INVESTIGATION OF AlGaN FILMS AND NICKEL/AlGaN SCHOTTKY DIODES USING DEPTH-DEPENDENT CATHODOLUMINESCENCE SPECTROSCOPY AND SECONDARY ION MASS SPECTROMETRY

DISSERATION

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ABSTRACT

AlGaN/GaN heterostructures and high Al mole fraction AlGaN films are used in a wide variety of applications, such as high power/high frequency transistors, UV photodetectors, solar-blind detectors, light-emitting diodes, and laser diodes. However, there are several important issues that need to be addressed in AlGaN/GaN heterostructures, such as the impact of surface roughness, impurities, and defect states on electronic properties such as mobility and two-dimensional electron gas (2DEG) sheet charge density and the role of surface processing on the Schottky barrier height. Also, Si doping of AlGaN with high Al mole fraction has been shown to be difficult and may be restricted by non-intentional impurities and their associated deep levels (such as O), as well as an increasing dopant donor energy with higher Al mole fraction. For the AlGaN/GaN heterostructures, correlations have been made between deep level defects and the 2DEG sheet charge density, interface broadening, surface roughness, and Ga-N ratios. Depth-dependent cathodoluminescence spectroscopy (CLS) and secondary ion mass spectrometry (SIMS) reveal the nature of deep level defects and their effect on Si doping of high Al mole fraction (25%-100%) AlGaN. SIMS results provide correlations between AlGaN deep level emissions from CLS and elemental impurities distributed through the epitaxial bulk films. The highest Al mole fraction ($x_{\text{Al}}$) samples exhibit deep level optical emissions that correlate with O and C impurities measured by SIMS. The CLS energy onset of near band edge peak emissions track the $b=1$ theoretical band gap
for \(0 \leq x_{\text{Al}} \leq 0.98\) while their peak emissions deviate monotonically. The absence of free carriers for \(x_{\text{Al}} > 0.80\) is consistent with Si donor compensation due to deep levels associated with oxygen. Cross-sectional CLS measurements of the AlGaN/sapphire interface reveal luminescence signatures which correlate with oxygen diffusing from the sapphire into the AlGaN. Internal photoemission spectroscopy (IPE) reveals changes in the Schottky barrier height of Ni on AlGaN/GaN heterojunction field effect transistor structures (HFETs) with pre-metallization processing conditions and post-metallization ultra-high vacuum (UHV) annealing. These variations in the IPE Schottky barrier height are correlated with AlGaN near band edge emissions from low energy electron-excited nanoluminescence spectroscopy (LEEN) and Ni/AlGaN interface impurities by SIMS. It is shown that changes in the Schottky barrier height and the appearance of dual barriers are dominated by changes in the local Al mole fraction. CL mapping reveals spatial variations in the AlGaN near band edge emission which could lead to the appearance of dual Schottky barriers. Interfacial oxygen and carbon have secondary but systematic effects as well. Future studies are proposed, which include the further examination of the role of impurities in AlGaN/GaN heterostructures and at the AlGaN/sapphire interface, Schottky barriers to AlGaN with higher Al mole fraction, electron beam induced current (EBIC) analysis of the minority carrier diffusion lengths and lifetimes in these films, and electro-chemical C-V profiling. This work demonstrates that spatially-resolved cathodoluminescence spectroscopy, when coupled with chemical information from SIMS, is very effective in understanding the physical mechanisms which determine the electronic properties of nitride semiconductors and device structures.
Dedicated to Patricia and Abby.
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1.1 Relevance of III-Nitride Materials: An Introduction

III-Nitride materials are of great interest for a wide array of device applications since there are many areas in which the use of conventional III-V materials is not feasible. GaN and the AlGaN ternary are currently being used in optoelectronic devices such as UV photodetectors, light emitting diodes (LEDs), and laser diodes. AlGaN and AlN are also promising materials for surface acoustic wave (SAW) devices and high temperature/high power transistors, and solar-blind detectors. When doped with transition metal elements, AlN is believed to be a promising material for the emerging field of spintronics. GaN and InGaN with small In mole fraction are well established as efficient light emitters for a wide range of optoelectronics, but pure InN has not received as much attention as GaN or AlN because of its poor light emitting efficiency and the fact that it is difficult to grow high-quality InN films consistently. Rapid progress in the performance of III-Nitride emitter devices occurred in the mid 1990s with blue and green LED commercialization and long lifetime short wavelength lasers. GaN based LED technology is now well established with blue and green emitter lifetimes determined by degradation of the packaging material, not the device. There is currently a large research thrust toward solid-state illumination applications and the InGaAlN alloy system is
targeted as being a major contender for such applications. AlGaN/GaN field effect transistors are being sought for microwave applications such as mobile-phone base stations, other wireless distribution systems, and military applications such as tracking systems and communications, but the wider use of these technologies is limited by cost since larger wafer sizes are desirable.\textsuperscript{8}

For the III-Nitrides GaN and AlN, the band gaps are direct and relatively large. The wide band gap of these materials gives rise to high breakdown fields, which permit devices to be scaled down to an order of magnitude less than devices made of conventional materials. Large conduction band offsets and piezoelectric properties in the AlGaN/GaN system allow sheet charges to be formed and high gain transistors to be developed. Table 1.1 provides a comparison of GaN semiconductor parameters to other conventional electronic materials. While GaN has a high band gap, high breakdown field, and maximum electron velocity, GaAs and SiC have a higher electron mobility and thermal conductivity, respectively. However, GaN has the highest combined figure of merit for high temperature/high power/high frequency applications.
Table 1.1 Comparison of common material parameters at 300 K for several semiconductors. The combined figure of merit (CFOM) provides a ratio of high temperature/high power/high frequency characteristics to those of Si.  

<table>
<thead>
<tr>
<th>Property</th>
<th>Si</th>
<th>GaAs</th>
<th>4H-SiC</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap $E_g$ (eV)</td>
<td>1.12</td>
<td>1.42</td>
<td>3.25</td>
<td>3.40</td>
</tr>
<tr>
<td>Breakdown field $E_B$ (MV/cm)</td>
<td>0.25</td>
<td>0.4</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Electron mobility $\mu$ (cm²/V/s)</td>
<td>1350</td>
<td>8500</td>
<td>1000</td>
<td>1400</td>
</tr>
<tr>
<td>Maximum velocity $v_s$ (10⁷ cm/s)</td>
<td>1.0</td>
<td>2.0</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Thermal conductivity $\xi$ (W/cm K)</td>
<td>1.5</td>
<td>0.5</td>
<td>4.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Dielectric constant $\varepsilon$</td>
<td>11.8</td>
<td>12.8</td>
<td>9.7</td>
<td>9.0</td>
</tr>
<tr>
<td>CFOM = $\frac{\xi\varepsilon\mu E_B^2}{(\xi\varepsilon\mu E_B^2)_{Si}}$</td>
<td>1</td>
<td>8</td>
<td>458</td>
<td>489</td>
</tr>
</tbody>
</table>

There is a large amount of research currently focused on the development of high-power/high-frequency AlGaN/GaN HFETs and n-type AlGaN with high Al mole fraction. Also, Schottky contacts are necessary for AlGaN/GaN HFET device operation as well as for some UV photodetectors made from high Al mole fraction AlGaN. The following sections will outline some of the past and present work in these sub-fields and describe some of the research challenges. Challenges for AlGaN/GaN HFET structures include an understanding of the impact of surface roughness, impurities, and defect states on electronic properties such as mobility and 2DEG sheet charge density. Schottky barriers to GaN and AlGaN are crucial for HFET device operation but their formation mechanisms are not totally understood. High n-type doping of high Al mole fraction
AlGaN is met with varied success due to many proposed factors. Challenges in this area include a fundamental understanding of the nature of intentional and unintentional impurities in a range of Al mole fractions and their effect on the luminescence spectra, Hall carrier density, and other electronic properties. The goal of this work is to address these challenges at a fundamental level using several characterization techniques and, as a result, reveal physical insights that may be useful to the device community.

1.2 AlGaN HFETs and HEMTs

A cross-sectional schematic of a typical heterostructure field effect transistor (HFET) layout is shown in the following figure.

![Cross-sectional schematic of a typical heterostructure field effect transistor (HFET) layout](image)

Figure 1.1. HEMT cross-section showing the source and drain ohmic metals and the Schottky gate. The gate of the HEMT structure is biased to modulate the depletion region of the channel and therefore the charge transfer characteristic between the source and drain.

This figure shows the typical metal-semiconductor field-effect transistor (MESFET) configuration with an additional semiconductor barrier layer forming a heterostructure with a buffer layer. MESFETs are usually composed of a single semiconductor and differ from metal-oxide field-effect transistors (MOSFETs) in that there is no intentional oxide layer formed between the metal and the semiconductor. HFETs and HEMTs
represent specific classes of MESFETs that stress the heterostructure and high mobility nature of the devices, respectively. As shown in Figure 1.1, the source and drain of the transistor are comprised of ohmic contacts to the material and the conductivity between the source and drain is controlled by a Schottky contact forming the transistor gate. MOSFETs are usually not created using III-V semiconductors because the native oxide for these materials is of poor quality\(^{10}\) and therefore the relatively high density of defects in the oxide and at the oxide/semiconductor interface affects the DC and AC performance of the device. However, there have been attempts to create MOSFETs using oxides that have been deposited via other methods, such as chemical vapor deposition and molecular beam epitaxy. Johnson, et al.\(^ {11}\) have demonstrated a Gd\(_2\)O\(_3\)/GaN MOSFET grown by plasma-assisted O source MBE and observe a high concentration of dislocations due to the oxide/GaN mismatch.

HFETs and HEMTs created from AlGaN/GaN have shown great performance in recent years, with power outputs of up to 9.8 W/mm at 8 GHz.\(^ {12}\) These device structures take advantage of the piezoelectric properties of the strained AlGaN film grown on GaN which forms a two-dimensional electron gas (2DEG) at the AlGaN/GaN interface. More about the piezoelectric properties of AlGaN and GaN will be discussed in the following paragraphs. HFETs and HEMTs can presently be consistently produced with room temperature mobilities in the range of 1400-1600 cm\(^2/V/s\) and 10\(^ {13}\) cm\(^{-2}\) sheet charge density.\(^ {13}\) Record high mobilities of the two dimensional electron gas (2DEG) at the AlGaN/GaN interface have been reported.\(^ {14,15}\) The potential for these devices has been well documented\(^ {2,5,16}\), but significant work is needed in order to make the technology viable in the marketplace. Electronic traps in the material limit the microwave
performance of the device. These traps may be due to dislocations, surface states, or deep level defects in the AlGaN layer or the buffer layer. Surface passivation has been shown to dramatically improve the microwave characteristics of AlGaN/GaN HFETs.\textsuperscript{17} However, there is evidence that DC current collapse is related to traps in the GaN buffer and that observed gate lag is associated with the surface of the device. C-related deep levels, similar in ionization energy to the famous yellow luminescence YL defect band, in the semi-insulating GaN buffer layer have been suggested to be the cause of the DC current collapse in AlGaN/GaN HFETs.\textsuperscript{18} This DC current collapse and hysteresis has been reported after hundreds of hours of stress, but cannot be totally eliminated by surface passivation. According to H. Dietrich from the Office of Naval Research, the next phase of HFET research will involve the optimization of HFET surfaces and interfaces.

The YL defect luminescence band has been observed in many GaN and AlGaN samples grown by MBE and MOCVD. Native point defects,\textsuperscript{19} residual impurities,\textsuperscript{20} and dislocations\textsuperscript{21} in the material have been attributed to possible YL causes. Calculations by Neugebauer, \textit{et al.} and positron annihilation spectroscopy (PAS) experiments\textsuperscript{22} have shown that Ga vacancies (V\textsubscript{Ga}) are most likely the deep level involved in the YL. Recent investigations by Hsu, \textit{et al.} using two-photon excitation have determined that the spatial distribution of YL in GaN was uniform and therefore independent of dislocations.\textsuperscript{23} Whether or not residual impurities have a role to play in the YL of GaN is still a matter of debate, but the currently accepted theory is that the YL involves a transition from a deep acceptor (V\textsubscript{Ga}) and a shallow donor (V\textsubscript{N, SiGa, O\textsubscript{N}}).
The 2DEG is formed with the assistance of the piezoelectric effect of the strained AlGaN barrier layer grown on the GaN buffer layer. The nitride system exhibits a higher amount of polarization (spontaneous and piezoelectric) than other conventional III-Vs by about an order of magnitude. For AlGaN alloys, the values of the piezoelectric and spontaneous polarization constants increase as the Al mole fraction is increased. Strain of AlGaN layer in the c-axis direction grown on a relaxed GaN buffer induces polarization sheet charges at the AlGaN surfaces. The polarity of these sheet charges depends on the orientation of the AlGaN layer. Figure 1.2 shows a diagram of the wurtzite AlGaN lattice and HFET layer structure and the directions of the polarization vectors for Ga- and N-face material. Part b) of this figure shows the location and polarity of the polarization sheet charges for each material face. The leftmost (Ga-face) arrangement is usually employed in HFET device applications. Free electrons tend to compensate the positive polarization sheet charge that forms at the lower AlGaN/GaN interface and, as a result, a two-dimensional electron gas (2DEG) may form near this interface. Also shown on the left side of Figure 1.2 is an AlN (or AlGaN) nucleation layer. The growth of this layer before GaN or AlGaN growth has been shown to define the polarity of the upper layers as Ga(Al)-face. This choice in growth provides opportunities to position the 2DEG at the interface desired by the device engineer.
Figure 1.2. Diagram of the effect of piezoelectric strain on the 2DEG position in an AlGaN/GaN HFET layered structure. Part a) shows the AlGaN wurtzite lattice for Ga (or Al)-face and N-face material in which the direction of the piezoelectric and spontaneous polarization vectors pointing along the c-axis depend on the face of the material. Part b) shows the distribution of polarization-induced sheet charges as a function of material face. The addition of an AlN or AlGaN buffer layer can control the polarity.

The resulting band diagrams for Ga-polar and N-polar AlGaN films are shown in Figure 1.3. In this figure, part (a) shows the desired band diagram for an AlGaN/GaN HFET device utilizing a 2DEG. From this band diagram, it is apparent that there is a large concentration of electrons confined near the AlGaN/GaN interface that produces a high-mobility, high carrier density channel that is desired for high-power and high-frequency HFET device applications. For N-polar AlGaN, a two-dimensional hole gas may form if holes are present (p-type GaN). This band diagram is shown in parts (b) and
(c) of Figure 1.3. This arrangement is not as good for HFET operation for a couple of reasons. First, the hole mobility in the nitride system is much lower than the electron mobility ($\mu_h=30 \text{ cm}^2/\text{Vs}$, $\mu_e=1000\text{ cm}^2/\text{Vs}$ for GaN). Second, creating p-type GaN is more of a challenge than creating n-type GaN because of compensation by native n-type defects in GaN and AlGaN. Shur, et al. have shown that a 2D hole gas can only be achieved for sheet densities higher than $\sim10^{13} \text{ cm}^{-2}$ and that the accumulation of such a hole layer could be applied to limit the AlGaN/GaN heterojunction bipolar transistor spreading resistance.
Figure 1.3. Band diagrams for AlGaN/GaN HFET structures with different Ga- and N-polarity. Part a) represents the desired band alignment with the accumulation of a high carrier density 2DEG at the AlGaN/GaN interface. It is also possible to achieve a hole gas with N-polar materials as shown in parts b) and c).

Growth morphology and interface roughness can potentially impact the 2DEG transport properties, and dislocations present due to the lack of well-matched substrates can affect surface morphology and electronic transport properties. Several studies have shown that Ga-rich MBE growth conditions produce higher quality AlGaN and GaN material than N-rich MBE material where an abrupt change in the surface morphology of GaN films occurs between these growth regimes. One such study found that MBE AlGaN films grown under N-rich conditions had an order of magnitude greater density of
dislocations than that of Ga-rich AlGaN films and that even though Ga-rich films had higher compositional disorder, they had higher photoluminescence efficiency and a lower concentration of non-radiative defects.\textsuperscript{34} Improvements in the reduction of these anomalous features could greatly improve AlGaN/GaN HFET performance and push these devices into high production instead of in relatively small batches for custom high-performance applications military and commercial applications.

1.3 Si Doping of High Al Content AlGaN

Successful doping of III-Nitride materials is required for the realization of many types of devices. For example, the cladding layers which surround the active regions of III-Nitride laser diodes are usually n-type or p-type AlGaN of higher Al mole fraction for transmission of shorter wavelengths. Similar cladding layers are used for UV photodetectors. Also, modulation doping of AlGaN/GaN HEMTs is sometimes employed by using a Si-doped layer of GaN or AlGaN near the desired 2DEG channel with excellent high-frequency characteristics.\textsuperscript{35} Unintentional n-type conduction is well documented for Al\textsubscript{x}Ga\textsubscript{1-x}N alloys and has been attributed to nitrogen vacancies (V\textsubscript{N}) or impurities such as oxygen.\textsuperscript{36} However, it has been shown recently that the V\textsubscript{N} formation energy is high for n-type GaN and AlN and therefore nitrogen vacancies will not form in high concentrations.\textsuperscript{37} A recent study by Nepal, et al.\textsuperscript{38} showed that V\textsubscript{N} in AlN have a large donor binding energy (260-300 meV) and therefore would not make a significant contribution to n-type doping of AlN. Intrinsic Al\textsubscript{x}Ga\textsubscript{1-x}N is also known to significantly drop in conductivity for increasing mole fraction, particularly for x>0.4.\textsuperscript{39} This decrease in conductivity for mole fractions greater that 0.4 also correlates with a large increase in the carrier localization energy.\textsuperscript{40} Also, for n-type samples doped with oxygen the shallow
oxygen donor is converted to a deep level by a DX transition for $x>0.4$.\footnote{41} Oxygen potentially poses a serious problem in the successful doping of high Al content Al$_x$Ga$_{1-x}$N since Al has a large affinity for oxygen and is a common contaminant during growth. This deep level can act as a compensating center and compete with intentional doping. Youngman and Harris have attributed deep level emissions in AlN to oxygen related defects.\footnote{42} Also, Youngman and Harris have found that the way that oxygen is incorporated in the lattice depends on the concentration of oxygen. For the lowest levels of oxygen incorporation, the oxygen is associated with an aluminum vacancy ($V_{\text{Al}}$). As the oxygen level is increased above 0.75%, the defect changes to Al atoms octahedrally coordinated with oxygen. This octahedral configuration leads to stacking faults and inversion domain boundaries and thus extended defects arise. The impact of these oxygen-related defects on the conduction properties and luminescence characteristics of AlGaN are relatively unexplored.
Silicon is the most widely used n-type dopant in the Al$_x$Ga$_{1-x}$N ternary system. For n-GaN, the Si donor level has been established to be near 20 meV. The Si donor energy increases with increasing $x_{Al}$ because of the smaller dielectric constant of AlN than GaN and the larger effective mass of the electron in AlN. However, the degree to which the Si donor energy changes with increasing mole fraction is disputed. Figure 1.4 shows the experimental and theoretical Si donor energies as a function of Al mole fraction. Some groups report that Si forms a localized deep level or DX state for higher mole fractions of Al$_x$Ga$_{1-x}$N while others report shallow Si donors up to AlN. Stutzmann, et al. have shown that the conductivity activation energies for $x_{Al}$=0.8 and $x_{Al}$=1.0 Si-doped Al$_x$Ga$_{1-x}$N alloys are 250 meV and 320 meV, respectively. These activation
energies are shown on the graph of Figure 1.4. A theory that states that the high frequency dielectric constant of a material must be used instead of the static dielectric constant when the donor ionization energy is larger than the transverse optical phonon energy has been applied by Hwang, et al. to explain the sudden change of Si ionization energy to the high values reported by Stutzmann for Al mole fractions greater than ~0.8. The previous figure shows these TO phonon energies as a function of Al mole fraction. A large increase in the Si activation energy has also been reported for mole fractions above 80% by Taniyasu, et al., although they only report a donor ionization energy of 86 meV for AlN—considerably less than the value by Stutzmann.

Native defects in GaN and AlN alloys play a role in determining the level of conductivity across the Al alloy range. In particular, gallium vacancies are known to be deep acceptors in GaN. For Al containing alloys, aluminum vacancies play a similar role as being deep acceptors in AlGaN and AlN. These deep acceptors can be singly, doubly, and triply ionized and potentially compensate one, two, or three ionized donors. As mentioned previously, $V_{Al}$ are formed when O is incorporated into AlN and AlGaN. Wagener, et al. show that the second and third ionization states of the Al vacancies degrade the n-type conductivity of Si-doped AlGaN up to an Al mole fraction of at least 50%.48

There have been various amounts of success in using Si as an n-type dopant in Al$_x$Ga$_{1-x}$N. Intentional n-type doping with Si has been reported for Al$_x$Ga$_{1-x}$N with x<0.5 with electron concentrations of over $10^{19}$ cm$^{-3}$ for MBE grown films.49 Taniyasu, et al. report carrier concentrations on the order of $5x10^{18}$ cm$^{-3}$ for Al$_{0.49}$Ga$_{0.51}$N films and $9.5x10^{16}$ cm$^{-3}$ for AlN, which is remarkable for pure AlN.50 Nam, et al. achieve $6.2x10^{17}$
cm$^3$ electron density for $x_{\text{Al}}=0.7$ and 2.1x10$^{18}$ cm$^3$ electron density for $x_{\text{Al}}=0.65$ for MBE grown films.$^{51}$ MBE Al$_x$Ga$_{1-x}$N from Cornell University (analyzed in this research) has produced electron concentrations of 8.5x10$^{19}$ cm$^3$ for $x_{\text{Al}}=0.8$ and electron concentrations of 1.25x10$^{20}$ cm$^3$ for $x_{\text{Al}}=0.5$. $^{52}$

1.4 Schottky Contacts to AlGaN

1.4.1 Metal-Semiconductor Contacts

In order to create a semiconductor device, an electrical contact to the semiconductor must be made. Braun discovered the first metal-semiconductor contact in 1874 without a good understanding of the physical principles.$^{53}$ Many theories over the years have been presented and only the most commonly accepted theories will be presented. Two of the most popular theories believed to govern the metal-semiconductor contact properties are the Schottky and Bardeen models.

