BT}}} \right]
\]

Equation 5

The decrease in resistivity with temperature for Mg doping was even greater than it was for Si doping, which indicates that an activation energy greater than 200 meV is expected for Mg in AlN. Therefore, \(p \ll N_D\) and \(p \ll N_A-N_D\) are valid assumptions which allows Equation 4 to be rearranged into a linear approximation of the following form.

\[
\ln\left(2pgT^{\frac{3}{2}}\right) \approx \ln\left(\frac{N_A-N_D}{N_D} \frac{2N_V}{T^2} \right) - \frac{E_a}{k_BT}
\]

Equation 6

Since the resistivity is proportional to the free carrier concentration, the slopes of the temperature dependence should be identical assuming a constant mobility making it possible to extract the activation energy. Even if the mobility did deviate with temperature, it shouldn’t change by more than an order of magnitude. Assuming such a large gradient in the mobility would still keep the extracted activation energy within the scatter of the measured values.
reported here. For Mg-doped AlN, $E_a$ was determined to be $591 \pm 30$ meV, which is more than twice the energy for the Si activation energy. Using this technique, $E_a$ was determined for multiple AlN and Al$_{0.75}$Ga$_{0.25}$N films. For GaN, Equation 5 was used since the free carrier concentration was measured directly through Hall effect measurements. All of the activation energies for Mg-doped films from these studies are given in Figure 4-37 along with values from the literature.\textsuperscript{148, 149, 151, 194-196} Only $E_a$ values reported in literature that were determined unambiguously through electrical measurements are included. These measured values are in relatively close agreement with the reported values. This data clearly indicates the deep nature of Mg and the main obstacle for achieving high p-type conductivity for Al-rich AlGaN based devices. The Mg activation energy increases linearly with Al-content which is different from the trend for Si which stayed constant until around 80 % at which point the activation energy increased exponentially.
4.3.2.4 Conductivity Overview in Mg doped Material

The minimum measured resistivity at 100 °C for the Mg-doped films shown in Figure 4-35 are given in Figure 4-38 (a) and plotted as a function of Al-content. The resistivity increased with an increase in Al-content which is expected since the Mg acceptor activation energy increased significantly with Al-content. A difference of nearly four orders of magnitude in the resistivity was measured between GaN and AlN. The free carrier concentrations associated with these lowest resistivity films are given in Figure 4-38 (b). The free carrier concentration given for GaN is a measured value by Hall effect, however, for Al\textsubscript{0.75}Ga\textsubscript{0.25}N.
and AlN $p$ was not able to be measured by Hall effect measurements reliably due to the relatively low Hall voltages. To properly measure the free carrier concentrations of these films with the systems that were available, a higher magnetic field would be required. The calculated carrier concentration for $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ and AlN is given using the resistivity measurements and assuming the given mobility values in Figure 4-38 (b). Using the Mg activation energies given in Figure 4-37, the free carrier concentration assuming no compensation was calculated providing a lower bound for the mobility of around 0.09 cm$^2$/Vs for $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ and 0.06 cm$^2$/Vs for AlN. The upper bound is assumed to be the measured mobility for GaN. More than $10^{15}$ cm$^{-3}$ free holes should be present in $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ at 100 °C. Furthermore, it is clear that compensation is even present in the films with the lowest measured resistivity.
Figure 4.38: Minimum resistivity (a) and maximum free carrier concentration (b) at 100 °C for Mg-doped films as a function of Al-content.
All of these results provide new insight on Mg-doped Al-rich AlGaN and AlN films grown on AlN substrates. The large Mg activation energies require high doping concentrations with low degrees of compensation in order to supply devices with enough free holes. Even with the state of the art high crystalline quality films, high resistivity films were realized with Mg-doping. Further work will be necessary to reduce the compensation in these Mg-doped films.

4.4 Point Defects Overview

Figure 4-39 provides a general overview of all the point defects which have been observed through PL studies presented in this dissertation along with the current identifications. Only the band-to-impurity and impurity-to-band transitions are given in Figure 4-39. Discussions on how these point defects were identified can be found in Sections 4.2 and 4.3. As mentioned previously, these emissions are not unique to MOCVD grown films. This plot provides a means for efficiently determining through luminescence measurements which defects are present in any GaN, AlGaN, or AlN material. Most importantly, upon identification of the defects, routes can be taken to control the optical and electrical properties of these III-nitride materials paving the way for their success in applications.
Figure 4-39: Energy values for band-to-impurity and impurity-to-band transitions present in room temperature PL spectra spanning the entire composition range from GaN to AlN.

4.5 Summary

In this chapter, the electrical and optical properties of Si- and Mg-doped AlGaN grown on native and foreign substrates spanning the entire composition range from GaN to AlN were studied. By growing high quality films on native AlN substrates, the overall conductivity was increased by over an order of magnitude compared to films grown on sapphire. The higher
dislocation density of the films on sapphire resulted in a higher incorporation of compensating point defects.