According to the Schottky theory, the Schottky barrier height, $\phi_B$, only depends on the difference between the work function of the contact metal ($\phi_M$) and the electron affinity of the semiconductor ($\chi$) as described by the following equation.

$$\phi_B = \phi_M - \chi$$  \hspace{1cm} (1)

Figure 1.5 shows the metal and semiconductor band alignments before and after contact for three separate cases. For the Schottky model, the Fermi levels of the metal and semiconductor align after contact due to charge transfer thus bending the bands of the semiconductor because of the resulting majority carrier depletion. In part (c) of this
particular diagram, the work function of metal is such that it causes an upward band bending in the semiconductor because the work function of the metal is greater than that of the semiconductor. Depending on the difference between the work functions of the semiconductor and the metal, one may obtain final band alignments as in case (a) showing accumulation and as in case (b) showing the flat band condition. The accumulation case is ideal for ohmic contacts which do not, by definition, show appreciable rectifying behavior.

![Figure 1.5. Band diagram of Schottky contact assuming the Schottky model for three different metal work functions. Part (a) represents accumulation for n-type materials, which is desired for ohmic contact formation. Part (b) represents the flat band condition. Part (c) shows depletion of electrons with the Schottky barrier and the depletion region noted on the diagram.](image)

Based on the Schottky theory, the Schottky barrier height is independent of the semiconductor doping. The carrier transport properties across the barrier can, however, be strongly affected by the doping level of the semiconductor. These current transport mechanisms will be discussed later.
It is usually quite difficult to vary the Schottky barrier by changing the work function of the contact metal because a phenomenon called *Fermi level pinning* tends to occur at the metal/semiconductor interface. The details of this pinning of the Fermi level are still controversial, but it is clear that imperfections at this interface and semiconductor surface states play an important role. This leads into a theory proposed by Bardeen\(^5\) that highlights the impact of surface states on the Schottky barrier height. The following figure shows states that are at the metal semiconductor interface and the very thin interfacial layer that is proposed to be involved in the surface states. In this case, the equation for the effective Schottky barrier height is much more complicated than the relationship derived from the Schottky theory.

![Schottky band diagram](image)

Figure 1.6. Schottky band diagram showing the impact of surface states and an interface oxide on the Schottky barrier height.
1.4.2 Schottky Contact Applications

A Schottky contact to a semiconductor differs from that of an ohmic contact in that the I-V characteristics of the Schottky contact exhibit diode-like rectifying behavior while an ohmic contact has linear or quasi-linear I-V characteristics. For typical device scenarios, a Schottky contact is used either as a diode for current rectifying or photodetection or carrier depletion region modulation in the semiconductor beneath the Schottky contact. Specifically, Schottky contacts are used to control the channel conductivity in MESFETs and HFETs as described previously in the AlGaN HFET section.

1.4.3 Variations of Schottky barriers to Nitrides

For GaN and AlGaN, several metals have been used for Schottky contacts. Platinum is shown to have the highest Schottky barrier values for GaN (~1.1 eV)\(^{56}\) while titanium tends to have the lowest for GaN (0.6 eV).\(^{57}\) However, other metals such as Ni tend to have a range of Schottky barrier heights. Different processing techniques, semiconductor surface treatments, surface roughness, local composition fluctuations, and film defects all affect the consistency of the barrier height. The effect of several types of surface processing on the GaN Schottky barrier height has been examined in recent studies, including plasma cleaning, UHV annealing/cleaning, wet chemical etches and treatments, interfacial oxides, electrochemical treatment, and sputtering.\(^{7,58,59,60,61,62}\) There have been several studies dealing with the Schottky barrier height of metals on AlGaN alloys of various Al mole fractions,\(^{63,64,65,66,67}\) but little work on the effect of processing conditions on the Schottky barrier height for the AlGaN system has been
The Schottky barrier height on AlGaN with increasing Al content is believed to increase, but the extent to which it increases is not entirely known.

1.4.4 Schottky Current Transport

Current transport across the Schottky barrier is ideally modeled using the theory of thermionic emission: \(^{68,69}\)

\[
I = I_s \left( \exp \left( \frac{\beta V_a}{n} \right) - 1 \right) \tag{2}
\]

where \(\beta = \frac{q}{k_B T}\) and the saturation current is given by:

\[
I_s = A^* A T^2 \exp(-\beta \phi_B) \tag{3}
\]

In this equation, \(A^*\) is the Richardson constant, \(A\) is the area of the diode, \(T\) is the temperature, and \(\phi_B\) is the Schottky barrier height. In these equations, \(n\) is called the ideality factor because it quantifies the deviation of the I-V curve from the ideal thermionic emission theory. The Richardson’s constant is defined by the relation \(A^* = 4\pi q k_B^2 m^*/h^3\) and in practice will deviate from the theoretical value. This constant may be found from a current-temperature measurement of the Schottky diode. From the equation for the saturation current one may see that increasing the Schottky barrier will reduce the saturation current (and therefore the reverse current) exponentially. The Schottky barrier energy band diagram for n-type semiconductors is shown in the following diagram. In Figure 1.7, two Schottky barriers are shown: \(q\phi_B\) and \(q\phi_{B0}\). The latter Schottky barrier represents the effective barrier due to the phenomenon of image
force lowering. Image force lowering, also known as the Schottky effect, is due to the formation of an image potential from an induced image charge in the metal under an applied electric field in the semiconductor. This potential interacts with the free electrons in such a way as to lower the barrier and the change in the effective barrier is not usually large.

Figure 1.7. Schottky barrier energy band diagram for an n-type semiconductor. The two Schottky barriers $q\phi_B$ and $q\phi_{B0}$ represent the ideal barrier and the effective barrier due to image force lowering, respectively.

From Figure 1.7, it is evident that the current in a Schottky barrier device is dominated by the majority carrier (electrons in this case) since it is the majority carriers that overcome the Schottky barrier from the semiconductor into the metal. This is true, however, only for low-injection conditions. For large forward biases, the minority carrier injection ratio (ratio of current due to minority carriers relative to the total diode current) may be significant. However, this effect is usually ignored because the rectifying nature of the Schottky barrier is emphasized in most devices.
As aforementioned, the ideality factor encompasses all of the deviations from the ideal thermionic emission. An increase in ideality can come from a variety of processes such as Schottky contact non-uniformity, tunneling through the Schottky barrier, interface recombination and trapping of carriers, recombination and generation within the space charge region, and barriers in series due to heterojunctions.\textsuperscript{69,70,71} Shah, \textit{et al.} have shown that the ideality factors due to carrier transport across a metal-semiconductor junction, a unipolar heterojunction, and a p-n junction would add linearly to increase the total ideality factor—which they use to explain the high idealities observed in GaN/AlGaN p-n junctions.

Schottky barrier carrier transport and barrier height are known to change with the addition of Al to GaN. Foremost, the Schottky barrier is expected to increase with increasing Al mole fraction due to the decreasing electron affinity of the alloy (GaN, \(\chi=4.2\) eV; AlN, \(\chi=2.05\) eV\textsuperscript{64,72}). It has been reported that Schottky contacts to GaN are not pinned by interface states, but it is unclear whether this hold true with the addition of Al. The ideality factor is observed to increase with the addition of Al, as will be described in the Chapter 5 discussion, due to a drastic deviation of thermionic emission theory.

1.5 Research Outline

The research objective is to correlate the electronic properties of AlGaN thin-film HFET structures and AlGaN:Si bulk films measured with LEEN spectroscopy and chemical information measured by SIMS and AES in order to develop an understanding of the nature of defects in these systems and how the defects relate to HFET electrical properties and AlGaN doping. An understanding of this relationship will have a positive
impact on the electronic material and device community. Another research thrust is to use these characterization techniques along with Internal photoemission spectroscopy (IPE) to examine the role of surface processing on the Ni/AlGaN/GaN Schottky barrier structure. These experimental techniques will be described in detail in the following section. Some of the issues that will be addressed in this research include:

- Relationship between deep levels, surface morphology, electronic properties, and chemical composition in AlGaN/GaN HFET structures.
- Role of impurities and associated defect states in the successful doping of high Al mole fraction AlGaN.
- Nature of Si donor in high Al mole fraction AlGaN.
- Role of impurities in the electronic properties of AlGaN/GaN HFET structures.
- Effect of surface preparation, defects, and impurities on the formation of Schottky barriers on AlGaN.
2.1 Cathodoluminescence

Cathodoluminescence (CL) is based on light emission from a sample excited by an electron beam. Typically, the emitted photons are resolved spectroscopically with a monochromator and a suitable photodetector. However, panchromatic CL is also used in some imaging applications. CL is related to photoluminescence—a common semiconductor characterization tool based on photon excitation—in that comparing each technique should yield similar results with the exception of some differences related to the specifics of the electron-hole pair generation processes. CL has many advantages as a characterization tool. A major strength of the CL technique is the ability to produce images that have high spatial resolution when used in a scanning electron microscope. Spectroscopic and imaging CL is commonly used in the fields of petrology and gemology, as well as in semiconductor characterization. Another great advantage of CL is the ability to obtain depth resolved spectral information by varying the electron acceleration voltage, as discussed in the following section. A disadvantage of this technique is the difficulty in the extraction of quantitative data from the CL results because of the dependence of the recombination processes on many factors, such as free carrier density, temperature, and local material non-uniformity. Of course, non-radiative
recombination mechanisms cannot be observed with the CL technique, thus revealing another limitation of CL. Non-radiative recombination characterization may be achieved by other methods, such as deep level transient spectroscopy (DLTS).

Many electron-hole pairs (EHPs) are produced per incident electron during typical cathodoluminescence conditions. The ionization energy \( E_i \) of the material is related to the band gap through the relation \( E_i = 2.8 \, E_g + M \). \(^{78} \) \( E_g \) is the band gap of the semiconductor in eV and \( M \) is a parameter in the range between 0 and 1 eV that is dependent on the material, not the electron beam energy. An improved expression for the local generation rate of EHPs per second is given by: \(^{79} \)

\[
G = \frac{V_b I_b (1 - \gamma)}{eE_i} = \frac{V_b I_b Q(1 - \gamma)}{eE_g}
\]  

(4)

where \( V_b \) and \( I_b \) are the electron beam voltage and current, respectively, \( E_i \) is the ionization energy, \( e \) is the electronic charge, \( E_g \) is the material band gap, \( Q \) is the EHP generation quantum efficiency, and \( \gamma \) is the fraction of the electron beam energy that is lost due to electron backscattering. Using this relationship, one can estimate the number of EHPs generated per incident electron by the ratio \( E_b/E_i \), where \( E_b \) is the electron beam energy in eV. For typical electron beam energies of 1-30 keV, this results in a very large number of EHPs being produced which can excite all luminescence mechanisms and therefore allows a greater probability in detecting luminescence from states which could not be easily detected by other methods. CL is also used with the sample at low temperatures (down to liquid helium temperatures) to enhance the signal to noise ratio and reduce thermal broadening.\(^{73,74} \) Also, the CL emission can be improved with higher beam currents, but sample heating and damage can occur.
2.2 LEEN Spectroscopy

Besides its high resolution imaging capability, a major strength of CL is the ability to take advantage of the electron beam penetration dependence on $E_b$ to probe electronic states versus depth. This non-destructive technique of depth profiling electronic states has been used with much success.\textsuperscript{80,81,82,83} This CL method utilizing a varying electron beam energy is known as Low Energy Electron-excited Nanoluminescence (LEEN) spectroscopy to stress the surface-sensitive nature of the technique. For very small electron beam energies, the electron penetration depth is quite surface sensitive and, in fact, can be as shallow as a few tens of angstroms.\textsuperscript{84} This is relevant to current methods of device processing and technology because many device structures such as HFETs and quantum wells have layer thicknesses on this scale. Everhart and Hoff\textsuperscript{85} introduced a fairly simple analytical approach to modeling the electron energy loss as a function of incident electron energy that is fairly accurate for electron probe energies in the range 1-25 keV and for low atomic numbers. However, this model begins to break down for very low electron probe energies and other methods such as Monte Carlo computer simulations are needed.

The Everhart-Hoff model begins with a relation for the electron energy loss per unit path length:

$$\frac{-\partial E}{\partial s} = \left(2\pi N_A e^4 \frac{Z \rho}{A}\right) \left[ \frac{1}{E} \ln \left( \frac{aE}{I} \right) \right]$$

where $N_A$ is Avogadro’s number, $e$ is the electronic charge, $Z$ is the atomic number, $A$ is the gram atomic weight, $\rho$ is the material density, $I$ is the mean excitation energy ($Z$
dependent), E is the electron energy, and a is a constant equal to 1.1658. The theoretical maximum range (R_B) for an incident electron is:

\[
R_B = \int_0^\xi \frac{\partial E}{\partial \rho(\rho_n)} = \int_0^{E_B} \frac{\xi \partial (\xi)}{\ln(\xi)}
\]  

(6)

with \( \xi = aE/I \). The factor \( \xi \) determines which empirical range formulas can be used since the model breaks down at low energies as the integral goes to infinity as \( \xi \) approaches 1.

Everhart and Hoff propose a universal depth dose function to generate depth dose curves for different electron probe energies. This function \( g(z) \) is empirically derived and is a third order polynomial \( g(z) = 0.60 + 6.21z - 12.40z^2 + 5.69z^3 \), where \( z \) is the depth normalized to \( R_B \) and is in the range 0<z<1. The electron range and low energy electron energy loss curves from the Everhart-Hoff model for GaN are shown in Figure 2.1. An electron probe energy of 0.5 keV is very surface sensitive with almost all of the electron energy loss occurring in the top five nanometers while higher probe energies at, say 2.0 keV, are able to probe down to a depth of 70 nanometers.
Figure 2.1 Electron range (left) and energy loss curves (right) using the Everhart-Hoff model of electron beam interactions in GaN. Low electron acceleration energies generate electron-hole pairs within the topmost tens of nanometers.

Modern methods of determining the nature of electron trajectories and energy loss in solids are based on Monte Carlo simulations. The simulations depend strongly on material density, which is directly related to the electron scattering cross-section of the material, and the energy loss per collision. A random number generator determines an electron scattering angle and the computer subtracts energy from the electron until the electron comes to rest in the solid. Then, the computer repeats the process by randomly generating the next electron’s scattering angle and so on. CASINO is a widely used shareware program that was developed to understand the electron/solid interaction. The user is able to select from many different models to model this interaction and the program supports and unlimited number of layers. CASINO has been used to model the
electron-solid interaction in the preliminary results of this research and tend to agree with the analytical predictions of the Everhart-Hoff model.

2.3 Auger Electron Spectroscopy

Auger Electron Spectroscopy (AES) is a method for determining the surface chemical composition of materials. This technique is based on a three-electron process where an incident electron ionizes a core level electron and then an electron in a higher energy shell then relaxes to the energy level of the ionized core electron. To conserve energy and momentum, some of the energy of the relaxed electron is then transferred to a third electron and this electron is emitted from the solid and is known as an Auger electron. The Auger electrons (as well as secondary electrons) are collected with an electron energy analyzer and the number of electron counts versus electron energy is recorded. The energies of the Auger electrons are characteristic of the atomic core energy levels and are thus useful in determining the elements present at the surface. Since the escape depth of typical Auger electrons is less than 3 nm\textsuperscript{88}, this technique is very surface sensitive and therefore ultra-high vacuum conditions are necessary to control the deposition of contaminants on the sample surface in order to properly analyze the specimen. However, this technique is routinely used to determine if there are indeed surface contaminants such as carbon and oxygen on the sample surface. AES is sensitive to compositions on the order of 1% and therefore typical dopants and bulk impurities cannot be observed. By using an inert sputter species such as argon, one can perform AES as a function of sputtering time to produce an Auger depth profile (ADP) in order to generate a profile of atomic species. Zinner\textsuperscript{89} has described some of the problems that must be taken into account with the interpretation of ADP scans due to sputter-specific
effects. These include preferential sputtering of species, redeposition of the sputtered material, sputter rate variation for different layers, sputter-induced mixing of species, and charging due to the sputter ions.

The following figure shows a representative AES spectrum of GaN. AES spectra are usually displayed in differential form, that is, the derivative of the N(E) spectrum or the E⋅N(E) spectrum. This spectrum also shows contaminant peaks from C and O along with the N and Ga peaks.

![AES Spectrum of GaN](image)

Figure 2.2. Representative differential Auger electron spectroscopy spectrum of GaN. The spectra also shows C and O peaks due to surface contamination.

Quantitative AES is difficult for several reasons. The response of the electron energy analyzer varies from instrument to instrument and therefore a careful calibration must be done for each instrument. Accuracies of quantitative analysis are on the order of 10% for calibrated standards with a measurement precision of 5% for semiconductors. Also, shifts in the AES energy levels can occur depending on matrix conditions such as
strain, chemical bonding, and impurity elements. Insulating samples also pose a problem since accumulated charge creates electric fields which alter the electron emission and collection efficiency. Relative sensitivity factors have been computed for many elements and can be found in books and tables which allow the user to get an approximate quantitative AES measurement.

2.4 Secondary Electron Microscopy

The scanning electron microscope (SEM) is commonly used in semiconductor characterization. An electron beam, or probe, is rastered over the sample surface and secondary electrons are collected in order to form a secondary electron image. Secondary electrons are usually collected with an Everhart-Thornley detector, which is based on a scintillation material that emits light when secondary electrons impinge on it. This light is guided to a photomultiplier tube (PMT) and the detected signal is used in conjunction with the electron probe rastering signal to form an image. The size of the electron probe defines the image resolution. An advantage of an SEM is the fact that one can achieve high resolution imaging in conjunction with other electron probe analysis techniques such as CL and LEEN (as discussed above), Auger electron spectroscopy (AES), electron beam induced current (EBIC), electron probe microanalysis, and voltage contrast. As with all electron beam techniques, a vacuum is required. Different types of SEMs have different specimen chamber vacuum ranges, but usually microscopes in which AES analysis is implemented require UHV (<10⁻⁹ torr). These microscopes are known as Auger microprobes.
A JEOL JAMP 7800F field emission Auger microprobe with Oxford MonoCL cathodoluminescence attachment is part of the Nanoscale Materials Laboratory at Ohio State University. The electron acceleration voltages can be varied in the range 0.1 keV to 25 keV with variable beam currents between $10^{-11}$ A and $10^{-8}$ A. The best secondary electron image resolution (~5 nm) occurs at 25 keV and smaller currents. There are two sample stages which can be interchanged: a variable high-tilt stage from JEOL designed for AES and high contrast secondary electron imaging and a liquid helium stage from Oxford Instruments capable of temperature dependent analysis from 10 K to 300 K. The CL apparatus includes a parabolic mirror that collects light from the sample and collimates the light into a grating monochromator. The monochromator is equipped with two gratings: one optimized for the UV/visible spectral regions and one optimized for the near IR/IR regions. Light exiting the monochromator is focused either on a photomultiplier tube or a liquid nitrogen cooled germanium detector, depending on the spectral area of interest. The MonoCL system also allows one to perform CL images in both a monochromatic and panchromatic fashion.
Figure 2.3. Schematic of JEOL JAMP-7800F with Oxford MonoCL cathodoluminescence attachment (not to scale). Light is collected using an \textit{in situ} parabolic mirror and focused into a grating monochromator for spectroscopic analysis. The hemispherical electron analyzer that is used to detect Auger electrons is also labeled.

In addition to secondary electron imaging and CL/LEEN, the system includes a hemispherical electron energy analyzer to detect Auger electrons for surface-sensitive elemental analysis for a particular spot or for imaging of elemental species. This is a powerful tool for semiconductor device analysis and high-resolution chemical mapping with nominal AES resolution on the order of 25 nm. An argon (Ar$^+$) ion sputter gun is also aligned to the analysis position for sputtering the specimen for charge compensation of insulating samples or Auger depth profiling (ADP). This ion etching tool is capable of
very low accelerating voltages (tens of volts) for charge neutralization of insulating samples both during analysis and before each analysis cycle. Typical sputter energies for the Ar ion etching devices are 4 keV for fast sputtering and 200-500 eV for slower sputtering. The sample stage may be rotated during sputtering using a technique called Zalar rotation. This technique increases the uniformity of the sputter crater thus reducing sputter-induced mixing and increasing the depth resolution of the Auger depth profile.

2.5 Secondary Ion Mass Spectrometry

Secondary Ion Mass Spectrometry (SIMS) is a powerful analytical technique for semiconductor characterization. This technique can detect all elements along with different elemental isotopes and molecules. SIMS is one of the most sensitive techniques used in semiconductor characterization and has detection limits for some elements in the range of $10^{14}$-$10^{15}$ cm$^{-3}$. SIMS is based on the removal of sample material and analyzing the masses of the removed material using a mass analyzer. Needless to say this is a destructive technique. SIMS is able to detect both activated and unactivated dopants that reside on any crystal lattice site and this information, combined with electrical techniques, can give insight into dopant diffusion and impurity activation. A primary ion beam (i.e., Ga) of typical energy 10-25 keV is focused on the sample and material is removed by sputtering. A very small fraction (~1%) of the ejected species is ionized either positively or negatively and can thus be collected by the extraction plates, which are biased to focus the secondary ions into the mass analyzer and the mass/charge ratio is recorded. Depending on the sample and extraction plate bias, SIMS can detect positive or negative ions. During the sputtering process, the primary ion tends to come to rest
within tens of nanometers of the sample surface, resulting in some degree of ion implantation. The escape depth of the sputtered secondary ions is on the order of a few monolayers for typical primary ion energies. This shallow escape depth leads to a very surface sensitive measurement of composition. The details of the sputtering process is quite complicated and will not be presented here, but it should be noted that different elements have different sputter yields per primary ion and these sputter yields can depend on the energy and angle of incidence of the primary ions, the crystal orientation of the sample, and the composition of the target material. SIMS is typically used in one of two modes: static or dynamic SIMS. Static SIMS uses very low primary ion currents and/or energies to probe the mass spectrum of the near surface region. Static SIMS is relatively non-destructive (compared to dynamic SIMS) in that little of the surface material is removed, but primary ions are implanted and some disorder does occur. Dynamic SIMS uses a higher sputter rate to depth profile samples and to acquire a total mass spectrum or the ion yield of particular masses of interest versus sputter depth. It should be noted that a total mass spectrum during a dynamic SIMS experiment is usually only acquired using time-of-flight SIMS since other SIMS methods acquire mass data much slower. Some of these other techniques will be discussed later.

It is important to realize that the secondary ion yield, not the sputter yield, is important in the SIMS process since only charged species can be detected. Several factors influence the secondary ion yield of elemental and molecular species. Sputtering the sample with electropositive or electronegative ions, typically Cs\(^+\) (negative ion yield) or O\(_2\)^+ (positive ion yield), respectively, can enhance the secondary ion yield of species of
opposite electronegativity. The periodic table shown in the following figure illustrates the elemental species that have either a dominant negative or positive ion yield.

Figure 2.4. Periodic table of the elements that shows the dominant secondary ion polarity (positive or negative SIMS) typically used for analysis. Oxygen sputtering is typically used to enhance the yield of positive ions while cesium is typically used to enhance the negative ion yield.

The secondary ion yield of a particular species is also dependent on the resident matrix. This is known as the matrix effect. For example, the Si ion yield in an SiO₂ matrix is approximately 100 times greater than the Si ion yield in crystalline Si. The relative sensitivity factors, or RSFs, for the elements in a Si matrix are shown in the following two figures. By definition, a low relative sensitivity factor means high ion sensitivity. Relative sensitivity factors and the methods used to determine them will be discussed in a later section. The purpose of these tables is to show that there are wide variations in ion sensitivity across the periodic table and as a function of secondary ion polarity. This observed variation stresses the fact that calibrated standards must be used
for a given matrix in order to perform quantitative measurements of atomic composition.

These calibrated standards are usually prepared by implanting impurity ions in a particular matrix. This calibration procedure will be discussed later in this document.

Figure 2.5. Relative sensitivity factors for the elements in a Si matrix with cesium primary ion bombardment and collecting negative ions. Low sensitivity factors mean high sensitivity of the species.
A Physical Electronics TRIFT III time-of-flight SIMS is available for use in the Nanoscale Materials Laboratory at Ohio State University. The primary ion beam is a liquid metal ion gun (LMIG), which uses gallium at energies of 15 keV to sputter the surface during the analysis cycle. A dual-source sputter column includes Cs\(^+\) and O\(_2\)\(^+\) for sputter depth profiling during the sputter cycle and electropositive and electronegative secondary ion yield enhancement. The specimen chamber and ion flight chamber are both maintained at UHV pressures. The TOF-SIMS technique gives much better mass resolution when compared with other types of SIMS techniques but has lower secondary ion signals because of the lower analysis beam currents employed.
Figure 2.7 shows a schematic of the PHI Trift III ion flight path. Primary ions composed of isotopically pure $^{69}$Ga$^+$ are pulsed and accelerated toward the sample. Secondary ions that are emitted from the sample are collected and filtered with the pre-spectrometer blanker. This component is composed of a set of biased plates that can selectively blank high ion masses for improved dynamic range. Secondary electrons can be diverted to the secondary electron detector (SED) for simultaneous imaging of the secondary ions and electrons. After the ions pass through the contrast diaphragm which reduces high angular dispersion ions, the ions pass through a series of electrostatic lenses (ESA) which guide the ion pulse through the flight tube. Along the way, the ions pass through a slit that, when inserted, can remove low energy metastable ions and thereby improve the detection limits of the instrument by lowering the background counts. Near
the end of the flight tube, the ions pass through the post-spectrometer blanker. This blanker has the ability to blank specific masses from entering the detector. Finally, the ions hit the detector and are time-resolved to determine their masses.

2.6 Current-Voltage Measurements: Schottky Contact Characterization

Current-voltage measurements (I-V) are a common method of device characterization, especially for the characterization of Schottky diodes and field-effect transistors. In essence, a voltage is varied across the device and the resulting currents are measured. An HP 4145B semiconductor parameter analyzer was employed to characterize the ohmic and Schottky contacts. In some cases when the HP 4145B was not available, a Keithley 2400 programmable sourcing meter and custom LabView data acquisition programming was used to measure the I-V characteristics.

Current-voltage measurements can be used to characterize the carrier transport properties across a semiconductor-metal interface. As mentioned previously in the Introduction and Background, current transport across an ideal Schottky barrier is described by thermionic emission theory. The equation for thermionic emission was also shown. The log of the forward current can be linearly fit and the ideality factor, \( n \), of the diode can be extracted from the slope. Also, assuming a value for the Richardson’s constant, the Schottky barrier can be computed. However, the accuracy of this method is only as good as the accuracy of the Richardson’s constant. Also, factors such as tunneling currents and heterostructure effects can render incorrect values of the Schottky barrier by this method.
Next, capacitance-voltage (C-V) measurement of the Schottky barrier height will be discussed briefly for comparison with I-V because the C-V method is a commonly used technique. Goodman\textsuperscript{99} has derived the capacitance expression for a Schottky diode as a function of doping and applied bias as shown in the following equation:

\[
C = A \cdot \frac{\pm qK_v \varepsilon_0 (N_A - N_D)}{2(\pm V_{bi} \pm V - kT/q)}
\]

(7)

where A is the diode area, \(K_v\) is the dielectric constant, \(V\) is the applied reverse bias, and \(V_{bi}\) is the diode built-in voltage. \(V_{bi}\) is negative for n-type samples and positive for p-type samples. The “+” sign is used for p-type samples and the “−” sign is used for n-type materials. The built-in voltage is related to the Schottky barrier by the expression \(\phi_B = V_{bi} + V_o\) where \(V_o = (kT/q)\ln(N_C/N_D)\) with \(N_C\) being the effective conduction band density of states. The C-V data is acquired by sweeping the applied DC voltage which rides on a modulated high frequency AC voltage and measuring the capacitance. Then, \(1/(C/A)^2\) is plotted versus applied voltage yielding a straight line. The x-intercept is then used along with \(V_o\) to determine the Schottky barrier height. The slope of line easily yields the effective doping density. This technique of finding the Schottky barrier height relies on knowing the intrinsic carrier density or the effective density of states.

What are the sources of error in using these voltage-based techniques to determine the Schottky barrier height? The current-voltage method is strongly affected by defects at the metal-semiconductor interface which can act as traps or recombination centers thereby altering the current transport characteristics. This action may cause the physical current transport mechanism to deviate from that of thermionic emission and increase the
ideality factor and lower the measured Schottky barrier height. Capacitance-voltage methods are not affected by this as much as I-V measurements are, but defects in the space-charge region can affect the resulting intercept voltage and consequently the measured Schottky barrier height. For C-V measurements, it is imperative that the data be frequency independent and, of course, be linear in order to apply the model described in the capacitance equation given above. In the case of a patchy contact with parallel conduction mechanisms, I-V measurements tend to be dominated by the lower barrier regions whereas C-V measurements tend to give the Schottky barrier component from the region of largest area, as shown by Ohdomari, et al. in parallel silicide contacts.100 All this aside, C-V measurements are usually regarded to be more indicative of the Schottky barrier height than I-V. However, the technique of internal photoemission spectroscopy (IPE) is generally regarded to provide the most reliable Schottky barrier height because it probes the barrier from the metal side of the junction instead of from the semiconductor side as with C-V and I-V. This technique, along with its merits and flaws, is discussed in the following section.

2.7 Internal Photoemission Spectroscopy

Internal photoemission spectroscopy (IPE) is a technique used to determine the Schottky barrier height of a metal-semiconductor junction. Figure 2.8 shows a schematic of the process of internal photoemission. Monochromatic light is focused on the thin Schottky metal from either the metal side or the semiconductor side of the junction. Light absorbed in the metal creates electron-hole pairs and if the electron energy is large enough, the electron may drift to the interface and be swept across the barrier by the
built-in field. This process leads to a photocurrent that can be measured by an external circuit, either by a lock in amplifier for an electrometer.

Figure 2.8. Schematic of the internal photoemission process. An incident photon excites an electron-hole pair in the Schottky metal (incident either through the metal or semiconductor side of the junction). If the energy of the photon is large enough to give an electron sufficient energy to be excited over the barrier, a photocurrent is generated and can be measured by an external circuit.

Typically, the incident light is first dispersed through a monochromator before impinging on the Schottky diode. An ohmic contact to the semiconductor material is also necessary to complete the circuit. A schematic of the internal photoemission circuit is shown in Figure 2.9.
Figure 2.9. Schematic of the internal photoemission circuit. Monochromatic light is focused on the Schottky diode either from the substrate or through the top of the Schottky metal. The resulting photocurrent is measured at the Schottky contact while the ohmic contact is grounded to complete the measurement circuit.

The theory of the photoemission of electrons from metals was first formulated by Fowler in 1931. From this theory, the photocurrent over the Schottky barrier per absorbed photon as a function of incident photon energy is described by the equation: \[ Y = B(h\nu - q\phi_B)^2 \] (8)

with \( h\nu \) is the incident photon energy, \( q\phi_B \) is the Schottky barrier in eV, and \( B \) is a constant. Using this equation, a plot of the square root of the photocurrent per incident photon yields a linear portion. This plot of the square root of the photocurrent per incident photon is usually called a Fowler plot. Extrapolation of this line to the photon energy axis gives the Schottky barrier height. Care must be taken in the determination of the number of incident photons at a given photon energy in order to yield the correct Fowler plot curve. A high incident photon flux is desired because not all photons will
participate in the generation of a photocurrent due to reflection at the metal (topside geometry) or at the substrate (backside geometry) and absorption in the metal or in the semiconductor away from the depletion region.

As mentioned in the previous section, IPE is generally regarded as providing a reliable Schottky barrier height measurement. IPE is not influenced by tunnel currents to nearly the degree that I-V measurements are affected, especially if the linear portion extends to photon energies much larger than the Schottky barrier height. In some cases, the Fowler theory as presented in the above equation may not be the appropriate model to describe the photocurrent because some of the higher order terms in Fowler’s original theory may be contributing. Sometimes it is difficult to find a linear portion of the Fowler plot, however, the derivative of $Y$ with respect to incident photon energy can usually yield a linear fit. This particular derivative method has been employed by Okumura and Tu,\textsuperscript{103} where the authors utilized this method to characterize non-uniform Schottky contacts of Pd and Ni silicides on n-type Si. The authors state that this differential method is more sensitive to contact nonuniformities, but the conventional approach will also detect non-uniformities. The ability of IPE to detect contact nonuniformities and to assign Schottky barriers to these patchy regions is a definite advantage over I-V and C-V methods, since those methods tend to provide either the lowest barrier or the barrier representative of the largest area patch, respectively. There are other issues with IPE, such as its ability to characterize small area Schottky contacts such as HEMT gates. Small area contacts such as these would have a small incident flux onto the Schottky metal and a perhaps a very small, noisy photocurrent or no detectable
photocurrent. Using a lock-in amplifier and modulation spectroscopy could help this to a
certain degree since this technique is commonly used to increase the signal-to-noise ratio.

The IPE apparatus in the Electronic Materials and Nanostructures Laboratory at
The Ohio State University consists of a ThermoOriel 450 W Xe arc lamp as the light source. The light is coupled by lenses into a ThermoOriel 260i grating monochromator and is dispersed into an F/# matcher to a fiber optic. The fiber optic is used to focus the monochromatic light onto Schottky diodes either from below or above. The sample was probed with a manual probe station in a light-tight, electromagnetically shielded box. With the ohmic contact grounded, the photocurrent was measured at the Schottky contact with a Keithley 6517A electrometer. A custom LabView program was used to scan the monochromator energies and filter settings and to read the current from the electrometer. Before the analysis of the Schottky diodes, the system photoresponse was calibrated with a calibrated Newport Corporation Si diode at the output of the fiber optic. This calibration provided the number of photons incident at the sample as a function of monochromatized photon energy, thus providing the necessary data to form the photocurrent Fowler plot. An optical chopper and SRS 830 DSP lock-in amplifier are also available to be used in place of the electrometer.

2.8 UV-Ozone Cleaning

UV-Ozone cleaning (UV/O$_3$) is a technique used to clean semiconductor surfaces
of carbon contamination and other residual impurities. Reactive species in oxygen (such
as atomic oxygen and O$_3$) following irradiation with an in situ UV lamp can react with
UV-excited organic contaminants on the semiconductor surface and make the
Thereafter, the contaminants will be removed from the surface because of their volatility. This method may also remove C that is trapped in the uppermost layers of the material. There is evidence that the reactive oxygen oxidizes the surface of GaN. This cleaning procedure is conventionally performed at atmospheric pressures with the UV source very close (1 cm) to the surface to be cleaned. However, samples may also be cleaned at much lower oxygen overpressures ($10^{-5}$ torr to 20 torr) but the process takes a much longer time (7 seconds in air compared to 1 hour at low pressure).

![Figure 2.10. Representation of the process of UV/O$_3$ cleaning.](image)

UV/O$_3$ cleaning was performed in the Electronic Materials and Nanostructures Laboratory using a UHV process chamber with a butterfly valve connected to the turbomolecular pump of the chamber. This valve allows the chamber background pressure to be easily varied from UHV to low vacuum while still operating the
turbomolecular pump. Oxygen (and other gases) can flow into the chamber with regulation from mass-flow controllers to control the background pressure of the gas. For UV/O₃ cleaning, 99.99% pure oxygen is used. A Hg lamp is positioned inside the UHV chamber approximately 5 cm from the sample surface. The oxygen background pressure is monitored using a convectron gauge.
3.1 Degradation of Two-dimensional Electron Gas

\( \text{Al}_x\text{Ga}_{1-x}\text{N/GaN} \) HFET structures analyzed in this work were grown by plasma-assisted MBE on (0001) \( \text{Al}_2\text{O}_3 \) substrates by Dr. William Schaff at Cornell University. The MBE system is a Varian Gen II molecular beam epitaxy system equipped with standard effusion cells and an EPI RF plasma source. The sapphire was backside coated with TiW to allow for more uniform heating of the entire wafer. An AlN buffer layer of thickness 7-20 nm was grown on the sapphire to control the polarity of the GaN layer. Next, an unintentionally doped GaN barrier layer of thickness 1-1.2 \( \mu \text{m} \) was grown, followed by an \( \text{Al}_x\text{Ga}_{1-x}\text{N} \) layer with nominal thickness of 25 nm. The final layer is a 2 nm unintentionally doped GaN contact layer. Many different samples were analyzed with varying \( \text{Al}_x\text{Ga}_{1-x}\text{N} \) thickness and Al mole fraction.
Figure 3.1. Cross-sectional schematic of the AlGaN/GaN HFET structures grown by MBE. By design, the location of the 2DEG is at the lower AlGaN/GaN interface because the structure was nominally grown in the Ga-polar orientation.

Presented in this section is an analysis of two samples that were grown under nearly identical growth conditions: one that exhibited 2DEG formation and one that did not. The goal of this study was to determine the reason that the 2DEG failed to form and to learn about the mechanisms involved. The buffer layer was composed of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ of nominal thickness 25 nm. LEEN depth profiles were performed in the JAMP 7800F Auger microprobe at room temperature at a constant excitation power of 1 $\mu$W and an electron probe raster area of $\sim 100 \, \mu\text{m}$. The LEEN spectra are corrected for the response of the monochromator grating and detector. CASINO simulations were performed for electron probe energies of 1, 2, and 3 keV as shown in Figure 3.2.
Figure 3.2. CASINO Monte-Carlo electron trajectory simulation of Al$_{0.3}$Ga$_{0.7}$N HFET structure for 1, 2, and 3 keV electron beam excitation. These three choices of electron beam energy provide localized spectroscopy of the AlGaN film, AlGaN/GaN interface, and the GaN buffer layer.

From this simulation it is clear that for increasing electron probe energy one can probe the near-surface region, the AlGaN layer, the AlGaN/GaN interface, and the GaN barrier layer in a well-controlled fashion.

LEEN depth profiles of the HFET structure with no 2DEG formation are shown in Figure 3.3. The spectra show “yellow” defect emissions at 2.18 eV and 2.34 eV, as well as AlGaN and GaN band edge emissions at 3.82 eV and 3.4 eV, respectively. As the electron probe energy is increased, the AlGaN and the GaN band edge emissions vary in intensity in a way that correlates with the CASINO simulations. Also, the 2.34 eV defect emission tracks the AlGaN band edge emission as the electron probe energy is increased. The 2.18 eV defect emission seems to scale with the GaN band edge emission. At the lowest electron beam energies, an emission at 3.25 eV is observed.
Figure 3.3. LEEN depth profile of HFET structure with no 2DEG formation (left). The peak intensities of the AlGaN and GaN band edge emissions and the peak intensity of the “yellow” defect emission is shown versus electron probe energy (right).

LEEN depth profiles of the HFET structure with 2DEG formation are shown in Figure 3.4. The spectra show a “yellow” defect emission at 2.18 eV, as well as AlGaN and GaN band edge emissions at 3.95 eV and 3.42 eV, respectively. The 2.18 eV defect emission seems to scale with the GaN band edge emission. This structure did not exhibit a 2.34 eV defect emission. In each spectra for each structure, the intensity increase for photon energies around 2.0 eV is found to be an artifact of the optical response correction and should be ignored.
3.2 Correlation of Properties on an AlGaN/GaN HEMT Wafer

In order to further investigate the nature of the defect emissions in HFET structures as observed in the samples of the previous section, a section of a 2-inch HFET structure wafer was analyzed. The AlGaN barrier layer thickness and the Al mole fraction for this specimen were nominally the same as those described in the previous section. This type of specimen offers a good opportunity to correlate LEEN spectra, chemical composition, and morphology as a function of position. Since the growth temperature near the center of the wafer is on the order of 25-75 °C more than the temperature at the edge of the wafer, the AlGaN and GaN growth conditions will definitely vary across the wafer. LEEN spectra were performed at constant power at 1, 2, and 3 keV at room temperature in the JAMP 7800F Auger microprobe at room
temperature as a function of radial position. These electron probe energies allowed localized stimulation of the AlGaN barrier layer, the AlGaN/GaN interface, and the GaN buffer layer as shown in Figure 3.2. Figure 3.5 shows LEEN spectra at 2 keV electron probe energy versus radial position as measured from the wafer center. The electron beam excitation at 2 keV has an energy loss peak which coincides with the AlGaN/GaN interface and therefore LEEN results provide information from this region. The defect emissions were fitted with a non-linear least-squares curve fitter (Origin 7.0) to model the behavior of the AlGaN defect emission and the GaN defect emission that were identified in the previous section, as well as the second order emission from the AlGaN band edge emission. Figure 3.6 shows LEEN spectra at 3 keV electron probe energy versus radial position with the AlGaN and GaN defects also deconvolved as with the 2 keV case.
Figure 3.5. LEEN spectra at room temperature of HFET wafer as a function of radial position. The spectra were taken at 2 keV electron probe energy. The defect luminescence was fitted to three Gaussian curves with the lowest energy curve taking into account the second-order grating transmission of the AlGaN near band edge emission. Arrows show the defect emissions with the highest relative intensity.
Figure 3.6. LEEN spectra at room temperature of HFET wafer as a function of radial position. The spectra were taken at 3 keV electron probe energy. The defect luminescence was fitted to three Gaussian curves with the lowest energy curve taking into account the second-order grating transmission of the AlGaN near band edge emission.

The 2 keV spectra show several interesting results. First, the AlGaN band edge emission energy is monotonically increasing with increasing radial position, suggesting that the Al content is varying. Also, this emission is not observed for radii less than 6 mm, suggesting that the AlGaN barrier layer did not grow because of the higher growth temperature near the wafer center. The ratio of the defect luminescence to the band edge emissions of GaN and AlGaN are highest at intermediate radii and tend to decrease toward the wafer edge as shown in Figure 3.7. A similar analysis for the LEEN spectra taken at electron probe energies of 1 keV and 3 keV reveal the same trend, but also show
that the AlGaN and the GaN defect to band edge ratios vary in a more independent manner. These are shown in Figure 3.8 and Figure 3.9.

Figure 3.7. Ratio of AlGaN defect to AlGaN band edge intensity and ratio of GaN defect to GaN band edge intensity versus radial position for 2 keV electron beam excitation. There is an increase in these ratios for intermediate radii and a general decrease in these ratios for the inner and outermost radii.
Figure 3.8. Ratio of AlGaN defect to AlGaN band edge intensity and ratio of GaN defect to GaN band edge intensity versus radial position for 1 keV electron beam excitation. The AlGaN defect emission and GaN defect emission clearly vary in an independent fashion with maxima in different spatial locations on the wafer.

Figure 3.9. Ratio of AlGaN defect to AlGaN band edge intensity and ratio of GaN defect to GaN band edge intensity versus radial position for 3 keV electron beam excitation. Again, it is clear that the AlGaN and GaN defect emissions vary independently across the wafer.
Also, the entire “Yellow” defect emission and near band edge emissions of the AlGaN and GaN layers were integrated and analyzed in order to further characterize the relative variation of defects across the wafer. The ratio of the total integrated defect emission to the AlGaN and GaN near band edge emissions for 2 keV excitation is plotted versus radial position in Figure 3.10. Again, there is a decrease in the relative intensity of the defect emission to the near band edge emissions for wafer radii greater than ~17 mm. It will be further elucidated in the following pages that there is a clear variation in other physical parameters (i.e., chemical composition and surface morphology) that correlate with the observations of a relative decrease in defect emissions.
Figure 3.10. Ratios of the total integrated defect emission (YL) to the total integrated AlGaN and GaN near band edge emissions as a function of radial position. There is a clear maxima of this ratio for intermediate radii and a sharp ratio decrease for radii > ~17 mm.

For 2 keV excitation, the peak widths for the AlGaN and GaN near band edge emissions as a function of wafer radius are shown in Figure 3.11. There is a clear broadening of the peaks for wafer radii greater than 16 mm which correlates with the observed decrease in the relative contribution of defects to the luminescence spectra.
Figure 3.11. NBE peak width (FWHM) of the GaN and AlGaN emissions with 2 keV electron beam excitation as a function of radial position on AlGaN/GaN HFET wafer. Peak widths increase dramatically for the outermost radii for both emissions.

Also plotted are the AlGaN and GaN near band edge emission peak positions as a function of wafer radius. These were performed for 1 keV, 2 keV, and 3 keV excitation and are shown in Figure 3.12, Figure 3.13, and Figure 3.14, respectively. In all cases, the AlGaN peak position shifts monotonically to higher energies with increasing wafer radius. The GaN peak position shifts dramatically at around 16 mm for the 1 keV and the 2 keV electron beam excitations. For the case of 3 keV excitation, the GaN peak position does not shift appreciably.
Figure 3.12. GaN and AlGaN NBE peak emission energies as a function of wafer radial position with a constant 1 keV electron beam excitation. The AlGaN NBE position gradually increases with increasing wafer radius until around 18 mm. The GaN NBE position drops dramatically in energy for radii greater than 16 mm.
Figure 3.13. GaN and AlGaN NBE peak emission energies as a function of wafer radial position with a constant 2 keV electron beam excitation. The AlGaN NBE position gradually increases with increasing wafer radius. The GaN NBE position drops gradually in energy for radii greater than 16 mm.
Figure 3.14. GaN and AlGaN NBE peak emission energies as a function of wafer radial position with a constant 3 keV electron beam excitation. The AlGaN NBE position gradually increases with increasing wafer radius until around 18 mm and then increases dramatically for larger radii. The GaN NBE position is relatively constant as a function of wafer radius.