With an increase in Al-content, there was a significant decrease in the free carrier concentration for both n- and p-type films. It was determined that the reduction in free carrier concentration was primarily caused by an increase in the Si and Mg activation energies. The Si donor activation energy increased from 15 meV for GaN to 244 meV for AlN with an increase in Al-content. The Mg acceptor activation energy was many times greater than the Si donor activation energy and spanned from around 141 meV for GaN to 591 meV for AlN.

An onset of self-compensation for donor and acceptor incorporations larger than a critical doping concentration was observed for both Si- and Mg-doped AlGaN, respectively. This onset of self-compensation by point defects was indicated by changes in both the electrical and optical properties. Hybrid DFT calculations were used to help identify point defects. It was determined that possible point defects in Si-doped films are C_N, V_{III}^{+3}O_N, V_{III}^{+2}O_N, and V_{III}^{+1}O_N defects, where only the V_{III}^{+3}O_N defect would not behave as a compensating defect. By controlling the V/III ratio during growth, the C_N incorporation could be managed, therefore providing a means to improve the conductivity in Si-doped AlGaN. In Mg-doped films, the V_N and Mg_{III}^{+}H_i defects are expected to be prevalent. The triply ionized V_N donors incorporate at high Mg doping levels and heavily compensate the films.

The results presented in this chapter provide information on how to realize the highest conductivity in n- and p-type AlGaN spanning the entire composition range from GaN to AlN. Furthermore, the provided point defect identifications make it possible for a quick evaluation of any AlGaN material to be grown in the future.
CHAPTER 5: Conclusions and Future Work

5.1 Conclusions

In this dissertation, the growth of Al-rich AlGaN and AlN on both polar and non-polar single crystal AlN substrates was investigated. These substrates provide a means of producing the highest quality III-nitride materials, which are required for improved performance in electronic and optoelectronic devices. This dissertation provides the first comprehensive understanding of how growth proceeds on these substrates. Moreover, by realizing the role of extended and point defects on the properties of these wide bandgap semiconductors, efforts can be made to further improve these materials.

In Chapter 2, a surface kinetic framework for control of surface morphology during Al-rich AlGaN and AlN growth on Al-polar surfaces by MOCVD was developed. Films grown with both high and low dislocation densities were investigated, indicating the importance of realizing low dislocation densities to achieve the desired long-range step-flow growth and flat surfaces. Mixed and screw-type dislocations promote spiral growth which roughens the surface. By growing pseudomorphically on a native AlN substrate with <10^3 cm^{-2} dislocations, parallel bilayer steps were observable free of step pinning and spiraling with RMS roughnesses of less than 50 pm for a 5x5 µm^2 AFM scan area. Step morphology dependence on substrate misorientation angle and vapor supersaturation, as demonstrated by changing the growth rate and growth temperature, were observed and explained. BCF theory was utilized to understand these dependencies. The surface energy, a critical parameter controlling surface kinetics during growth, of the Al-polar surface of AlN was experimentally determined to be 149 ± 8 meV/Å^2 using the proposed model. The onset of 2D nucleation and step flow growth was found to
depend on the surface diffusion length with respect to the terrace width. The same surface morphology could be achieved either by changing the misorientation angle, which controlled the terrace width, or vapor supersaturation, which controlled the surface diffusion length. For a fixed vapor supersaturation, a critical misorientation angle existed for the transition between bilayer steps and step bunches, however, this critical misorientation angle could be controlled by the vapor supersaturation to some degree. A dependence on the terrace width with the Al composition was observed and explained through the BCF theory. Furthermore, step bunching resulted in compositional inhomogeneity. Strained AlN homoepitaxial films exhibited both micro-cracking and nano-pitting of varying degrees. Pitting and cracking occurs as the main partial strain relaxation mechanisms in epitaxial Al-rich AlGaN and AlN thin films as opposed to misfit dislocation formation. Hillocks on the surfaces of Al-rich AlGaN and AlN were investigated and it was found that by properly cleaning the substrate, the density of hillocks could be reduced by more than one order of magnitude. In addition, all of the surface defects studied in this dissertation caused compositional inhomogeneity in AlGaN films. All of the results in Chapter 2 indicate the importance of controlling the surface morphology and present a control scheme for achieving surface defect-free and atomically smooth bilayer stepped surfaces for Al-rich AlGaN and AlN epitaxial thin films.