RMS roughness values versus radial position measured by atomic force microscopy (AFM) are shown in Figure 3.15. This value represents a general figure of merit for the quality of the material since high quality epitaxial material should theoretically be atomically smooth. The AFM analysis was performed in tapping mode at The Ohio State University and the rms roughness was calculated for a 10 µm square area. This reveals that there is a large change in the roughness values around $R_w=17$ mm in that the surface is much smoother at the outermost radii. This transition correlates with Figure 3.10 in that regions of higher defect to band edge ratio there is increased surface
roughness and regions of lower defect to band edge ratios show reduced surface roughness. Representative AFM images are shown in Figure 3.16, Figure 3.17, and Figure 3.18. The first two images are from the rough regions of the sample surface while the third image is from nearer the sample edge where Ga droplets were present on the surface.

Figure 3.15. RMS roughness as measured by AFM as a function of radial position. There is a large drop in the roughness for $R_W > 17$ mm, demarking two regions of similar morphology.
Figure 3.16. Tapping mode AFM image (5 µm square) of AlGaN/GaN HFET wafer at $R_w=12.5$ mm. There exists a very irregular morphology with ~50 nm deep pits.

Figure 3.17. Tapping mode AFM image (5 µm square) of AlGaN/GaN HFET wafer at $R_w=17$ mm. There exists a very irregular morphology at this wafer position, but there is not as much pitting as at the 12.5 mm position.
Auger electron spectroscopy was also performed versus position to monitor chemical composition trends in order to compare these trends with the observed rms roughness and the luminescence characteristics. Two types of measurements were performed. The first measurement involved using an Ar$^+$ ion sputter source at low energies (1 keV or less) to gently sputter the C and O contaminants from the surface until no carbon AES signal appeared. After the cleaning process, the near-surface N and Ga AES signals were measured as a function of radial position. The results were that the ratio of N (KLL) to Ga (LMM) AES differentiated signals decreased with increasing wafer radius with a value of 1.2 for radii less than 18 mm and 0.9 for radii greater than 18 mm. This implies that the Ga to N local atomic ratio is increasing with increasing wafer radius.
The second AES measurement was performed by Auger depth profiling. At each point on the wafer, the N, Ga, and Al AES differential peak was monitored as a function of 500 eV Ar$^+$ sputter time. These measurements were performed at four positions: 13.5, 17.5, 20.5, and 22.5 mm. Figure 3.19 shows the ADP results for these positions. The 13.5 mm ADP result was very similar to the 17.5 mm result, as was the 22.5 mm results to the 20.5 mm result. For each profile, the N composition was normalized to 50% and appropriate sensitivity factors (from JEOL) were used for the Al and Ga signals. This figure shows that the AlGaN/GaN interface is much broader for $R_w<17.5$ mm and is more narrow for $R_w>17.5$ mm even though the Ga and Al concentrations remain approximately constant in the center of the AlGaN film for each measured position.
Figure 3.19. Auger depth profiles of Al, Ga, and N normalized to 50% N concentration in the center of the film. The depth profiles for Rw<18 mm revealed a significantly broadened AlGaN/GaN interface when compared with the depth profiles for Rw>18 mm.

SIMS depth profiles of negative ion yields as a function of position also reveal the trend of Figure 3.19. Two representative SIMS depth profiles of the total ion, O<sup>-</sup>, <sup>71</sup>GaN<sup>-</sup>, AlN<sup>-</sup>, Al<sup>-</sup>, and C<sup>-</sup> are shown in Figure 3.20 and Figure 3.21 for wafer radii of 17 and 18 mm, respectively. The Cs<sup>+</sup> sputter source was set to 1 keV in order to achieve good depth resolution for these thin films. These particular profiles were taken on each side of the position where the surface morphology changes abruptly. SIMS depth profiles were performed at 1 mm intervals from Rw=13 mm to Rw =23 mm. The broadened
AlGaN/GaN interface is evident in each of the depth profiles of $R_W \leq 17$ mm and the sharper AlGaN/GaN interface is evident in the depth profiles of $R_W \geq 18$ mm. Therefore, the other SIMS depth profiles are not displayed. For these experimental conditions, the C ion counts are on the order of the noise level because the analysis beam current was intentionally set to a relatively low value. This low value of the beam current was chosen because none of the secondary ions were blanked and a higher beam current would saturate the ion detector.

Figure 3.20. Secondary ion mass spectrometry depth profiles of wafer radius 17 mm on the AlGaN/GaN HFET wafer. The depth profiles for $R_W < 17$ mm are very similar to the 17 mm case and are not displayed.
Figure 3.21. Secondary ion mass spectrometry depth profiles of wafer radius 18 mm on the AlGaN/GaN HFET wafer. The depth profiles for \( R_w > 18 \) mm are very similar to the 18 mm case.

From the SIMS depth profiles that were taken as a function of radial position, the O/GaN ratio was extracted from the center of the AlGaN film thickness in order to characterize the O concentration as a function of radial position. These results are shown in Figure 3.22. This plot shows a clear trend of increasing O/GaN negative ion ratio as the radial position is increased. Utilizing the relative sensitivity factors that were derived from implanted SIMS standards (See Chapter 4), the O concentration at a wafer radius of 13 mm was determined to be on the order of \( 10^{19} \) atoms/cc. The O concentration at the edge of the wafer is nearly twice this amount.
Figure 3.22. SIMS O/GaN negative ion ratio as a function of wafer radius on the AlGaN/GaN HFET wafer. The O/GaN ratio is monotonically increasing with increasing wafer radius. Using the relative sensitivity factors for O in AlGaN for this Al mole fraction, the O concentration was determined to be on the order of $10^{19}$ cm$^{-3}$ for $R_w=13$ mm.
Also from the SIMS depth profiles, the AlN/GaN negative ion ratio as a function of radial position is plotted in Figure 3.23. This ratio represents an average of the AlN/GaN ratio over the AlGaN film thickness away from the surface and AlGaN/GaN interface regions. There is a clear decrease in this ratio with increasing radius. Also shown on the diagram are the locations of N-rich and Ga-rich regions as defined by the AES measurements. On the right of the figure, Al mole fractions for the highest and lowest AlN/GaN ratios are given as determined by a SIMS calibration procedure described later in Chapter 4. This calibration procedure involved many samples and many measurements of the AlN/GaN ratio for samples of varying Al mole fraction across the AlGaN alloy series.
Figure 3.23. SIMS AlN/GaN negative ion ratio as a function of wafer radius on the AlGaN/GaN HFET wafer. N-rich and Ga-rich regions, as shown by AES measurements, are shown on the figure. Using the AlN/GaN curve as a function of Al mole fraction (Figure 4.8), the Al mole fraction variation is also shown.

3.3 HFET Structures with Varying Al Mole Fraction and Electrical Properties

In order to further elucidate the relationship between electronic states measured by LEEN, mobility, 2DEG sheet charge density, and morphology, more HFET structures grown by MBE at Cornell University were investigated. The sheet densities and mobilities for each structure were measured by Hall effect measurements at Cornell and the Al mole fraction was measured by X-ray diffraction at Cornell. The HFET layer structure is the same as that described in the beginning of section 3 with the exception that the AlGaN layer thicknesses are smaller for these structures (~15 nm for higher mole fractions and ~25 nm for lower mole fractions). Atomic force microscopy measurements
were also performed for each sample. Table 3.1 shows the Al mole fraction for the strained AlGaN, sheet density (electrons/cm$^2$), mobility at room temperature (cm$^2$/V/s), AlGaN near band edge emission at 2 keV electron energy and associated full width half maximum, and the mean rms roughness and standard deviation measured by AFM. This table shows that a wide range of samples properties exist for these structures.

Table 3.1. List of measured sample properties of AlGaN/GaN HFET structures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al fraction</th>
<th>Sheet Density</th>
<th>Mobility</th>
<th>AlGaN NBE (eV)</th>
<th>AlGaN FWHM</th>
<th>Mean Rms Roughness (nm)</th>
<th>Roughness SD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gs1041</td>
<td>34.42</td>
<td>1.40E+13</td>
<td>729.9</td>
<td>3.725</td>
<td>0.33</td>
<td>9.213</td>
<td>1.965</td>
</tr>
<tr>
<td>gs1044</td>
<td>36.94</td>
<td>3.708</td>
<td>0.26</td>
<td>7.317</td>
<td>1.873</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gs1059</td>
<td>58.47</td>
<td>2.28E+13</td>
<td>433.8</td>
<td>3.97</td>
<td>0.23</td>
<td>7.447</td>
<td>8.555</td>
</tr>
<tr>
<td>gs1235</td>
<td>32.45</td>
<td>1.06E+13</td>
<td>805.4</td>
<td>3.801</td>
<td>0.14</td>
<td>14.843</td>
<td>3.255</td>
</tr>
<tr>
<td>gs1236</td>
<td>28.42</td>
<td>9.78E+12</td>
<td>1046.5</td>
<td>3.801</td>
<td>0.16</td>
<td>8.395</td>
<td>0.73</td>
</tr>
<tr>
<td>gs1240</td>
<td>29.85</td>
<td>1.42E+13</td>
<td>471.4</td>
<td>3.813</td>
<td>0.19</td>
<td>6.578</td>
<td>0.851</td>
</tr>
<tr>
<td>gs1241</td>
<td>29.85</td>
<td>9.31E+12</td>
<td>889.6</td>
<td>3.801</td>
<td>0.22</td>
<td>14.519</td>
<td>5.347</td>
</tr>
<tr>
<td>gs1243</td>
<td>75.31</td>
<td>3.08E+13</td>
<td>268</td>
<td>4.264</td>
<td>0.24</td>
<td>15.753</td>
<td>0.163</td>
</tr>
<tr>
<td>gs1244</td>
<td>82.3</td>
<td>1.74E+13</td>
<td>60.1</td>
<td>none observed</td>
<td>1.931</td>
<td>0.181</td>
<td></td>
</tr>
<tr>
<td>gs1246</td>
<td>83.15</td>
<td>1.30E+13</td>
<td>129.8</td>
<td>none observed</td>
<td>3.391</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>gs1248</td>
<td>79.1</td>
<td>ins</td>
<td>ins</td>
<td>3.742</td>
<td>low intensity</td>
<td>7.362</td>
<td>0.493</td>
</tr>
<tr>
<td>gs1264</td>
<td>30.32</td>
<td>8.79E+12</td>
<td>1014.9</td>
<td>3.742</td>
<td>0.14</td>
<td>1.551</td>
<td>0.145</td>
</tr>
<tr>
<td>gs1271</td>
<td>30.32</td>
<td>7.29E+12</td>
<td>1114.5</td>
<td>3.685</td>
<td>0.23</td>
<td>4.151</td>
<td>1.613</td>
</tr>
<tr>
<td>gs1273</td>
<td>76.61</td>
<td>9.85E+12</td>
<td>971.6</td>
<td>none observed</td>
<td>2.593</td>
<td>1.102</td>
<td></td>
</tr>
<tr>
<td>gs1274</td>
<td>53.76</td>
<td>2.01E+13</td>
<td>772.1</td>
<td>4.003</td>
<td>0.23</td>
<td>3.014</td>
<td>0.653</td>
</tr>
<tr>
<td>gs1282</td>
<td>77.09</td>
<td>2.48E+13</td>
<td>720.9</td>
<td>4.11</td>
<td>0.23</td>
<td>19.707</td>
<td>1.684</td>
</tr>
<tr>
<td>gs1283</td>
<td>68.73</td>
<td>2.92E+13</td>
<td>260.8</td>
<td>none observed</td>
<td>1.779</td>
<td>0.433</td>
<td></td>
</tr>
<tr>
<td>gs1286</td>
<td>67.27</td>
<td>2.54E+13</td>
<td>350.1</td>
<td>4.227</td>
<td>0.33</td>
<td>6.27</td>
<td>4.845</td>
</tr>
</tbody>
</table>

From this tabular data, several property comparisons can be made. First, the 2DEG sheet density is plotted as a function of Al mole fraction as shown in Figure 3.24.
This data shows an increase in the 2DEG sheet density with increasing Al mole fraction, with several exceptions that are encircled. The outlying samples did not exhibit AlGaN near band edge emission.

![Graph showing 2DEG sheet density vs. Al mole fraction]

Figure 3.24. 2DEG sheet density (cm$^{-2}$) as a function of Al mole fraction for AlGaN/GaN HFET structure in Table 3.1. There is a clear increase in the sheet density as the Al mole fraction is increased. Three of the outlying data points are encircled.

The Hall mobility as a function of Al mole fraction is shown in Figure 3.25. In this plot, there is a clear decrease in Hall mobility with increasing Al mole fraction with a few outlying data points.
Figure 3.25. Room temperature Hall mobility as a function of Al mole fraction for AlGaN/GaN HFET structures in Table 3.1. There is a clear decrease in mobility as the Al mole fraction is increased.

Since defect emission was not observed with LEEN for most of this sample set, the data set was examined to correlate rms surface roughness with the electrical properties. These plots are shown in Figure 3.26 and Figure 3.27. From these plots, no correlation between roughness and mobility for 2DEG sheet density.
Figure 3.26. Hall mobility versus mean rms roughness as measured by AFM for the AlGaN/GaN HFET samples in Table 3.1.

Figure 3.27. 2DEG sheet density versus mean rms roughness measured by AFM for the AlGaN/GaN HFET samples in Table 3.1.
3.4 Discussion

There are some luminescence features which correlate with AlGaN/GaN 2DEG confinement and some that do not. The additional emission at 3.25 eV in the near-surface region of Figure 3.3 and Figure 3.4 is present in both samples at the same intensities and therefore does not correlate with 2DEG formation. This feature may be due to surface states, however the continuous shift of this feature to the GaN band edge as the electron probe energy is increased suggests a strain-induced red shift of the band edge emission due to strong piezoelectric fields or large surface band bending. The fact that the 2.34 eV defect emission that is observed in the structure with no 2DEG formation tracks with the AlGaN band edge emission as a function of electron probe energy suggests that this particular defect emission is localized in the AlGaN barrier layer. A possible explanation for the difference in the structures is that excess charge may be trapped in the AlGaN layer and could alter 2DEG confinement. If only electrostatic processes are considered, the defect density throughout the 25 nm AlGaN layer should be \( \sim 10^{13} \text{ cm}^{-2} \) or more in order to compensate the positive charge induced near the 2DEG AlGaN/GaN interface. This corresponds to a volume density of \( 4 \times 10^{17} \text{ cm}^{-3} \), comparable to GaN n-type doping levels. Hubbard, et al. have examined AlN/GaN MISFET structures with varying Hall mobilities and 2DEG densities.\(^{107}\) In their work, they discover an increase in 1.9-2.3 eV defect luminescence (similar to our YL) with decreasing Hall mobility. Therefore, this defect has been observed in different material growth methods (MBE vs. MOCVD) and this defect correlates with 2DEG degradation. The authors also use an Oxford Instruments MonoCL monochromator system and a
Hamamatsu high-sensitivity PMT in conjunction with a scanning electron microscope for their cathodoluminescence measurements. Therefore, the luminescence signatures could be compared with reasonable confidence.

The spectra taken at 1, 2, and 3 keV excitation for the AlGaN/GaN growth wafer as a function of radial position show that the AlGaN and GaN defect emissions peak at separate spatial positions along the wafer radius. This suggests that there are indeed two separate contributions to the defect luminescence. The nature of these defects could be related to Al and Ga vacancies or other cation-specific native defects.

This result of a decreasing N/GaN AES ration as a function of increasing wafer radius agrees with the observation of Ga droplets near the edge of the wafer—a consequence of the cooler growth temperatures near the wafer edge. The increase in yellow defect emission in the region of decreased Ga to N AES ratio is consistent with the Ga vacancy origin of yellow defect luminescence in GaN. Also, observations of Ga-rich versus N-rich growth conditions have also shown a consistency between yellow defect emission and Ga-deficient conditions. An increase in trap concentration in n-GaN measured by DLTS has been correlated with Ga-lean conditions, degraded surface morphology, and lower bulk electron mobility.

The increase in the AlGaN and GaN NBE peak width in Figure 3.11 correlates with observations of increased photoluminescence peak widths due to increased compositional disorder in Ga-rich AlGaN films. The authors also state that despite the increased compositional disorder observed in Ga-rich AlGaN films, these films do not exhibit more defect luminescence than N-rich AlGaN films. This helps to confirm our
observation of cation-rich conditions near the AlGaN/GaN wafer edge and the fact that more YL is observed in the less Ga-rich (or N-rich) regions of the wafer.

Since the broadened interface exhibited in the AES depth profiles and the SIMS depth profiles of the AlGaN/GaN wafer at various radii also correlates with increased RMS roughness, these roughness variations may contribute to the apparent interface broadening. Because of this correlation, it is not obvious as to which mechanism is related to the observed change in luminescence features. Interface broadening has been observed in structures with degraded electrical properties such as mobility and 2DEG density by LEEN spectroscopy and ADP.\textsuperscript{109}

AlGaN NBE shifts have been observed in the LEEN spectra as a function of position across the wafer. It is well known that the absorption and emission band edge may shift due to high fields in the semiconductor. This has been attributed to the Franz-Keldysh effect. Essentially, this describes the theory that the electric field tilts the energy bands and therefore the probability of photon-assisted tunneling of carriers across the band gap increases. Halliday\textsuperscript{110} has presented an expression for the apparent change in the band gap as a function of applied electric field:

\[
\Delta E_g = \left( \frac{3q\hbar E}{4\sqrt{2m^*_e}} \right)^{2/\gamma}
\]

where \( m^*_e \) is the electron effective mass and \( E \) is the applied field. Using a value of 0.2 for the GaN effective mass, the apparent band gap shift calculated using this equation with applied electric field is shown in Figure 3.28.
Figure 3.28. Calculated shift in the AlGaN NBE energy as a function of internal electric field using the previous equation. An applied field of at least $10^5$ V/cm is required to achieve an appreciable band edge shift.

In this figure, it is clear that an electric field of at least $10^5$ V/cm is required to make a considerable difference in the AlGaN band edge emission energy. Field magnitudes of 10 MV/cm are theoretically possible for strained AlN/GaN heterojunctions and AlGaN/GaN HFETs can also exhibit very large electric fields.

Using the results from this figure, one may extract the electric field as a function of position on the AlGaN/GaN HFET wafer. Taking into account the Al mole fraction extracted from SIMS depth profiling as a function of position, the LEEN 2 keV AlGaN NBE energy, and the theoretical AlGaN NBE, Figure 3.29 shows the internal electric field as a function of position. This figure shows a decrease in the internal electric field (therefore a decrease in the strain) with increasing wafer radius. This could mean that the AlGaN film thickness for wafer radii greater than 18 mm is experiencing strain relaxation.
from an increase in the thickness above the critical thickness. Nitrides grown by MBE exhibit less cation desorption for cooler growth temperatures and therefore the films would exhibit a faster growth rate because the cation arrival rate minus the desorption rate at the surface is the rate-limiting step for MBE film growth. For wafer radii greater than ~ 18 mm there are numerous Ga droplets on the surface which support this claim.

![Electric Field vs Position](image)

Figure 3.29. Calculated internal electric field as a function of radial position on the AlGaN/GaN HFET wafer utilizing the Al mole fraction deduced from the SIMS AlN/GaN negative ion ratio and the AlGaN NBE energy at 2 keV.

An alternate explanation for the upward shift of the AlGaN NBE energy with increasing wafer radius involves the growth kinetics under group-III-rich MBE growth. Iliopoulos, *et al.* have found that films grown by MBE under group-III-rich conditions exhibit a higher Al mole fraction than N-rich films for the same Al/Ga flux ratio. The authors state that the Al-N bond is stronger than the Ga-N bond therefore the N would
prefer to bond with the Al under group-III-rich conditions. This would give rise to a higher sticking coefficient for the Al and a lower sticking coefficient for the Ga and thus a higher Al mole fraction. Also, when the group-III flux is increased from the N-rich growth regime to the group-III-rich growth regime and beyond, the Al incorporation probability has been determined to be near unity while the Ga incorporation probability decreases as shown in Figure 3.30.\textsuperscript{113} This figure shows that for higher total group-III fluxes at a fixed Al/Ga flux ratio, Al is incorporated more readily than the Ga and the resulting film has a higher Al mole fraction. The referenced paper states that Ga is incorporated only with nitrogen flux that is left over from the nitrogen that is not consumed by the Al. This means that precise flux control is necessary to grow these films with a repeatable Al mole fraction. Iliopoulos, et al. also mention that the Ga adlayer during group-III-rich growth serves as a surfactant that participates in the film growth but does not fully incorporate into the films.
Figure 3.30. Al and Ga incorporation probabilities in MBE grown AlGaN films for a growth temperature of 750 °C. For a fixed Al/Ga flux ratio, Ga is not readily incorporated at the higher fluxes, leading to a film with a higher Al mole fraction.

While the wafer edge of our AlGaN is believed to be 25-75 °C cooler than the wafer center during MBE growth, I believe that there are non-uniformities in the atomic fluxes that intercept the growth substrate, especially the nitrogen plasma source flux. Ga would tend to incorporate more readily at lower growth temperatures (at the wafer edge) but also the available nitrogen flux at the wafer edge is probably not as much as the available nitrogen flux near the wafer center due to plasma non-uniformities.

Increased group-III total fluxes would therefore tend to give rise to a higher energy AlGaN NBE. It has been determined that the outer portion of the AlGaN/GaN wafer is Ga-rich by AES measurements and also by the observation of Ga droplets nearer the wafer edge. SIMS analysis of the AlN/GaN negative ion ratio suggested that the edge of the wafer had a higher Ga/Al ratio, but this method has an error of ±2% Al mole
fraction and therefore the method of Al mole fraction determination is not a reliable metric given the relatively small spread in AlN/GaN ratio versus radius.

The O impurity concentration is observed to increase with increasing wafer radius as shown in Figure 3.22. This result correlates with the observation that the AlGaN NBE energy is increasing with increasing radius. If the increase in the observed AlGaN NBE energy is due to the increase in Al mole fraction, then it makes sense that the O impurity concentration would increase with radius. This is because AlGaN films with higher Al concentration are shown to have higher O impurity concentrations due to the strong affinity that Al has with O. The increase in O with increasing Al mole fraction has been observed in both MOCVD-grown\textsuperscript{114} and MBE-grown\textsuperscript{115} AlGaN films. The O impurity concentration distribution also correlates with observations by Elsass, \textit{et al.} that N-rich and III-rich AlGaN films grown by MBE at lower temperatures have a higher O concentration than those grown at higher temperatures.\textsuperscript{116} Elsass, \textit{et al.} also find that group-III-rich AlGaN films have 3× less oxygen than N-rich films under the same growth conditions. In the case of our AlGaN/GaN HFET wafer, the temperature varies across the wafer during growth so we cannot fully compare our results with the latter findings.

The increasing O concentration with increasing wafer radius correlates with the observed decrease in defect luminescence. It was discussed previously that gallium vacancies are believed to the at least partially responsible for the “yellow” luminescence in GaN. The LEEN measurements on the AlGaN/GaN HFET wafer correlate with this theory. Other proposed theories regarding the nature of the AlGaN and GaN defect luminescence involve gallium vacancies forming complexes with O substituting on a nitrogen site (V$_{Ga-O_N}$) or with other impurities such as C\textsuperscript{20,117,118}, Si\textsuperscript{21,119}, and H\textsuperscript{120}. The
observed decrease in defect luminescence with increasing O concentration argues against
the theory that O plays a role in defect luminescence. The SIMS depth profiles did not
show C and Si above that of the noise level for the given experimental conditions,
therefore no claims can be made regarding these impurities and defect luminescence.

LEEN of the HFET structures listed in Table 3.1 reveals an AlGaN near band
edge emission that is significantly lower than what is predicted by a band gap curve with
b=1. This suggests that the films are heavily strained and that the luminescence is shifted
by a Franz-Keldysh effect. For all of these structures, with the exception of gs1041,
gs1044, and gs1059, no deep level defect luminescence is observed by LEEN. This does
not allow for a comparison of the electrical properties with deep level luminescence as
presented in the previous sections. At this time, no correlations with LEEN have been
observed for 2DEG sheet density and mobility except the absence or presence of the 2.34
eV YL and 2DEG confinement. With the current data, one cannot rule out defects inside
the AlGaN barrier layer or surface roughness as being factors in degrading the electrical
properties of the HFET structure. Further investigation of the relationship between these
physical parameters is warranted.

There are correlations of the 2DEG sheet density and electron mobility with Al
mole fraction as shown in Figure 3.24 and Figure 3.25. In these figures, the sheet density
increases with increasing mole fraction and the mobility decreases with increasing mole
fraction. This can be explained as follows. For a fixed AlGaN thickness, the
piezoelectric field in this layer increases with increasing Al content. This happens mostly
because the strain increases due to the change in the lattice parameters from the addition
of Al. The piezoelectric field will increase since this field is proportional to the strain in
the c-plane and therefore more piezoelectric sheet charge will form at the AlGaN/GaN interface. Consequently, electrons gather at the AlGaN/GaN interface in an attempt to cancel this positive charge and therefore the 2DEG concentration increases. The mobility decreases primarily due to the increase in the 2DEG density. With increased 2DEG density, the electrons will gather closer to the AlGaN/GaN interface and interface scattering will occur and limit the electron mobility.

Figure 3.31 shows the room temperature mobility for MBE grown AlGaN/GaN HFET structures from Dr. William Schaff’s group at Cornell University as a function of time. There is a wide scatter in the mobility data demonstrating that these film structures are difficult to reproduce. Figure 3.26 and Figure 3.27 also exhibit wide scatter in the electrical properties versus rms roughness. Taking this into account, it is not surprising that correlations between roughness, defects, and electrical properties from the set of AlGaN/GaN HFETs listed in Table 3.1 would be difficult to obtain.
Figure 3.31. Room temperature mobility for Cornell AlGaN/GaN HFETs as a function of time. The line is a guide to the eye provided by the MBE growers at Cornell.
CHAPTER 4

SI DOPING OF ALGaN WITH HIGH AL CONTENT

4.1 LEEN Spectroscopy of AlGaN:Si

Si doped AlGaN was grown at Cornell University in a turbomolecular pumped Varian Gen II MBE system which uses standard effusion cells for the group III elements. An EPI RF plasma source was used for the nitrogen source. Two-inch Al$_2$O$_3$ wafers were used as the substrate and were backside coated with TiW, as done with the HFET structure growth. A 20 nm AlN nucleation layer was grown, followed by a 400 nm thick Si doped Al$_x$Ga$_{1-x}$N layer grown at 800 °C. Al mole fraction was determined by X-ray diffraction. Many samples were grown with different Al mole fractions and Si fluxes. Table 4.1 lists the Al mole fraction, room temperature mobility in cm$^2$/V/s, Hall doping density, and Si effusion cell temperature for the samples that were analyzed in this study. The goal of this study is to determine the nature of doping in this system and determine the physical reasons behind the compensation at high Al mole fractions.
Table 4.1. List of material parameters for Si doped AlGaN samples.

<table>
<thead>
<tr>
<th>sample #</th>
<th>Al fraction</th>
<th>Hall mobility</th>
<th>doping density (#/cm^3) (Hall)</th>
<th>Si Temp(°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>gs1420</td>
<td>25%</td>
<td>45</td>
<td>6.00E+18</td>
<td>1300</td>
</tr>
<tr>
<td>gs1421</td>
<td>33%</td>
<td>68</td>
<td>3.60E+18</td>
<td>1300</td>
</tr>
<tr>
<td>gs1422</td>
<td>52%</td>
<td></td>
<td></td>
<td>1300</td>
</tr>
<tr>
<td>gs1423</td>
<td>48%</td>
<td>22.5</td>
<td>3.50E+19</td>
<td>1375</td>
</tr>
<tr>
<td>gs1424</td>
<td>100%</td>
<td></td>
<td></td>
<td>1375</td>
</tr>
<tr>
<td>gs1425</td>
<td>47%</td>
<td>19.8</td>
<td>1.25E+20</td>
<td>1425</td>
</tr>
<tr>
<td>gs1426</td>
<td>98%</td>
<td></td>
<td></td>
<td>1425</td>
</tr>
<tr>
<td>gs1427</td>
<td>65%</td>
<td>17.5</td>
<td>8.8E+19</td>
<td>1425</td>
</tr>
<tr>
<td>gs1555</td>
<td>78%</td>
<td>5.1</td>
<td>4-8E+19</td>
<td>1450</td>
</tr>
<tr>
<td>gs1564</td>
<td>79%</td>
<td>2.7</td>
<td>3.00E+19</td>
<td>1470</td>
</tr>
<tr>
<td>gs1590</td>
<td>76%</td>
<td>18.7</td>
<td>6.00E+17</td>
<td>1340</td>
</tr>
</tbody>
</table>

Depth-dependent LEEN spectra of the AlGaN:Si films were acquired at electron probe energies of 1 keV, 5 keV, and 10 keV at constant power in the JAMP 7800F Auger microprobe. These energies were chosen because they would excite different regions of the film: the near surface, the bulk, and the Al₂O₃/AlGaN interface. CASINO simulations of the electron energy loss curves for Al₀.₅Ga₀.₅N are shown in Figure 4.1. The 1 keV and 5 keV electron beams are localized within the top 20 nm, 200 nm of the AlGaN film, respectively. The 10 keV beam penetrates the entire film and into the sapphire substrate with peak energy loss around 300 nm inside the AlGaN film.
Figure 4.1. CASINO Monte Carlo electron trajectory simulation of Al$_{0.5}$Ga$_{0.5}$N:Si film. Electron beam excitation at 1 keV excites the near surface region, while 5 keV and 7 keV electron beam excitations excite the film center.

Figure 4.2 shows the low temperature 5 keV LEEN spectra for all of the AlGaN:Si films in Table 4.1. The spectra are offset vertically for clarity. These spectra show a wide variation in the AlGaN near band edge emission shape and width. The signal intensities in this figure cannot be compared between the different samples because the spectra were taken on different days. Mid-gap emissions were only observed in the four samples with the highest Al mole fraction. These mid-gap emissions will be discussed later.
Figure 4.2. 5 keV low temperature (10-12 K) LEEN spectra for AlGaN:Si films described in Table 4.1. The spectra are offset vertically for clarity.

The high-energy onset of the near band edge emission and the peak of the near band edge emission taken at 12 K and 5 keV excitation are shown in Figure 4.3. The high-energy onset of the near band edge emission tracks the theoretical band gap (with $b=1$)\textsuperscript{121} while the peak of the near band edge emission deviates from the theoretical band gap in a nearly linear fashion. The deviation of the peak energy position from the theoretical band gap is plotted in Figure 4.4. It is interesting to note that the near band edge emission peak for gs1424 does not follow the linear trend.
Figure 4.3. Near band edge emission high energy onset energy and peak emission energy versus mole fraction for AlGaN films of Al mole fractions from 0.25 – 1.0 for a 5 keV electron beam. The theoretical band gap with b=1 is also shown.
Figure 4.4. Deviation of the near band edge emission peak shown in Figure 4.3 from the b=1 theoretical band gap. There is a linear dependence versus mole fraction up to x=0.98.

In order to characterize the thermal quenching activation energies of the near band edge emissions, temperature dependent cathodoluminescence measurements were performed at 5 keV electron probe energy for each sample. The total near band edge emission was integrated and the activation energy of the thermal quenching was found by least square fitting of the intensity data using the standard equation: \( I = \frac{I_o}{1 + a \cdot e^{\frac{E_g}{kT}}} \) (10)

where I is the intensity of the emission, \( I_o \) is the baseline intensity, a is a radiative recombination efficiency constant (a=\( \tau_R/\tau_{NR0} \), the ratio of the radiative and nonradiative
lifetimes), k is the Boltzmann constant, $E_a$ is the activation energy, and $T$ is the temperature. These results are shown in the following figure.

Figure 4.5. Activation energy of total integrated near band edge emission for AlGaN samples excited with a 5 keV electron beam. The reduced activation energies are circled.

Figure 4.5 shows that the activation energy is significantly less for the four highest Al mole fraction samples (~36 meV) than the ~54 meV activation energies of the lower Al samples. SIMS reveals enhanced O concentrations in these AlGaN films compared with films of lower Al mole fraction, shown in Table 4.2.

Changes in the AlGaN near band edge emission with the addition of Si are noted for samples of Al mole fraction ~50%. Low temperature LEEN spectra for three samples—GS1422, GS1423, and GS1425—are shown in Figure 4.6. While these samples have very similar Al mole fractions, the Si flux during growth was varied. With increasing Si flux, the near band edge features shift to lower energies. This can be
explained by the formation of a Si donor band near the conduction band edge with higher concentrations of Si donors. This phenomenon is known as band-tailing\textsuperscript{124} and reduces the effective band gap due to an increased density of states below the conduction band edge. This increased density of states below the original conduction band allows for excited electrons to thermalize down to a lower state in the conduction band and therefore light may be emitted at an energy below that of the original band gap if the electrons recombine radiatively with valence band holes.

![Luminescence Intensity vs Photon Energy Graph](image)

Figure 4.6. Change in AlGaN near band edge emission with the addition of Si for Al mole fraction of ~0.5. There is a shift in the AlGaN near band edge emission to lower energies as the Si concentration is increased.

4.2 SIMS Impurity Calibration

In order to quantify the amount of Si, O, and C impurities in the AlGaN films, separate pieces of some of the samples listed in Table 4.1 were implanted with Si\textsuperscript{28}, O\textsuperscript{16},
and C\textsuperscript{12} using an ion implanter at a dose of 3x10\textsuperscript{15} cm\textsuperscript{-2}. Samples encompassing a wide range of Al mole fractions were implanted with impurities such that calibration factors could be generated for the entire alloy series to account for matrix effects. For pure GaN, a separate set of samples from another source were implanted with Si\textsuperscript{30}, O\textsuperscript{18}, and C\textsuperscript{12} for calibration purposes. The peak concentrations of the implanted species were found using SRIM/TRIM 2000, an ion implantation simulator\textsuperscript{125}. This program takes into account the implant species, the implant dose, the implant energy, the target material stoichiometry, and the target material density to generate an implant profile. Negative SIMS depth profiles using a 3 keV Cs\textsuperscript{+} sputter beam were performed on these implanted standards in the TRIFT III TOF-SIMS. Several spots on each sample were analyzed to account for material variations and for statistical purposes. Calibration factors were calculated using a variation of the relative sensitivity factor method\textsuperscript{126}. Generally, a relative sensitivity factor (RSF) is a conversion factor between the impurity SIMS counts and the impurity concentration in the material. This is described by the following equation:

\[
RSF_M = C_I \frac{I_M}{I_I}
\]

where \(C_I\) is the concentration of the impurity, \(I_M\) is the SIMS counts for the matrix species \(M\), and \(I_I\) is the SIMS counts for the impurity. In order to reduce to influence of instrument tuning on the RSF measurements, the MN\textsuperscript{−} matrix ions were chosen (AlN\textsuperscript{−} and GaN\textsuperscript{−}) instead of the M\textsuperscript{−} matrix ions (Al\textsuperscript{−} and Ga\textsuperscript{−}) as suggested by Chu, et al.\textsuperscript{127} For each RSF analysis, the impurity concentration at the peak of the implant profile was determined using SRIM 2000. The SIMS impurity counts were divided by the SIMS AlN\textsuperscript{−} (GaN\textsuperscript{−}) counts at the peak of the implant profile and this ratio was used with the
peak impurity concentration to calculate the RSF\textsubscript{AlN} (RSF\textsubscript{GaN}). RSFs were calculated for each of the analysis points on each of the samples and standard errors for each RSF were computed. As aforementioned, this is a variation of the RSF method. The traditional RSF measurement involves integrating the entire implant profile and using a depth profilometer (i.e., Dektak) to find the sputter crater depth and thereby calculating the impurity concentration from the implant dose. The lack of access to a profilometer to characterize each of the many SIMS analysis craters dissuaded us from using this method to determine relative sensitivity factors.

An increase in the oxygen SIMS counts with increasing sputter time has been observed in similar AlGaN films. This has been attributed to background oxygen in the analysis chamber. However, sputter times for the samples analyzed in the research are relatively small and therefore a very small amount of oxygen is expected to have been due to the background oxygen. Figure 4.7 shows data from one study of the background oxygen contribution to the SIMS O signal. In this study, an oxygen implanted AlGaN sample of Al mole fraction 0.33 was depth profiled with a 3 keV Cs\textsuperscript{+} sputter beam using different Cs currents. Higher Cs currents result in faster sputtering. The background oxygen ion counts and the implant peak oxygen counts were monitored. Assuming an AlGaN film thickness of 400 nm, a sputter rate was assigned for each current setting. The Cs current is controlled by aperture settings, denoted Ap 5, Ap 10, etc. The Cs currents are listed in the figure for each setting. This figure shows the O/GaN ion ratio as a function of the inverse of this sputtering rate. For almost all of the SIMS experiments, the highest sputter rates (smallest sputter times) were used (Ap 50). This setting yielded
the lowest oxygen background levels so it appears as if the oxygen background
correction has been minimized for these experimental conditions.

Figure 4.7. SIMS O/GaN negative ion ratio of O-implanted GS1421 measured at the
background level as a function of inverse sputtering rate assuming an AlGaN thickness of
400 nm. A linear fit is also shown. For very slow Cs sputtering rates, the apparent O
concentration is approximately eight times that of the O concentration at the fastest
sputtering rates. The Cs current for each aperture setting is listed in the figure.

In an effort to extract the Al mole fraction from a SIMS depth profile, the
AlN/GaN negative ion ratio versus Al mole fraction was analyzed. Figure 4.8 shows the
average of this ion ratio at each Al mole fraction and the associated error bars that were
computed from the statistics of many measurements at each point. The points were fitted
with an exponential curve weighted with the error bars. The curve did not fit the data
points for Al mole fractions greater than 70% and therefore this calibration data is only

99
used for mole fractions less than 0.50. The error of this curve fit yields an error in the Al mole fraction of ±2%. An exponential curve fit was assumed with no physical basis.

![Graph showing AlN/GaN SIMS ratio as a function of Al mole fraction.](image)

Figure 4.8. AlN/GaN SIMS negative ion ratio as a function of Al mole fraction. This plot represents many measurements of samples at each mole fraction with the average value and representative error bar plotted for each Al mole fraction. The plots were fitted using an exponential function weighted by the error bars.

4.3 SIMS Analysis of AlGaN:Si

Negative SIMS depth profiles were performed on each of the AlGaN:Si samples in order to characterize the impurity profiles and concentrations. Si, O, and C impurities were found in each of the samples with varying concentrations. Generally, the O and C concentrations were larger at the surface than in the middle of the film and the Si concentration profile was constant throughout the film. There was also some degree of O out-diffusion from the sapphire substrate into the AlN buffer layer and beyond. An example of this type of O profile is shown in the following SIMS depth profile from
which the largest amount of O diffusion of the sample set was observed. Note that the oxygen profile reveals a larger concentration near the AlGaN/AlN interface near 400 nm.

![SIMS depth profile of Si and O impurities for sample gs1555](image)

Figure 4.9. Negative SIMS depth profile of Si and O impurities for sample gs1555. This profile revealed the largest amount of diffusion into the AlGaN of the entire sample set.

The following table summarizes the Si and O bulk concentrations for each of the samples. The O concentration was taken from the middle of the AlGaN film. From this data it is clear that there is a relatively large amount of O in these samples and the general trend is that the O concentration is higher for the larger Al mole fraction samples (with the exception of gs1424/AlN). This trend is expected since Al has a large affinity for O. Also, there is good agreement between the measured Si concentration and the Si effusion cell temperature across the Al mole fraction range as shown in Figure 4.10.
Table 4.2. Si and O bulk concentrations for AlGaN:Si samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al mole fraction</th>
<th>[Si] (atoms/cm$^3$)</th>
<th>[O] (atoms/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gs1420</td>
<td>0.25</td>
<td>5.1e18</td>
<td>8.6e18</td>
</tr>
<tr>
<td>Gs1421</td>
<td>0.33</td>
<td>2.5e19</td>
<td>3.4e19</td>
</tr>
<tr>
<td>Gs1422</td>
<td>0.52</td>
<td>3.6e18</td>
<td>6.4e18</td>
</tr>
<tr>
<td>Gs1423</td>
<td>0.48</td>
<td>1.6e19</td>
<td>6.6e18</td>
</tr>
<tr>
<td>Gs1425</td>
<td>0.47</td>
<td>7.6e19</td>
<td>1.3e19</td>
</tr>
<tr>
<td>Gs1427</td>
<td>0.65</td>
<td>7.1e19</td>
<td>1.3e19</td>
</tr>
<tr>
<td>Gs1590</td>
<td>0.76</td>
<td>2.1e19</td>
<td>4.4e20</td>
</tr>
<tr>
<td>Gs1555</td>
<td>0.78</td>
<td>2.6e20</td>
<td>7.1e20</td>
</tr>
<tr>
<td>Gs1564</td>
<td>0.79</td>
<td>2.5e20</td>
<td>3.4e20</td>
</tr>
<tr>
<td>Gs1426</td>
<td>0.98</td>
<td>7.5e19</td>
<td>1.4e20</td>
</tr>
<tr>
<td>Gs1424</td>
<td>1.00</td>
<td>6.0e19</td>
<td>2.2e19</td>
</tr>
</tbody>
</table>

Figure 4.10. Relationship between measured Si concentration and Si effusion cell temperature for AlGaN samples across the alloy series. There is a clear correlation of increasing Si concentration with increasing effusion cell temperature.
The Si concentration and the Hall electron density are plotted as a function of the Al mole fraction in Figure 4.11. For Al mole fractions less than ~ 0.75, the Hall density tends to be higher than the measured Si concentration. However, for Al mole fractions greater than 0.75, the Si concentration tends to be higher than the Hall density. The arrows on the figure point from the Si concentration to the electron concentration. There is definitely a large change in the effectiveness of the Si doping at ~ 75% Al mole fraction.

Preliminary electrochemical C-V profiling measurements of the lowest Al mole fraction samples were performed by Dr. Edward Stutz at the Air Force Research Laboratory at Wright-Patterson Air Force Base. This profiling involved etching the AlGaN films electrochemically with an electrolyte solution and incident light while measuring the electron concentration. This method yields the carrier concentration as a function of depth. The results along with the SIMS impurity profiles for O, Si, and C are shown in Figure 4.12 and Figure 4.13 for gs1420 and gs1421. In these depth profiles, the electron concentrations are lower than that of the impurity concentrations. If the error of the SIMS relative sensitivity factors for each of impurities is taken into account, then the electron concentration overlaps the range in SIMS impurities defined by the RSF error bars. Higher Al mole fraction samples could not be etched by this electrochemical C-V profiler because the light source did not produce enough UV light to be absorbed by these high band gap materials.
Figure 4.11. Hall electron density and SIMS Si concentration as a function of Al mole fraction for AlGaN:Si. The arrows on the diagram point from the Si concentration to the electron concentration and serve as a guide to the eye.

Figure 4.12. Electrochemical C-V profiling electron concentration and O, Si, and C SIMS impurity concentrations versus depth for gs1420 AlGaN:Si (25%). The electron concentration is lower but reasonably close to the impurity concentrations.
Figure 4.13. Electrochemical C-V profiling electron concentration and O, Si, and C SIMS impurity concentrations versus depth for gs1421 AlGaN:Si (33%). The electron concentration is below but reasonably close to the impurity concentrations.

4.4 Deep Levels in High Al Mole Fraction AlGaN

As previously mentioned, mid-gap luminescence was only observed in the four samples with the highest Al mole fraction. Low temperature cathodoluminescence for the Al$_{0.98}$Ga$_{0.02}$N and AlN samples are shown in Figure 4.14 and Figure 4.15. These figures show depth-dependent CLS spectra taken at 12 K for 1, 5, and 10 keV electron probe energies for AlN and Al$_{0.98}$Ga$_{0.02}$N samples. For the AlN film in Figure 4.15, the near band edge emission is observed at 6.03 eV with a line width of 120 meV and is in agreement with a near band edge emission at 5.99 eV with a corresponding line width of 150 meV reported by Tang, et al. for AlN on sapphire measured at a comparable sample temperature.$^{128}$ In addition, broad deep levels appear at 3.2-3.5 eV and at 4.4 eV.
Figure 4.14, a broad deep level is also observed in the Al$_{0.98}$Ga$_{0.02}$N film, but the emission has a peak at a slightly lower energy of 3.1 eV. Figure 4.15 shows that as the electron beam is varied from 1 keV up to 10 keV in the AlN film, there is a continuous shift of the broad deep level emission from 3.51 eV to 3.18 eV. In contrast, Figure 4.14 shows virtually no shift of the 3.1 eV peak as the electron beam energy varies from 1 to 10 keV in the Al$_{0.98}$Ga$_{0.02}$N film. Also, a relatively broad near band edge emission at 5.46 eV is observed in the Al$_{0.98}$Ga$_{0.02}$N film. Mid-gap emissions are observed at 3.1 eV in Al$_{0.98}$Ga$_{0.02}$N and in the range of 3.3-3.5 eV in AlN and the near band edge emission peaks are 5.46 eV and 6.03 eV, respectively. These deep mid-gap emissions have been attributed to O-related defects as previously mentioned. A surface-related emission is observed only with 1 keV excitation in Al$_{0.98}$Ga$_{0.02}$N at 4.76 eV, i.e., 0.6 eV below the near band edge emission peak. Broad emissions are observed with 10 keV excitation in both samples at 4.29 eV and 5.54 eV in AlN and 4.16 eV and 4.59 eV in Al$_{0.98}$Ga$_{0.02}$N.
Figure 4.14. Low temperature cathodoluminescence of Al\(_{0.98}\)Ga\(_{0.02}\)N as a function of electron beam excitation energy. The peak position of maximum energy loss for each electron probe energy from CASINO simulations are shown in the plot.