In Chapter 3, Al-rich AlGaN and AlN epitaxial films were grown on (1-100) m-plane AlN single crystal substrates using MOCVD. Pre-growth substrate preparation resulted in a surface chemically and morphologically comparable to that of c-plane substrates prepared in the same manner, as confirmed by XPS and AFM. The AlN homoepitaxial surface consisted of macrosteps oriented along the ±[0001] directions for films grown at and below 1350 °C.
Films grown at temperatures above 1350 °C contained atomically smooth surfaces with no preferential faceting, which provided an ideal surface for subsequent Al-rich AlGaN growth. High-resolution XRD symmetric rocking curves possessed FWHM values of 12-25 arcsec. In addition, PL spectra revealed several sharp DBX peaks with a FWHM as narrow as 550 µeV, demonstrating the highest quality films ever reported. SIMS measurements showed that as the growth temperature increased, the oxygen concentration in the film decreased from \(~10^{20}\) cm\(^{-3}\) to less than \(10^{18}\) cm\(^{-3}\). This unintentional incorporation of oxygen made it possible to identify for the first time the DBX transition at 6.006 eV as originating from the neutral-oxygen-donor (O°X) in AlN. Additionally, defect luminescence peaks between 3.2 and 3.8 eV, similar to those seen in Si-doped c-plane and m-plane homoepitaxial films, appeared and increased in intensity as a function of oxygen concentration. The assignment of these transitions was made possible for the first time in this dissertation by hybrid DFT calculations. High-resolution XRD and TEM studies were performed to investigate strain and dislocation behavior in the non-polar epitaxial films. Both studies indicated that no basal plane stacking faults were present, which was in contrast to results on non-native substrates. All of these findings bring about new insight on m-plane Al-rich AlGaN and AlN epitaxial growth which is crucial to the development of AlN based non-polar devices.

In Chapter 4, Si- and Mg-doped AlGaN thin films spanning the entire composition range from GaN to AlN were grown by MOCVD on (0001)-oriented native (single crystalline AlN and GaN) and foreign (sapphire) substrates. Multiple doping levels were used to differentiate compensation arising from the presence of dislocations from those related to the intrinsic formation of point defects; either native defects or unintentional impurities. A
reduction in dislocation density of the films grown on AlN, as compared to sapphire, resulted in films with much lower resistivity. It was found that with an increase in Al-content, there was a significant decrease in the free carrier concentration for both n- and p-type films. The reduction in free carrier concentration was primarily caused by an increase in the Si and Mg activation energies. The Si activation energy increased exponentially with Al-content whereas a linear increase was observed for the Mg activation energy. It was observed that up to a critical Si or Mg doping concentration, the carrier concentration was always proportional to the dopant source flow. Any further increase in doping led to a reduction of the carrier concentration. This trend was observed for all compositions studied and was a strong indication of self-compensation for donor and acceptor incorporations larger than the critical concentration. The incorporation of native compensating defects was correlated with a change in the PL spectra. The peak positions in PL spectra related to the compensating defects was correlated to calculations performed using hybrid DFT. It was determined that possible point defects present in Si-doped films are C_N, V_{III}^{+3}O_N, V_{III}^{+2}O_N, and V_{III}^{+1}O_N defects. More specifically, at low doping levels the C_N and V_{III}^{+3}O_N are predominately present in the films, but as the Si doping level reaches a critical concentration, the V_{III}^{+2}O_N and V_{III}^{+1}O_N defects begin to overcompensate the donor causing a significant reduction in the conductivity of the films. In Mg-doped films, the V_N and Mg_{III}^{+}H_i defects are expected to be prevalent. The triply ionized V_N donors incorporate at high Mg doping levels and heavily compensate the films. With this knowledge, different point defect control schemes were discussed involving growth condition changes and above band gap illumination during growth in order to further improve the conductivity in AlGaN thin films.
5.2 Future Work

The following provides suggested future work on each of the main topics discussed in this dissertation:

- Preliminary results suggest that the hillock formation is dependent on the substrate polishing condition. Since the hillocks are related to dislocations, the density should match that of the substrate in the best case. Future work will include determining if the subsurface polishing damage can be removed prior to growth. Also, the vapor supersaturation and substrate misorientation angle should be considered to potentially find a condition where the surface defect doesn’t form even with the presence of the dislocations.

- The substrate misorientation angle not only affects the surface morphology but also affects the composition of AlGaN films as discussed in Section 2.5. The growth parameter space will need to be considered in order to potentially find a more stable regime for AlGaN.

- The dependence of surface morphology on the misorientation angle of the substrate has been demonstrated for (0001) and (1-100) growth. It will be necessary to conduct a more detailed study on (1-100) growth in order to better understand the surface kinetics of Al and Ga adatoms on AlGaN. In particular, the faceting behavior was not present in (0001) growth and its origin is still unknown. Once this has been achieved, the expected potential of non-polar device structures can be realized. With atomically smooth AlGaN, quantum wells can be grown and characterized. The internal quantum
efficiency can be measured and studied in order to provide experimental evidence of
the negative consequence of the quantum-confined Stark effect seen in c-plane
quantum wells.

- Compensating point defects in Si- and Mg-doped AlGaN have been revealed. Increasing the V/III ratio during growth was shown to result in lower point defect
centations, however, further work is needed to find more effective ways of
removing these defects.
REFERENCES