Figure 4.15. Low temperature cathodoluminescence of AlN as a function of electron beam excitation energy. The peak position of maximum energy loss for each electron probe energy from CASINO simulations are shown in the plot.
The SIMS depth profiles for the $\text{Al}_{0.98}\text{Ga}_{0.02}\text{N}$ sample and the AlN sample are shown in Figure 4.16 and Figure 4.17, respectively. The $\text{Al}_{0.98}\text{Ga}_{0.02}\text{N}$ sample exhibits a higher O concentration than the AlN and also has a very different O profile than any of the AlGaN:Si samples in that there is a relatively high level of O extending from the surface into the middle of the film. Also, the $\text{Al}_{0.98}\text{Ga}_{0.02}\text{N}$ shows a significant level of O diffusion at the AlN/$\text{Al}_2\text{O}_3$ interface. The depth scale for both AlN and $\text{Al}_{0.98}\text{Ga}_{0.02}\text{N}$ are based on the AlN and the O profile crossover for the 400 nm films. There is an enhanced oxygen concentration near the sapphire substrate for both films and an increased oxygen concentration near the surface of the $\text{Al}_{0.98}\text{Ga}_{0.02}\text{N}$ film, as shown by the arrows. In Figure 4.17, the O concentration exhibits a well-defined shoulder that extends ~100 nm into the AlN from the $\text{Al}_2\text{O}_3$ with a magnitude ~100x larger than the baseline O concentration of $2\times10^{19}$ cm$^{-3}$ in the bulk. Surface O concentration increases significantly but is uncalibrated due to matrix effects. In Figure 4.16, the O content in the $\text{Al}_{0.98}\text{Ga}_{0.02}\text{N}$ is relatively high, ~5-7$\times10^{20}$ cm$^{-3}$, within a few hundred nm of the surface compared to a minimum value in the bulk of ~$2\times10^{19}$ cm$^{-3}$. The O concentration again exhibits a pronounced shoulder that extends ~100 nm into the AlGaN alloy. However the shoulder intensity is approximately the same as near the surface. The Si in the AlN exhibits a non-uniform profile. Increased SIMS ion counts of Si and C in the $\text{Al}_2\text{O}_3$ are due to an enhanced ion yield from the secondary ion matrix effect$^{129}$ and are not significant.
Figure 4.16. Negative SIMS depth profiles for Al\textsubscript{0.98}Ga\textsubscript{0.02}N. The Si, O, and C impurity concentrations are shown on the left axis while the AlN\textsuperscript− matrix ion counts are shown on the right axis.

Figure 4.17. Negative SIMS depth profiles for AlN. The Si, O, and C impurity concentrations are shown on the left axis while the AlN\textsuperscript− matrix ion counts are shown on the right axis.
Deep level emissions were also observed by LEEN in two other samples: gs1564 and gs1555. A luminescence emission around 4.0 eV is observed for both samples under 10 keV electron beam excitation. These LEEN depth profiles are shown in Figure 4.18 and Figure 4.19.

Figure 4.18. Low temperature LEEN depth profile for sample gs1564 (79% Al). This sample exhibits deep level emissions similar those with the highest Al mole fractions as well as an emission around 4.0 eV for 5 keV and 10 keV excitation.
Figure 4.19. Low temperature LEEN depth profile for sample gs1555 (78% Al). This sample exhibits deep level emissions similar those with the highest Al mole fractions as well as an emission around 4.0 eV for 10 keV excitation. The rise in signal at 2.5 eV is due to the second order signal of the near band edge emission.

4.5 Cross-sectional CLS of AlGaN:Si

In order to determine the nature of defects near the AlGaN/sapphire interface, cross-sectional CL measurements were performed on cleaved pieces of AlGaN and AlN. This experiment was conceived in order to further elucidate the nature of the defects that were observed in plan-view CLS. The sample was held at a temperature of 11 K in the JAMP 7800F Auger microprobe and excited with a 10 keV electron beam. From CASINO simulations, this electron beam excites a depth of approximately 400 nm—well below the free surface—in order to reduce the contribution of luminescence from the cleaved surface. This high excitation energy degrades the lateral CL resolution in that the
electron cascade has a lateral spread on the order of the excitation depth (~ 800 nm). Automatic probe tracking was used to keep the electron beam in its specified place.

Figure 4.20.  SEM image of Al$_{0.98}$Ga$_{0.02}$N sample (gs1426) showing the spots where cross-sectional CL was taken. The SEM was operated in spot mode in order to place the electron probe at these points. The sapphire is on the upper left and the AlGaN film is on the lower right. The film thickness is 400 nm.

Figure 4.21 shows the CL spectra as a function of distance from the AlGaN/sapphire interface for the points shown in Figure 4.20. There are several different emissions observed to vary as a function of position. In this figure, positive distances denote measurements in the sapphire. The AlGaN near band edge emission is observed at ~5.5 eV in the AlGaN film. This peak position correlates with the value found from plan-view measurements. Defect emissions at 3.3 eV and 3.8 eV are also observed in the AlGaN film and the sapphire. An additional broad defect emission is also observed at an energy position of ~ 4.5 eV. This 4.5 eV broad defect emission continues to increase into the sapphire.
Figure 4.21. Cross-sectional CL of gs1426 (98%) AlGaN as a function of distance from the AlGaN/sapphire interface. Positive distances correspond to measurements in the sapphire. The arrows designate the near band edge emission and the defect emissions.

The integrated luminescence features from this set of spectra are plotted as a function of distance from the interface in Figure 4.22. In this figure, the AlGaN near band edge emission is a maximum at the center of the AlGaN film. The 3.3 eV and 3.8 eV features exhibit maxima near the AlGaN/GaN interface but are present to varying degrees throughout the measured spectra.
Figure 4.22. Luminescence features of from cross-sectional LEEN of AlGaN gs1426. The AlGaN near band edge emission peaks in the center of the AlGaN films, while the 3.3 eV and 3.8 eV defects peak near the AlGaN/sapphire interface. Negative distances refer to the AlGaN film.

4.6 Discussion

The SIMS and CLS measurements are consistent with strong deep level emissions due to oxygen and carbon. For the AlN, the mid-gap defect exhibits a trend in that the peak continuously shifts to lower energies as the electron probe energy is increased. This shift correlates with the increased O at the interface of the sapphire and thus with the observations by Youngman, et al. shown in Figure 4.23. In this study, the deep level luminescence peak energy position is found to increase in wavelength from 305 nm (4.07 eV) to 375 nm (3.31 eV) as the atomic percent of oxygen increases from 0.1% to around 1%. This relationship is shown in the following figure.
Hence, the energy shift in Figure 4.15 from 3.51 to 3.18 eV with increasing excitation depth observed in our AlN film is consistent with the increased O percentage from ~0.1% in the film bulk to >1% at the interface with the sapphire. Likewise, the absence of any shift of the 3.1 eV peak in Figure 4.14 with increasing probe depth is consistent with the high O concentration at almost all depths within the Al<sub>0.98</sub>Ga<sub>0.02</sub>N. Also, its 3.1 eV value coincides with the energy expected for such O concentrations. The Al<sub>0.98</sub>Ga<sub>0.02</sub>N sample has a mid-gap state with a slightly lower energy than that of the AlN sample; this could also be accounted for by the higher overall O concentration observed in the Al<sub>0.98</sub>Ga<sub>0.02</sub>N film. However, for O concentrations greater than 1%, no further decrease in energy of the cathodoluminescence peak energy was shown to occur.

Depth-dependent CLS and SIMS also identify a C-related deep level. The 4.4 eV emission in AlN at 1 keV and 5 keV has been reported in MOCVD carbon-doped AlN by
Tang, et al. and in unintentionally doped, vapor sublimation-recondensation grown AlN by Slack, et al.\textsuperscript{130} Tang, et al. observed a dramatic increase in the 4.44 eV emission for slightly C-doped AlN versus unintentionally doped AlN. The 4.76 eV emission at 1 keV excitation in the Al\textsubscript{0.98}Ga\textsubscript{0.02}N film may be related to the high O and C concentrations observed in the near surface region in the SIMS depth profile, but the exact origin is not known. One possible explanation for this isolated emission is that the increased impurity concentrations in the near-surface region could contribute to an increased donor-acceptor pair emission associated with O donors and C acceptors.

Figure 4.14 and Figure 4.15 show that new states emerge with 10 keV electron beam excitation in both samples. Since the electron beam at this energy is also penetrating into the sapphire substrate, one needs to distinguish any bulk Al\textsubscript{2}O\textsubscript{3} luminescence features from the luminescence features that are related to the interfacial region. An O-vacancy related emission has been observed at 3.8 eV and has been studied in electron-irradiated sapphire.\textsuperscript{131} An emission with an approximate energy of 4.25 eV might be expected to occur from an excited state of an O-vacancy in sapphire to the ground state, according to a model proposed by Brewer, et al.\textsuperscript{132} Thus, the 4.29 eV peak in AlN and the 4.16 eV peak in Al\textsubscript{0.98}Ga\textsubscript{0.02}N may correspond to this excited state. Such luminescence has not been reported. Taking this into account, the 4.29 eV and 5.54 eV emission bands in AlN and the 4.59 eV emission band in Al\textsubscript{0.98}Ga\textsubscript{0.02}N may be related to the AlGaN/Al\textsubscript{2}O\textsubscript{3} interface since these states have not been observed in the Al\textsubscript{2}O\textsubscript{3} bulk. The 4.29 eV peak does, however, appear to be due to the sapphire since cross-sectional measurements show that the intensity of a broad ~ 4.5 eV emission is a maximum in the sapphire as shown in Figure 4.22.
Cross-sectional study of the Al\textsubscript{0.98}Ga\textsubscript{0.02}N sample has further elucidated the nature of the defects that are observed with depth-resolved CLS in plan view. As mentioned in the previous paragraph, Figure 4.22 shows that the 4.5 eV emission increases into the bulk of the substrate. Therefore, it is most likely that this feature is due to the sapphire and not the interface. Also shown in Figure 4.22, the 3.3 eV emission and 3.8 eV emission are of maximum intensity at the AlGaN/sapphire interface. The 3.3 eV emission correlates with the plan-view CL defect observation and is most likely the O-related defect emission. In the previous paragraph, the 3.8 eV emission is attributed to O vacancies. The maximum of these peaks at the interface agrees with oxygen diffusing from the sapphire into the AlGaN film during growth and leaving behind O-vacancies. The 3.8 eV emission is in the range of O-related emission wavelengths as shown in Figure 4.23. However, this emission is unlikely to be due to O in the AlN material since, according to Figure 4.23, the O concentration as measured by SIMS is higher than the value required to give such an emission. Also, the plan-view CL of this particular sample revealed an O-related emission around 3.1 eV which is close to 3.3 eV. A high O concentration near the sapphire interface is observed in Figure 4.16 for this sample which appears to have diffused from the sapphire. This diffusion would lead to the creation of O vacancies in the sapphire and therefore could lead to an emission at 3.8 eV. A 3.8 eV emission maximum has also been observed with cross-sectional CL by Goss, et al. near a GaN/sapphire interface.\textsuperscript{133} The authors attribute this emission along with a resulting O donor-related emission in the GaN to O diffusing from the sapphire into the GaN film. Therefore, these cross-sectional measurements strengthen the argument that O is
diffusing from the substrate leaving O vacancies in the sapphire and taking part in creating deep levels observed by depth-dependent cathodoluminescence.

Figure 4.3 and Figure 4.4 showed that the luminescence emission peak energy deviated from the high energy onset of the luminescence peak with increasing Al mole fraction. The deviation of the near band edge peak from the band gap shows that the peak lies deeper into the gap at higher mole fractions. This is consistent with observations from other researchers that the Si and O donor/DX energies increase as the Al mole fraction increases. Bremser, et al. have observed a linear deviation of donor-acceptor pair (DAP) luminescence from the AlGaN near band edge with increasing Al mole fraction. The high-energy onset of the near band edge emission is more likely the free exciton or band-to-band transition and is expected to follow the theoretical band gap.

The activation energy of the quenching of the 5 keV LEEN luminescence was shown in Figure 4.5. The observed reduction in the activation energy of the near band edge emission in higher Al mole fractions differs from previous results showing the Si donor energy increasing strongly for Al mole fractions greater than 0.8. However, Nam, et al. have observed that there is a sharp reduction in the activation energy of the total integrated near band edge emission in Al$_{0.45}$Ga$_{0.55}$N for Si concentrations greater than 1x10$^{18}$ atoms/cm$^3$. They suggest that this is a critical concentration for achieving n-type conductivity since the localized states are filled and carriers can transport through extended overlapping states. Extended state hopping could be responsible for the reduced $E_A$ in our samples, assuming that both Si and O are acting as donors, since SIMS shows that the sum of the O and Si concentrations for these samples are higher than those of the other Al mole fraction samples. Transport through such overlapping states is likely for
concentrations exceeding the Mott limit, i.e., \( N_D = (0.24/a_B)^3 \geq 1 \times 10^{19} \text{ cm}^{-3} \), where \( a_B \) is the donor electron Bohr radius.\(^{43,138}\) Indeed Table 4.2 shows that the four samples with the highest Si and O concentrations have the lowest \( E_A \) values. Likewise, the Si and O concentrations of the AlGaN film with \( x = 0.52 \) are below this value and the film is insulating. Thus, both the \( E_A \) and the excess carrier concentration values can be accounted for by assuming O is a donor. However, the proposal of overlapping donor states does not explain the lack of conductivity for the AlGaN films with the Al mole fractions of 0.98 and 1.0. The highest Al mole fraction films could be less conductive because of impurity compensation yet still exhibit a reduction in activation energy caused by the extended overlapping states. Another explanation is that the donor level broadens with the higher O and Si concentrations so that higher lying states are closer to the conduction band. This would effectively reduce the observed activation energy. Significantly, the samples with reduced \( E_A \) and relatively large Si and O concentrations are the only samples of the series that exhibit mid-gap cathodoluminescence emissions, suggesting both deep as well as relatively shallow states related to oxygen. Further investigations are necessary to examine the correlation between increased Si and O concentrations, increased mid-gap cathodoluminescence, and reduced near band edge activation energy in these high Al mole fraction AlGaN films.

Figure 4.11 shows that the Hall carrier density tends to be larger than the Si concentration as measured by SIMS for \( x_{Al} < 0.76 \) and vice versa for \( x_{Al} \geq 0.76 \). This reduction in Hall carrier density for these higher Al mole fraction samples correlates with the reported Si activation energy increase, the increased O concentration, and the increased intensity of mid-gap emissions. This could mean that O is changing roles from
a shallow donor at lower mole fractions to a compensating center at higher mole fractions. Oxygen at the interface has been shown to increase the measured conductivity in GaN\textsuperscript{139} and therefore could play a role in the observed increase in Hall carrier density for the lower mole fraction samples. A degenerately doped interfacial layer has been shown to affect Hall-effect measurements in the GaN/Al\textsubscript{2}O\textsubscript{3} system and a two-layer Hall model has been proposed in order to correct for this highly conductive layer.\textsuperscript{140} A new donor level whose intensity correlates with O concentration near the interface demonstrates the donor nature of O in GaN. According to Youngman and Harris, O is shown to incorporate with Al vacancy complexes and can form other extended complexes at higher O concentrations. Youngman and Harris state that as the oxygen level is increased above 0.75\%, the V\textsubscript{Al}-O defect progressively changes to Al atoms octahedrally coordinated with oxygen. This octahedral configuration leads to stacking faults and inversion domain boundaries and thus extended defects arise. The exact electronic nature of these extended defects is not known. However, aluminum vacancies have been shown to act as compensating centers and therefore affect the conductivity of high Al mole fraction AlGaN. In addition, Taniyasu, et al., have reported Si self-compensation in AlN for [Si]>3x10\textsuperscript{19} cm\textsuperscript{-3} and this phenomenon could also contribute to the reduction of the Hall carrier density at high Al mole fractions. Further electrochemical-CV profiling measurements are planned to determine the carrier concentration versus depth in the AlGaN films at higher Al mole fractions. The results will be compared with the SIMS impurity profiles and cathodoluminescence spectra in order to determine the contributions of impurities to the observed carrier concentrations.
Figure 4.24 shows most of the elements from Figure 4.3 with the addition of the luminescence states believed to be due to C and O impurities. It is interesting to note that the points labeled as *defect emission* lie at about the same energy as the points believed to be due to C impurities. If the *defect emission* features are also due to C, this would mean that C gives rise to a state that is constant in the band gap.

Figure 4.24. Luminescence features as a function of Al mole fraction from 5 keV LEEN spectroscopy. This figure is similar to Figure 4.3 but with the addition of the assigned C and O defect emissions.
5.1 UHV Deposition of Ni/AlGaN Contacts

The importance of surface preparation on the formation of Schottky barriers to nitrides was discussed in previous sections. In order to study the relationship between surface preparation, Schottky barrier height, and current transport, Schottky diodes were created on selected AlGaN/GaN HFET structures from Cornell University. In this study, only Ni was used as the Schottky contact, but other Schottky metals such as Au and Pt were available for use. Before the Schottky surface preparation and deposition of the Schottky contacts, ohmic contact bars were formed on each piece of material. These ohmic contact schemes were based on a commonly used layered structure of Ti/Al/Ti/Au with Ti deposited on the sample surface and Au deposited on top of the layer stack. The thicknesses of each of the metals were 200 Å, 500 Å, 600 Å, and 550 Å, respectively. A standard organic solvent clean of acetone, methanol, and isopropanol followed by a DI water rinse was employed to degrease the sample. An acid etch of buffered HF followed the degrease procedure in order to remove the native oxide for a more intimate metal/semiconductor contact. Following the acid etch, the samples were rinsed in DI water and blown dry with nitrogen gas. Tantalum clips were used to hold the sample and to serve as a shadow mask for the ohmic deposition and the samples was then introduced
into the vacuum chamber for metal deposition. Typical background pressures were in the low $10^{-10}$ torr range before ohmic metal deposition. After the ohmic layers were deposited, the sample was removed from the vacuum chamber and placed on a UHV heating mount and then reintroduced into the chamber for annealing of the ohmic contact. The temperature of the sample ohmic anneal was monitored using an optical pyrometer focused on the molybdenum heater mount through a sapphire viewport. An emissivity of 0.2 was assumed for the molybdenum. The sample was heated to 850 °C for 30-45 seconds and then returned to room temperature before removal from the vacuum chamber. Annealing ohmic contacts has been shown to significantly reduce the contact resistance and thus reduce ohmic losses during the Schottky barrier I-V measurements. The ohmic contacts were then checked for linearity using the probe station and HP4145 semiconductor parameter analyzer.

Next, the Schottky processing steps and Schottky contact deposition were performed in the regions of the samples between the ohmic contact bars. A representative contact arrangement is shown in Figure 5.1.
The surface preparation schemes included a combination of acids to remove surface contamination and UV-ozone cleaning to remove carbon contamination. Following the various surface treatment steps, the samples were rinsed in DI water, blown dry in nitrogen, and then masked for patterning of the Schottky contacts. Circular shadow masks with inner hole diameters of 1 mm and 0.5 mm were overlaid on the samples and fastened with tantalum clips. The samples were immediately loaded into the UHV metal deposition chamber with a base pressure of $10^{-10}$ torr. Ni Schottky metal deposition was performed with an electron beam evaporator at a rate of approximately 0.1 nm/s to a total thickness of around 24 nm. For wafer 1, a 10 nm Au layer was then deposited on top of the Ni to facilitate probing and wire bonding. Wafer 2 contacts did not have this Au layer. Following the deposition, the samples were removed and
characterization was performed by I-V and IPE. In certain cases, the samples were then subsequently annealed using the same UHV molybdenum heater that was used to anneal the ohmic contacts.

5.2 Description of Surface Processing Conditions

Schottky contact studies were performed on two different AlGaN/GaN HFET structures: GS1044 and GS1235. A comparison of the material properties are shown in Table 5.1. These two pieces are from the same batch of samples grown at Cornell University as previously described. These HFET structures have similar Al mole fractions and Hall mobilities, but exhibit slightly different degrees of quality as exemplified by the difference in AlGaN near band edge emission width and different intensities of defect luminescence (YL).

Table 5.1. Comparison of material properties for two AlGaN/GaN HFET structures used for Schottky deposition studies.

<table>
<thead>
<tr>
<th></th>
<th>Al mole fraction</th>
<th>Mobility (300K)</th>
<th>AlGaN FWHM</th>
<th>YL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1235</td>
<td>0.33</td>
<td>805</td>
<td>140 meV</td>
<td>Little YL</td>
</tr>
<tr>
<td>(Wafer 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1041</td>
<td>0.35</td>
<td>730</td>
<td>330 meV</td>
<td>Higher YL</td>
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<tr>
<td>(Wafer 2)</td>
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The different surface processing steps are described as follows. All AlGaN surfaces were cleaned with organic solvents (acetone/methanol/isopropanol), rinsed in DI water, and blown dry with N₂ gas. After the organic clean, the AlGaN surfaces were
processed in three ways. Process A (HF) involved a simple acid etch (buffered HF) to remove the native oxide, DI water rinse and N₂ dry, and then the sample was shadow masked for Ni patterning and immediately loaded into the load chamber for introduction into UHV. Process B (UV/O₃) involved all of the wet processing steps of the first process followed by exposing a selected area of the wafer by shadow masking with tantalum foil. The sample was immediately loaded into a custom UV-ozone processing chamber with an internal Hg lamp positioned approximately 5 cm from the sample surface for UV irradiation. UV-ozone cleaning was performed at an oxygen background pressure of 300 milliTorr for two hours. Process C (UV/O₃ + HF/HCl) involved the elements of the first two processes but with an additional buffered HF and concentrated HCl acid etch and DI water rinse and N₂ dry to remove the surface oxide that was formed by the UV-ozone cleaning step.

Subsequent surface processing steps were performed on each of the wafers in order to minimize the effects of sample nonuniformities which could result from using different pieces of wafers that could potentially have different material characteristics. For example, wafer 1 was exposed to Process A. After these diodes were characterized by I-V and IPE, an adjacent part of the wafer was exposed to a UV-ozone clean (Process B) and the existing diodes were shielded with tantalum clips. Then, new diodes were created in the newly processed UV-ozone region and characterized. Next, all of the diodes were annealed in steps with I-V and IPE characterization performed after each annealing step. Finally, a new region of the sample which had been exposed to the UV-ozone cleaning process was etched in buffered HF (Process C) and diodes were deposited in this region and then characterized. Similar process steps were performed for wafer 2.
5.3 Internal Photoemission Spectroscopy and I-V versus Surface Processing

Wafer 1 Results:

Internal photoemission spectroscopy and current-voltage characterization were performed on wafer 1 following the surface HF treatment (process A), UV/O$_3$ (process B) and subsequent UHV anneals at 325 °C for 10 minutes and 425 °C for 10 minutes. After the diodes were annealed, new diodes were created by process C adjacent to the existing diodes. A representative IPE spectrum is shown below.

Figure 5.2. Representative internal photoemission Fowler plot of Ni/AlGaN Schottky diodes showing two slopes. The first slope is designated as being the less steep slope. Two different Schottky barriers are observed for this particular diode, but some diodes exhibited one slope. The signal oscillations in the line of the steeper slope are due to optical interference in the AlGaN HFET structure.
Figure 5.3. Representative internal photoemission Fowler plot of Ni/AlGaN Schottky diodes showing a single slope. Again, the oscillations in the line are an artifact of optical interference.

Some of the IPE spectra exhibit a nonlinear region near the turn-on of the photocurrent that closely mimics the measured output of the IPE setup and thus appears to be an artifact of the measurement. Wafer 1 IPE spectra before anneal exhibit a single slope which can be used to extrapolate to zero photocurrent and yield a single measured Schottky barrier height as shown in Figure 5.3. After annealing, the spectra exhibit another IPE slope which turns on before the original slope as shown in Figure 5.2. The Schottky barriers are denoted the first slope Schottky barrier and the second slope Schottky barrier.

The second slope Schottky barrier as a function of processing is shown in Figure 5.4. In this figure, diodes D1-D4 were processed by process A, diodes D5-D9 were processed by B, and diodes 9 and 10 were processed by process C. D8 overlapped the
ohmic metallization and therefore did not produce a diode. Only D1-D7 were subjected to annealing. Following the first post-metallization anneal at 325 °C, all of the diodes were characterized by IPE and I-V. Then, after another anneal at 425 °C the diodes were again characterized by these methods. Process C was then performed on an adjacent region and diodes were deposited there and then characterized. There is a significant increase in the observed Schottky barrier height for process A and process B diodes after the 325 °C anneal. After a subsequent 425 °C anneal, there are mixed results. D5 does not exhibit an IPE Schottky barrier at any point in the annealing.

![Figure 5.4](image)

Figure 5.4. Internal photoemission Schottky barrier height (second slope) of diodes fabricated on wafer 1 as a function of processing and post-metallization annealing. Diodes D1-D4 were subjected to process A, diodes D5-D9 were processed via process B, and diodes 9 and 10 were subjected to process C. Only D1-D7 were subjected to annealing.

After the 325 °C anneal, two Schottky barriers were observed. These two Schottky barriers are plotted versus diode number in Figure 5.5. Diodes processed by
process B exhibit higher values of the second slope Schottky barriers than the process A diodes. The first slope Schottky barrier tends to track the changes in the second slope Schottky barrier, except for D6.

Figure 5.5. Internal photoemission Schottky barrier heights (slope 1 and slope 2) of wafer 1 diodes subjected to process A and process B after the 325 °C anneal. Process B diodes exhibit a larger second slope SBH than process A diodes.

The reverse current density at a reverse bias of -2 V exhibits changes which correlate with the observed increase of the IPE Schottky barrier height as a function of post-metallization annealing. The reverse current as a function of processing is shown in Figure 5.6. The absolute numbers of the reverse current should not be relied upon for inter-diode comparisons since the distance between the ohmic contact and the Schottky contact was different for each diode. Intra-diode comparisons are valid, however.
Figure 5.6. Reverse current density at a reverse bias of -2 V for wafer 1 diodes as a function of process and annealing. The decrease in the reverse current is consistent with observed increases in the IPE Schottky barrier height.
Figure 5.7 shows the I-V curves for D4 after process A and after a post-metallization anneal at 325 °C. Two linear regions are observed in the forward bias case with a prominent current plateau. This current plateau is observed for most diodes, but not all. In this figure, the reverse current and the small forward bias current decreased following the 325 °C anneal. The log of the absolute value of the current is commonly displayed in I-V curves, as shown here.

For each of the diodes, the ideality factor was found from the slope of the forward bias linear regions. In most cases, two linear regions were observed in the plots of the logarithm of the current versus voltage. The slopes of these linear regions were determined by least-squares linear fitting using the Origin software package. This factor is a figure of merit for the diode with values ranging from unity. Figure 5.8 shows the
extracted ideality factor of the lower voltage slope—assuming the thermionic emission model—for the diodes of wafer 1. These ideality factors are much greater than unity and vary widely from diode to diode and as a function of processing. There seems to be a certain degree of grouping at n~6 and n~2-3. These higher ideality factors mean that the current transport mechanism is not governed by thermionic emission alone.

Figure 5.8. Ideality factors extracted from the first slope (lower voltage) of forward I-V curve for wafer diodes as a function of processing. The solvent + HF diodes of process A (D1-D4) are listed with the UV-ozone only column. The ideality factor for each diode is much larger than unity. There are no clear trends in the ideality factor as a function of processing.

Figure 5.9 shows the ideality factor of the larger linear voltage region for the wafer 1 diodes as a function of processing. For this part of the I-V curve, the diodes exhibit a very tight grouping around n=2.5, except for D7. This particular diode deviates greatly from the other diodes. D5 and D8 did not exhibit any linear regions and therefore no ideality factors were computed for Figure 5.8 and Figure 5.9.
Figure 5.9. Ideality factors extracted from the second slope (higher voltage) of forward I-V curve for wafer 1 diodes as a function of processing. The solvent + HF process A diodes (D1-D4) are listed with the UV-ozone only column. The values are generally close to 2.5 for most diodes and processes except D7, which is significantly higher.

**Wafer 2 Results:**

For wafer 2, processing and characterization steps very similar to those of wafer 1 were performed. Process A (D1-D4) and Process C (D5-D11) diodes were created, annealed, and characterized as a function of processing and subsequent post-metallization annealing. D9 overlapped the ohmic metallization and thus did not form a diode. The annealing steps were 325 °C, 425 °C, and 500 °C for 20 minutes each. Process B was not performed on these diodes. IPE revealed two slopes for all processing steps, unlike wafer 1 where two slopes were only observed after annealing.

Figure 5.10 shows the second slope IPE results for wafer 2 diodes as a function of processing and post-metallization annealing. Some diodes from process C did not exhibit
a measurable Schottky barrier height until the later anneals. After the first annealing steps, the Schottky barriers for each process show a clear bifurcation in that the process C diodes exhibit a lower Schottky barrier height than the process A diodes.

Figure 5.10. Second slope IPE Schottky barrier heights for wafer 2 as a function of processing and post-metallization annealing. Following the first annealing step, the process C diodes (UV/O\textsubscript{3}+HF) exhibit lower Schottky barrier heights than the process A diodes (HF+HCl). Some diodes did not exhibit a measurable Schottky barrier height until later in the annealing process.

Figure 5.11 shows the first slope IPE results for wafer 2 diodes as a function of processing and post-metallization annealing. Some diodes from process C did not exhibit a measurable Schottky barrier height until the later anneals, particularly D10 and D11. Most of the diodes exhibit Schottky barrier heights around 1.45 eV with the exception of these diodes.
Figure 5.11. First slope IPE Schottky barrier heights for wafer 2 as a function of processing and post-metallization annealing.

Both the first and second slope IPE Schottky barriers for each diode are shown in Figure 5.12 after the 500 °C process step. For the first and second slopes, the process C diodes exhibit lower Schottky barrier heights than the process A diodes. D10 and D11 show further decreases in the first slope Schottky barrier. D5 and D8 do not exhibit measurable Schottky barriers.
Figure 5.12. Internal photoemission spectroscopy Schottky barrier heights for wafer 2 diodes after a 500 °C anneal. Two Schottky barriers are observed for diodes processed using process A (HF) and process C (UV/O₃+HF+HCl). Process C generates lower IPE SBHs than process A for all diodes. Diodes 10 and 11 exhibit further first slope SBH shifts to lower energies.

The I-V curves for the wafer 2 diodes before post-metallization annealing are shown in Figure 5.13. These curves demonstrate a wide variation in the forward and reverse current characteristics. The diodes D5, D8, and D11 exhibit higher forward and reverse currents at small bias levels. Consequently, these diodes did not produce a measurable IPE Schottky barrier.
Figure 5.13. Wafer 2 diode I-V curves before post-metallization annealing. The diodes exhibit a wide variation in the forward and reverse bias regions. D5, D8, and D11 show the largest low bias reverse and forward currents and did not show a measurable Schottky barrier at this process step.

5.4 LEEN spectroscopy of Diodes Following Processing

Wafer 1:

Following the final annealing step for the process A (D1-D4) and process B (D5-D7) diodes, and the deposition and characterization of the process C (D8-D10) diodes, LEEN spectroscopy was performed. Wafer 1 was loaded into the JAMP 7800F Auger microprobe and the sample was cooled to a temperature of 12 K. Two types of scans ensued: characterization through the Ni contact and characterization of the free AlGaN surface near each contact. An electron beam of energy 2 keV was chosen to characterize the Ni/AlGaN interface through the Ni contact. CASINO simulations show that this
choice of electron energy is very interface sensitive. Electron beam energies of 1 keV, 2 keV, and 4 keV were employed to characterize the AlGaN free surface near each diode.

Figure 5.14 shows LEEN spectroscopy at 1 keV electron beam excitation of the free AlGaN surface near each diode. The electron beam was rastered over a 100 µm square area. These spectra show multiple peaks. The GaN near band edge emission is clearly visible at 3.49 eV with a broad GaN donor-acceptor pair (DAP) emission around 3.35 eV. The AlGaN near band edge emission is composed of several peaks. There exists a high energy component at ~ 3.95 eV, a sharper component at ~ 3.85 eV, and what appear to be phonon replicas of these emissions at ~ 3.75 eV and ~ 3.65 eV. The polar optical phonon energies in the GaN and AlN are 91.2 eV and 99.2 eV, respectively. The energy between these luminescence emission peaks are on the order of these phonon energies. It is interesting to note that when the highest energy AlGaN NBE contribution at 3.95 eV is higher, the 3.75 emission is also higher. These emissions seem to be strongly coupled together.
Figure 5.14. LEEN spectroscopy at a sample temperature of 12 K and 2 keV electron beam excitation for the diodes of wafer 1. These spectra were taken with excitation of the AlGaN free surface near the Ni regions of each diode. D1 (process A), D8, D9, and D10 (process C) exhibit an enhanced high energy peak contribution.

Figure 5.15 shows LEEN spectra for each diode taken through the Ni contact with an electron beam excitation of 2 keV. For D1-D7, the diodes exhibit similar luminescence characteristics to those in Figure 5.14. However, D8-D10 (process C) diodes exhibit AlGaN NBE luminescence features shifted to lower photon energies. Also, the process C diodes fail to exhibit the phonon replicas that the other diodes exhibit. The shift of the AlGaN NBE highest intensity emission is approximately 60 meV.
Figure 5.15. LEEN spectroscopy at a sample temperature of 12 K and 2 keV electron beam excitation for the diodes of wafer 1. These spectra were taken through the Ni regions of each diode. D8, D9, and D10 (process C) exhibit a shift in the luminescence peak to lower energies.

In order to further characterize the components of the AlGaN near band edge emission, the 1 keV LEEN spectra of the free AlGaN surface near D1 was easily deconvolved into four Gaussian contributions: E1, E2, E3, and E4. The curve fitting of this spectrum is shown in Figure 5.16. Also, a temperature dependent study was performed at this analysis point and the thermal activation of each of the Gaussian contributions was calculated.
Figure 5.16. Gaussian curve fitting of 1 keV LEEN spectra of the AlGaN free surface near diode D1 at 20 K. The AlGaN near band edge emission is easily deconvolved into four Gaussian curves. The contributions are labeled E1, E2, E3, and E4.

Low temperature CL maps were also performed with the Auger microprobe in order to characterize the AlGaN luminescence distributions. Figure 5.17 shows complementary CL images at 7000x and 1 keV electron beam excitation near D5 for the 3.94 eV AlGaN NBE and the 3.85 eV AlGaN NBE features. These maps demonstrate that there is a spatial dependence of the AlGaN NBE emissions for different regions of wafer 1.
Figure 5.17. Complementary low temperature monochromatic CL images at 1 keV electron beam excitation of wafer 1. The left image maps the 3.85 eV AlGaN NBE while the right image maps the 3.94 eV AlGaN NBE.

**Wafer 2:**

Before the post-metallization annealing steps, LEEN spectroscopy was performed for each of the diodes of wafer 2 under the same experimental conditions as those employed for the wafer 1 diodes. Figure 5.18 shows the 1 keV AlGaN NBE LEEN spectra of the free AlGaN surface near each of the diodes. In this set of spectra, there is a clear difference between the AlGaN NBE luminescence for process A diodes and process C diodes. Process C diodes (D5-D11) show a shift in the AlGaN near band edge emission peak to lower energies than the process A (D1-D4) diodes. This shift is on the order of 200 meV. Diodes D10 and D11 exhibit further shifts to lower photon energies. The process C diodes show a luminescence contribution close to the dominant contribution of the process A spectra but of much smaller intensity. Process A diodes also show a small feature at 3.79 eV. Spectra taken through the Ni contacts with 2 keV electron beam excitation show very similar spectra to those in Figure 5.18 but with much...
lower signal intensities. No shifts in the luminescence spectra were observed through the Ni contacts and therefore the spectra will not be displayed here.

Figure 5.18. Low temperature (12 K) AlGaN near band edge emission for diodes using LEEN spectroscopy as a function of processing. The diodes numbers are shown in the legend. Diodes 5-11 were processed by process C (UV/O$_3$+HF+HCl) exhibit lower AlGaN near band edge energies than diodes 1-4 by process A (HF). Diodes 10 and 11 exhibit further shifts of the AlGaN near band edge to lower energies which correlate with further shifts in the IPE barrier.

SEM microscopy and CL mapping was also performed with a 1 keV electron beam on the AlGaN free surface for process A and process C regions of wafer 2 in order to determine the nature of the processing effects. These images are shown in Figure 5.19. The SEM image and the monochromatic CL image at 3.91 eV (AlGaN NBE peak) are relatively uniform with the exception of larger scale defects. Figure 5.20 shows a monochromatic CL image of the same region for the 3.79 eV contribution to the AlGaN LEEN signal. The contribution of the 3.79 eV feature is small compared to the 3.91 eV feature, and the relative area contributions in the CL maps also show this difference.
Figure 5.19. SEM micrograph (left) and monochromatic CL image at 3.91 eV (right) for the AlGaN free surface in the process A (HF) region with an electron beam energy of 1 keV and magnification of 5000x. Despite the large scale features present in these images, the SEM image appears relatively smooth. Also, the CL image appears uniform beyond the large scale defects.

Figure 5.20. Monochromatic CL image at 3.79 eV for the same region as Figure 5.19. This luminescence feature has a much smaller contribution than the 3.91 eV peak to the total LEEN signal.
5.5 SIMS Analysis of the Ni/AlGaN Interface

SIMS was performed on selected diodes for wafer 1 and wafer 2 following all of the characterization steps. All of the wafer 1 diodes were depth profiled, but only select wafer 2 diodes were profiled so that future studies could be performed on the diodes of this wafer. The wafers were loaded and the SIMS analysis chamber was allowed to pump down to $1 \times 10^{-9}$ torr or less in order to reduce the contribution of residual oxygen on the
SIMS spectra. SIMS depth profiling was performed in negative ion collection mode with a 15 eV Ga primary beam and 3 keV Cs sputter beam. The Cs beam was rastered over a 350 µm square area and the Ga analysis beam was rastered over a much smaller 20 µm square area in the center of the Cs crater. Figure 5.22 shows the SIMS depth profile of diode D6. All of the expected elements and fragments are observed, such as Ni, Au, AlN, GaN, O, C, Cl, and F. For the Au containing diodes, excess Cl contamination is observed in the Au film.

For each diode, the AlN/GaN ratio was found over the thickness of the AlGaN films from the SIMS depth profiles. The ratio was averaged point-by-point over the thickness of the AlGaN and the error was computed. These values are shown in Figure 5.23 for each diode. Diodes D1-D4 have a slightly lower ratio (Al mole fraction) than the other diodes. From the AlN/GaN calibration procedure described in Section 4.2, AlN/GaN=6.5 corresponds to an Al mole fraction of about 35% (see Figure 4.8), close to the growth target. This figure shows a variation in the local Al concentration as a function of diode position. Diodes D1-D4 are positioned in a collinear fashion to one side of wafer 1. This portion of the wafer seems to show a lower Al mole fraction due to MBE growth variations similar to those described in Chapter 3.
Figure 5.22. SIMS depth profiles of diode D6 on wafer 1. The Ni contact was sputtered through in about 15 seconds while the AlGaN film took about 25 seconds.

Figure 5.23. AlN/GaN ratio from AlGaN layer of SIMS depth profiles for wafer 1.
The Ni/AlGaN interface impurities were also analyzed from the diode depth profile data. Figure 5.24 shows the interface impurities for each diode formed on wafer 1. The impurity ion counts were divided by the total ion counts in order to compare the relative intensities. Process B diodes (D5-D7) show more O at the interface than the other diodes. Process C diodes (D8-D10) show more F and C than the other diodes. There is more Cl contamination for process A diodes (D1-D4). D7 shows the most F, but this is an artifact due to surface contamination.

![Figure 5.24](image-url)

**Figure 5.24.** Ni/AlGaN interface relative impurity contributions for the wafer 1 diodes. The impurity SIMS counts were divided by the total ion counts at the Ni/AlGaN interface. Diodes D5-D7 exhibit larger O counts at the interface than the other diodes. Diodes D8-D10 exhibit enhanced F and C concentrations.

Figure 5.25 shows the interface impurities and AlN 90/10 width at the Ni/AlGaN interface for selected diodes formed on wafer 2. The impurity ion counts were divided by the total ion counts in order to compare the relative intensities. Process A diodes (D2, 149
D3) exhibit higher F, Cl and C counts than process C diodes (D7-D10). The AlN 90/10 ion profile width is also a factor of two greater for the process C diodes. This larger ion profile width correlates with the observed increase in surface roughness shown in the SEM image of Figure 5.21.

Figure 5.25. Ni/AlGaN interface relative impurity contributions for selected wafer 2 diodes. The impurity SIMS counts were divided by the total ion counts at the Ni/AlGaN interface. The right axis shows the 90/10 AlN ion profile width at the Ni/AlGaN interface. Process C diodes have a larger interface width than process A diodes by a factor of two.

The IPE Schottky barrier height exhibits a correlation with the interface C impurities measured by SIMS. The second slope IPE barrier height is plotted versus interface C concentration for both wafer 1 and wafer 2 in Figure 5.26 and Figure 5.27. The correlation is much stronger for the wafer 2 diodes than for the wafer 1 diodes.
Figure 5.26. IPE second slope Schottky barrier heights after a 500 °C anneal versus SIMS interface C counts for wafer 2. There is a good correlation between increased C and increased Schottky barrier height.

Figure 5.27. IPE second slope Schottky barrier heights before an anneal versus SIMS interface C counts for wafer 1. There is a loose correlation between increased C and increased Schottky barrier height.
Figure 5.28 shows the AlN/GaN negative ion ratio versus sputter time (depth) for two wafer 2 diodes. Diode D2 was formed using process A while diode D7 was formed using process C. The D2 ratio exhibits oscillations in this ratio as a function of depth, while D7 shows a significantly smeared profile.

5.6 Discussion

On wafer 1, diodes were processed either by process A (HF) or by process B (UV/O₃). Figure 5.4 shows the second slope IPE Schottky barrier as a function of processing and annealing. The observed SBH of each diode increased following the 325 °C anneal by 0.15-0.20 eV. This has been observed in for Ni/Al₀.₁₁GaΝ₀.₈₉N contacts and is explained by Ni diffusing through a surface contamination layer forming a more intimate contact.²¹² Two Schottky barriers (Fowler plot slopes) are observed following
this anneal denoted as first and second slopes in Figure 5.5. The diodes treated by process B exhibit larger second slope Schottky barriers than diodes treated with process A. SIMS reveals increased levels of oxygen at the Ni/AlGaN interface for the UV/O\textsubscript{3} treated diodes as shown in Figure 5.24. An interface oxide could account for the increased effective Schottky barrier as reported by Cao, et al.\textsuperscript{59} for GaN Schottky barriers. Essentially, the interface oxide has a larger band gap than the semiconductor material and therefore the effective Schottky barrier is larger. The interface oxide would need to be sufficiently thick to reduce the tunneling probability. It was shown in Figure 5.23 that diodes D1-D4 exhibited a lower Al mole fraction than the other diodes. Diodes D6 and D7 (Process B) had slightly higher SBHs than the Process A (D1-D4) diodes after the 325 °C anneal. This IPE SBH difference could also be explained by the local variation in the Al mole fraction.

Figure 5.12 shows the IPE barriers for wafer 2 after a post-metallization 500 °C anneal for 10 minutes. On wafer 2, diodes were processed either by process A (HF) or by process C (UV/O\textsubscript{3}+HF+HCl). Similar results were obtained for process A and process C diodes for each wafer. After annealing, the process C diodes exhibited lower SBHs than the process A diodes. These lower second slope SBHs correlate with a ~200 meV shift of the LEEN AlGaN near band edge emission energies to lower energies as shown in Figure 5.18. This shift in NBE emission corresponds to a shift in Al mole fraction from 0.25 to 0.16 using a bowing parameter of unity. Assuming a linear increase of the AlGaN electron affinity with decreasing Al mole fraction (using a bowing parameter of unity), this corresponds to a ~190 meV shift in SBH -- in agreement with the ~200 meV decrease measured by IPE. Further shifts of the AlGaN near band edge
emission to lower energies are shown for diodes 10 and 11 in Figure 5.18. These shifts correlate with the shift of the first slope IPE SBH to even lower energies as shown in Figure 5.12. Oxidation-annealing pre-metallization processing has shown that an oxidation of the AlGaN surface followed by an acid etch to remove the oxidation leaves the surface with a lower Al mole fraction.

Auger electron spectroscopy of the AlGaN surface as a function of processing on a control piece of wafer 2 shows that UV-ozone cleaning of the AlGaN wafers increases the O/Ga ratio and that a subsequent HF and HCl etch reduces this ratio. This data is shown in the following table. In this experiment, pieces of wafer 1 and wafer 2 were subjected to the same processing steps that were used in the creation of the diodes. LEEN and AES were performed in UHV after each processing step in order to characterize surface chemical changes and to recreate the luminescence changes observed during the diode processing. Wafer 2 exhibited an increase in a lower energy AlGaN near band edge emission as a function of processing (process A→process B→process C), shown in Figure 5.29, which mimics the changes observed during the diode processing. The AES O concentration for the wafer 2 control studies showed an increase in the relative O concentration with process B (UV/ozone cleaning) and a reduction in this value with an additional oxide etch. Wafer 1 exhibited identical AES changes during processing, but did not exhibit any changes in the control wafer luminescence as a function of processing (Figure 5.30). The Ga relative concentration increased as a function of processing, possibly meaning that either the impurity concentrations were decreasing or the Al concentration was decreasing. Al was not observed during the AES measurements because of the low signal-to-noise in the Al AES region.
Table 5.2. Auger electron spectroscopy relative concentrations as a function of processing on a control piece of wafer 2. Standard sensitivity factors were used to compute the relative concentrations.

<table>
<thead>
<tr>
<th>Process</th>
<th>Ga</th>
<th>O</th>
<th>N</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process A</td>
<td>0.219</td>
<td>0.068</td>
<td>0.177</td>
<td>0.536</td>
</tr>
<tr>
<td>Process B</td>
<td>0.346</td>
<td>0.111</td>
<td>0.335</td>
<td>0.208</td>
</tr>
<tr>
<td>Process C</td>
<td>0.415</td>
<td>0.097</td>
<td>0.275</td>
<td>0.213</td>
</tr>
</tbody>
</table>

Figure 5.29. Change in room temperature AlGaN band edge cathodoluminescence at 1 keV with subsequent processing for wafer 2. There is a clear increase in the lower energy AlGaN NBE contribution with successive processing.

155
LEEN mapping of wafer 2 following process C (UV/O$_3$+HF+HCl) exhibits a nonuniform AlGaN near band edge emission and a rougher secondary electron image showing a larger degree of AlGaN disorder from selective removal of Al from the surface region. This AlGaN disorder could contribute to the two observable Schottky barrier heights by IPE shown in Figure 5.12. As mentioned previously in the IPE and I-V experimental discussion in Chapter 2, two parallel Schottky barrier heights are observable with IPE. Spatial variations of the local Al concentration could exhibit patchy Schottky contact formation with multiple contributions. Figure 5.31 shows a schematic of a Schottky band diagram with a spatial variation in the Schottky barrier height.

Figure 5.30. Change in room temperature AlGaN band edge cathodoluminescence at 1 keV with processing for wafer 1. This sample shows no observable changes with processing.
These spatial fluctuations have several effects on the IPE and the forward I-V characteristics. First, nonuniform Schottky barriers tend to increase the ideality factor of the forward biased I-V curve, where Tung has reported that deliberate introduction of inhomogeneity in the Schottky barrier height has been shown to produce large $n$. This is in contrast to an alternate explanation of GaN and AlGaN interface states being the cause of anomalous forward I-V characteristics. In this work by Hasegawa, et al., the authors argue that unintentional donors—most likely N vacancies—in the GaN near surface region act to facilitate carrier transport mechanisms other than thermionic field emission. They propose that this surface state changes the forward current in a bias-dependent manner as shown in Figure 5.32. This diagram shows a current plateau similar to what is observed with wafer 1 and wafer 2 diodes. Kim, et al. have also proposed thermionic field emission due to O-donor enrichment of the AlGaN surface as being a reason behind the anomalous forward characteristics.
Seghier, et al.\textsuperscript{145} have performed a study of Au Schottky contacts to AlGaN with Al mole fractions of 0.1 and 0.3. In their study, they conclude that higher Al content AlGaN exhibits an enhanced surface roughness and thereby a Schottky barrier lateral variation which acts to reduce the Schottky barrier as measured by I-V and C-V. The authors note that the rough surface acts as an interfacial layer with a continuum of surface states which reduces the SBH as described by the Bardeen model.\textsuperscript{55} Wafer 2 exhibited a similar surface roughness after Process C which resulted in a lowered SBH by IPE. The corresponding LEEN results of wafer 2 showed a shift to lower AlGaN NBE energies which is most likely due to a shift in the Al mole fraction. However, it is possible that the roughening of the surface by Process C also disrupted the band structure and therefore band-tailing could occur which could shift the luminescence peak to lower energies. The average Al mole fraction did decrease as measured by SIMS. Further characterization by
Al Auger mapping and depth profiling is necessary for the diodes that were not sputtered in order to determine the exact nature of the correlated shift in IPE and AlGaN NBE.

Another explanation of the anomalous forward I-V characteristic is dual Schottky barriers in parallel due to the second Schottky barrier formed at the AlGaN/GaN interface. This model was proposed by Chen, et al. to model the current conduction across an AlGaAs/GaAs HFET structure. Their proposed model is shown in Figure 5.33. The authors show that this model acts like two Schottky barriers connected in series.

Figure 5.33. Diagram of AlGaAs/GaAs HFET structure showing the two Schottky barriers connected in series. The conduction band offset at the AlGaAs/GaAs interface creates a virtual Schottky diode which also controls the carrier flow through the device.

The ideality factor has also been reported to increase with the addition of Al to the AlGaN system. Table 5.3 shows selected ideality factors from different groups as a function of Al mole fraction. The increase in ideality factor with increasing Al mole
fraction indicates that the current transport mechanism is changing from thermionic emission to thermionic field emission or another type of current conduction. In this work, the high ideality factors observed by I-V are not much larger than these published ideality factors.

Table 5.3. Ideality factors for Schottky diodes to AlGaN with different Al mole fractions.

<table>
<thead>
<tr>
<th>x_{Al}</th>
<th>n</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>1.4</td>
<td>145</td>
</tr>
<tr>
<td>0.11</td>
<td>1.1-1.34</td>
<td>142</td>
</tr>
<tr>
<td>0.23</td>
<td>1.37</td>
<td>64</td>
</tr>
<tr>
<td>0.30</td>
<td>2.5</td>
<td>145</td>
</tr>
<tr>
<td>0.35</td>
<td>2.11</td>
<td>63</td>
</tr>
<tr>
<td>0.40</td>
<td>3.5</td>
<td>147</td>
</tr>
</tbody>
</table>

There are also concurrent changes in the slopes of the IPE Fowler plots and the I-V characteristics for diodes D6 and D7 on wafer 2. Figure 5.34 shows the I-V characteristics of D6 as a function of annealing. After the 425 °C anneal, the I-V characteristics change from having two slopes to a single slope. A similar phenomenon occurs in the IPE spectrum after the 425 °C anneal as shown in Table 5.4. Taking this into consideration, the IPE dual Schottky barriers and the I-V dual slopes seem to come from a similar origin. This could mean that the dual IPE barriers correspond to a patchy oxide at the Ni/AlGaN interface with a higher Schottky barrier for the oxidized regions. After annealing, the metal may diffuse through the oxide and then only a single Schottky barrier is measured.
Figure 5.34. Change in I-V characteristics for wafer 2 diode D6 as a function of annealing. The forward characteristics change from having two slopes to a single slope. This change correlates with a similar concurrent change in the IPE results.

Table 5.4. IPE Schottky barrier heights and I-V extracted Schottky barrier heights for diode D6 on wafer 2 as a function of annealing.

<table>
<thead>
<tr>
<th></th>
<th>IPE SBH</th>
<th>325 °C</th>
<th>425 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>First $\phi_b$</td>
<td>1.466</td>
<td>1.480</td>
<td></td>
</tr>
<tr>
<td>Second $\phi_b$</td>
<td>1.611</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>I-V SBH</th>
</tr>
</thead>
<tbody>
<tr>
<td>First $\phi_b$</td>
<td>0.706</td>
</tr>
<tr>
<td>Second $\phi_b$</td>
<td>0.745</td>
</tr>
</tbody>
</table>
Low temperature LEEN spectra and mapping of the wafer 1 diodes showed both spectral and spatial variations. The LEEN spectra shown in Figure 5.14 show multiple AlGaN NBE features that were nearly equally spaced by approximately the energy of the optical phonons in AlGaN. It was noted that the 3.95 eV, 3.75 eV, and 3.65 eV emissions were strongly correlated in that an increase in the 3.95 eV emission resulted in a corresponding increase in the 3.75 eV and 3.65 eV emissions and a decrease in the 3.85 eV emission. This could be due to increased compositional disorder broadening the total AlGaN NBE to higher and lower photon energies. Also, the increase of the 3.75 eV and 3.65 eV emissions could be due to the increase of an underlying donor-acceptor pair emission due to native defects or residual impurities. The 3.95 eV emission could be due to higher Al mole fraction regions shown spatially in the CL maps of Figure 5.17. Since Al has a large affinity for O, these regions could have larger O concentrations and potentially a larger donor-acceptor pair emission. AES or SIMS mapping would help to identify this. In the CL maps of Figure 5.17, the 3.95 emission is localized around a large area defect. This defect could be due to dislocations or pinholes in the AlGaN growth. Scanning Kelvin probe microscopy has revealed that the surface termination of threading dislocations in GaN and AlGaN/GaN HFET structures are negatively charged. Theoretical investigations of n-type GaN show that acceptors are present below the Fermi level at the threading dislocations and are therefore negatively charged. These negatively charged regions are believed to attract impurities and native defects. Therefore it is plausible that enhanced donor-acceptor pair emission could occur near these types of threading dislocations and be associated with the high Al content regions.
SIMS analysis of the diodes also reveals F, Cl, and C impurities at the Ni/AlGaN interface. F and Cl do not correlate with the IPE barriers. Cl does correlate with the presence of Au. This indicates that the Au source is contaminated with Cl. AES measurements of the freshly deposited Au verify Cl contamination. This contamination could be reduced or eliminated by a more rigorous cleaning of the crucible and the tungsten filament. Increased C levels at the interface show a weak correlation with larger SBHs which can, however, be accounted for entirely by changes in Al content. Figure 5.26 shows the Schottky barrier height of diodes on wafer 2 as a function of C concentration at the Schottky interface. The C concentration is reduced for the diodes that were subjected to process C. Process C involves a UV/O$_3$ clean which readily removes C contamination from surfaces. Therefore, it seems as if the C concentration variation is simply due to the cleaning procedure since large AlGaN NBE changes correlated with Al variations appear to be dominant. In addition, the AlN/GaN ratio found in the SIMS depth profiles for each of the diodes correlates with the IPE Schottky barrier heights. This further strengthens the argument that local changes in the Al mole fraction dominate the Schottky barrier formation. However, C acts as an acceptor in GaN and AlGaN when it lies on a nitrogen site (C$_N$).$^{151,152}$ Carbon acting as an acceptor near the Schottky interface could make the near surface region p-type. This would lower the Fermi level in the near surface region and could increase the Schottky barrier height. This is an alternate explanation to the SBH lowering, but the shift in the AlGaN NBE energy to lower energies suggests a change in the local Al mole fraction as being the primary cause in the lowering of the SBH.
The AlN/GaN SIMS negative ion ratio depth profiles presented in Figure 5.28 exhibit oscillations that could be the result of ordering in the AlGaN layer during growth. Long-range ordering of AlGaN alloys grown by MOCVD\textsuperscript{153} and MBE\textsuperscript{154,155} has been reported. Iliopoulos, \textit{et al.} have observed that the ordering of the AlGaN film can vary with the ratio of the group-III and group-V growth fluxes using transmission electron microscopy (TEM) and x-ray diffraction (XRD). They observe that N-rich fluxes give rise to a shorter superlattice period (2 monolayers) while group-III-rich fluxes give rise to either 7 or 12 monolayer superlattice periods. The diodes were grown on nominally Ga-rich AlGaN/GaN HFETs by MBE, therefore such ordering is quite possible. This could explain the observed oscillations in the SIMS depth profile in Figure 5.28. As for diode d7, the oscillations were not observed. This is probably because of the effect of surface roughening on the depth profile resolution (shown in the SEM images for process C).
LEEN allows one to resolve defects in different heterostructure layers on a nanometer scale. The presence of the intense 2.34 eV defect emission localized in the AlGaN barrier layer correlates with the absence of the 2DEG measured electrically. The defect luminescence at 2.18 eV is localized in the GaN buffer layer regardless of 2DEG confinement. Large variations in the GaN and AlGaN band edge emissions, yellow defect emission, and elemental composition across an AlGaN/GaN heterostructure growth wafer have been observed. SIMS reveals O impurity variations as a function of wafer position. AFM shows a distinct variation in the surface morphology across the wafer which correlates with N-rich and Ga-rich growth conditions. AES and LEEN spectroscopies of the growth wafer suggest that variations in the stoichiometry and impurities may play a role in the mechanism responsible for the yellow defect emission in the AlGaN barrier layer. The depth-resolved LEEN technique provides detailed measurements in these nanometer-scale structures that can be used along with MBE growth to reduce layer-specific defects in AlGaN/GaN HEMT structures.

Deep levels in high Al content \( \text{Al}_x\text{Ga}_{1-x}\text{N} \) observed by depth-dependent cathodoluminescence spectroscopy correlate with Si and O impurity distributions in SIMS depth profiles. Cross-sectional CLS measurements confirm the existence of O-
related states at the AlGaN/sapphire interface. The reduction in carrier density for the largest Al mole fraction films (>80%) is consistent with compensation due to deep O-related levels. Correlations between optical properties observed with depth-resolved luminescence spectroscopy and impurity concentrations from SIMS provide a physical basis for understanding the dopant and deep level electronic properties of high Al content AlGaN.

AlGaN surfaces treated with UV-ozone cleaning and then subjected to an HF + HCl oxide strip exhibited lower SBHs by IPE that correlate with an observed shift in the AlGaN near band edge emission to lower energies. Dual IPE barriers also correlate with dual LEEN NBE interface features. AlGaN surfaces treated with organic solvents and UV-ozone cleaning exhibited the largest SBHs observed by IPE and O observed by SIMS, indicating SBH enhancement from an interface oxide. With the exception of interfacial O, SBH changes are dominated by changes in the local Al mole fraction rather than relative concentrations of interface impurities.

The results presented in this work underscore the importance of local and chemical measurements to help identify electronic transport behavior at surfaces and interfaces. LEEN is able to probe these buried interfaces and surfaces on the nanometer scale. The techniques of SIMS, AES, and IPE are powerful complements to LEEN and can help explain interesting physical phenomena in the nitride semiconductor system.

**Proposed Future Work**

As shown in the work completed to date, a large body of samples with different Al mole fractions and Si content have been characterized and are available for future
studies. Several of the samples show differences in the near band edge emissions for different Si concentrations. These near band edge emissions are relatively broad and can be deconvolved into several Gaussians. Further analysis is needed to understand the nature of these deconvolved peaks versus mole fraction and versus Si doping for the same mole fraction. Samples already are available to analyze these trends and more may be acquired from Cornell as needed.

In order to ascertain the role of interface-related states in the observed Hall carrier density, further electro-chemical C-V profiling studies should be employed in order to determine the level of conduction at the AlGaN/Al$_2$O$_3$ interface, as well as throughout the film, for selected samples that encompass the entire Al mole fraction range. The data presented in Chapter 4 is from lower Al mole fraction samples only. It would be interesting to see what happens at higher mole fractions. It is at these higher Al mole fractions that compensation of the donors occurs. Also, this information can be compared with SIMS in order to determine the role of impurities in the AlGaN film.

It has already been established that O and C produce deep level emissions in high Al mole fraction AlGaN. Emissions have already been observed which correlate with these impurities in AlGaN. Future studies would include cross-sectional cathodoluminescence analysis of the AlGaN/Al$_2$O$_3$ interface region in order to identify the effect of diffused O on the luminescence characteristics of AlGaN. This would provide insight on the effect of O impurities on the electronic properties of AlGaN. Also, SIMS analysis of AlGaN/GaN HFETs could provide insight into the effect of impurities on the electronic and luminescence properties that have already been observed. A remote rf-plasma processing chamber is available to process the semiconductor surface and
could be used to clean the AlGaN surface of O and C contamination (or to oxidize it). Chemical pre-treatments of the material may also be employed. This plasma chamber is linked by UHV to a LEEN/AES analysis chamber for \textit{in situ} characterization of the material. One would be able to study the effect of adding (oxidation) or removing (cleaning) impurities to the semiconductor surface on the LEEN spectra and gain insight on the effect of impurities on the electronic properties of AlGaN.

The contributions due to residual O in SIMS would be significantly reduced with an analysis technique called an \textit{interleaving profile}. In this method, the Ga and Cs sputter beams are pulsed at a rate on the order of 5 kHz with the analysis beam interleaved with the Cs sputter beam. This would leave a very small time window for residual O to deposit on the surface and contribute to the total O signal. At this time, this feature on the TRIFT III SIMS is not operational. Future studies should involve using this analysis mode to characterize AlGaN and AlGaN/GaN HFETs.

An electron beam induced current (EBIC) measurement system is now implemented in the JAMP 7800F Auger microprobe. This allows for monitoring and recording the current measured by a contact to the semiconductor as a function of electron probe position from the contact and also for imaging the collected current by rastering the electron probe over the sample. This technique is used to determine the minority carrier diffusion length, minority carrier lifetime, and the distribution of defects. As shown previously, the incident electron beam creates electron-hole pairs in the sample. Once a metal/semiconductor contact is implemented and the contact is connected to a current measurement system, the changes in the electron beam induced current are recorded as a function of electron beam position. Some of the minority
carriers diffuse to the metal/semiconductor junction and are collected. This junction may be either a Schottky contact or a pn junction because only these are suitable for the collection of minority carriers. Surface recombination has been shown to play an important role in EBIC and must be taken into account in the analysis of the data. Variation of the electron beam induced current with respect to the position of the electron probe can give rise to the minority diffusion length. A pulsed electron beam at a stationary position away from the metal contact can be used to extract the minority carrier lifetime. This pulsed electron beam deflection system will also be implemented on the JAMP 7800F using a signal generator control voltage to also allow for these types of measurements.

The electron probe beam near the presence of a minority carrier collection region generates a charge-collection current \( I_{cc} = \eta_{cc} GI_b \) which flows in the reverse-biased direction. In this equation, \( G \) is the generation rate of electron hole pairs from Equation 4, \( \eta_{cc} \) is the charge collection efficiency of the built-in field, and \( I_b \) is the electron probe current. Thus, in the presence of the diode current \( I_d \), the observed EBIC signal is \( I = I_{cc} - I_d \). This equation applies to the aforementioned methods of the determination of the minority carrier lifetime and diffusion length as well as to the analysis of extended defects in imaging mode. A charge collection contrast may be observed at extended defects, such as dislocations, which reflects the difference in the charge collection efficiency from defect recombination. This mode will be useful in identifying the locations of extended defects and then further analysis, such as LEEN, AES, and SIMS could be used to analyze the defect.
This method could be used to determine the minority carrier lifetimes and diffusion lengths in both the AlGaN thin film HFETs and the Si-doped AlGaN as well as to map the locations of extended defects. These extracted parameters will be correlated with impurity concentrations, impurity distributions, LEEN spectra, and measured electrical properties in order to provide insight into the physical nature of the impurities and extended defects in the material and their effect on the n-type doping in the high Al content AlGaN. This method may also be used to enhance the study of surface processing. Since a Schottky contact is required for this technique, EBIC measurements could give insights into the process of Schottky contact formation.

A future research avenue would include the further study of Schottky contacts to AlGaN HFET structures and high Al mole fraction AlGaN films. Various surface treatments may be employed on the semiconductor surface which may include a combination of annealing, remote plasma processing with O, N, or H, Ar or N$_2$ sputtering, and ex situ wet chemical pre-treatment. The barrier height can be obtained by I-V measurements and internal photoemission. The eventual goal would be to find a way to reliably produce high barrier height Schottky contacts and to develop a fundamental understanding of the metal/semiconductor interface in the formation of these contacts.

In Chapter 5, variations in the Schottky barrier height were correlated with shifts in the AlGaN NBE emission as a function of surface pre-metallization processing. Auger mapping with the JAMP 7800F Auger microprobe are planned in order to determine the spatial variation of the Al concentration as a function of processing and to correlate this result with the CL mapping that has already been performed. At present, the Auger electronics are not operational but will be in the very near future.
The variation of the Schottky barrier height as a function of Al mole fraction is also of interest with regards to possible Fermi level pinning with the addition of Al. A reduction of the observed Schottky barrier height with increasing Al mole fraction after a particular mole fraction of Al is observed.\textsuperscript{64,145} However, the observed reduction in SBH occurs only with a single data point in each of the referenced studies. A more complete study of the effects of Fermi level pinning as a function of Al mole fraction should be performed. This study may be performed with the sample sets listed in Chapters 3 and 4. IPE could be performed as a function of Al mole fraction similar to the work of Qiao, \textit{et al.}\textsuperscript{64} In addition, the JEOL JAMP 7800 allows for the determination of work functions of materials by the onset of secondary electron emission from the sample. This could be used to characterize the changes of the electron affinity with increasing Al mole fraction.

For wafer 2 (discussed in Chapter 5), some diodes were not sputtered by SIMS and could be used for future annealing studies. It has been shown in a recent study by Hull, \textit{et al.}\textsuperscript{156} that annealing Ni/AlGaN contacts to high temperatures (on the order of 900 \textdegree C) may cause a reaction between the Ni and the AlGaN and subsequent removal of the Ni by wet etch processes leaves the AlGaN surface Al-rich. The effect of this reaction on Schottky barrier formation could be explored with IPE and depth-resolved CLS, as well as SIMS.

Schottky metal studies with different metals would also be interesting in order to determine the variation of Schottky barrier height with metal work function. Lin, \textit{et al.}\textsuperscript{157} have studied the Schottky barrier height on strained AlGaN/GaN structures with 0.25 Al mole fraction by C-V and I-V for Ir, Ni, and Re contacts. The authors find that higher metal work functions tend to show a decrease in Schottky barrier height due to
interactions with the 2DEG layer. Further work by IPE on such structures is being pursued by the Electronic Materials and Nanostructures Laboratory at OSU at present.

Lastly, non-radiative defects were not investigated in this study. Techniques such as deep level transient spectroscopy (DLTS) and deep level optical spectroscopy (DLOS) could be used to characterize the non-radiative deep levels and traps in AlGaN as a function of Al mole fraction, doping, and electrical properties.
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