

Abstract

COOK, JR., TED EDWIN. Photoemission investigation of the electronic properties of Ga-face GaN(0001)-dielectric interfaces. (Under the direction of Robert J. Nemanich).

The characteristics of clean n- and p-type GaN (0001) surfaces and the interface between this surface and SiO₂, Si₃N₄, and HfO₂ have been investigated. Both n- and p-type Ga-face GaN (0001) surfaces have been cleaned via an 860 °C anneal in an ammonia atmosphere, and carbon and oxygen contaminants were reduced to below the detection limits. Layers of SiO₂, Si₃N₄, or HfO₂ were carefully deposited to limit the reaction between the plasma and the GaN surface. After stepwise deposition, the electronic states were measured with x-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). A valence band offset (VBO) of 2.0 ± 0.2 eV with a conduction band offset (CBO) of 3.6 ± 0.2 eV was determined for the GaN/SiO₂ interface. The large band offsets suggest SiO₂ is an excellent candidate for passivation of GaN. For the GaN/Si₃N₄ interface, type II band alignment was observed with a VBO of 0.5 ± 0.2 eV with a CBO of 2.4 ± 0.2 eV. While Si₃N₄ should passivate n-type GaN surfaces, it may not be appropriate for p-type GaN surfaces. A VBO of 0.4 ± 0.2 eV with a CBO of 2.0 ± 0.2 eV was determined for the GaN/HfO₂ interface. An instability was observed in the HfO₂ film, with energy bands shifting ~ 0.5 eV during a 650 °C densification anneal. The electron affinity measurements via UPS were 3.0, 1.1, 1.8, and 2.9 ± 0.1 eV for GaN, SiO₂, Si₃N₄, and HfO₂ surfaces, respectively. Electron affinity measurements, along with band alignment data, allow a deviation from the electron affinity model due to a change of the interface dipole to be observed. Interface dipoles of 1.7, 1.1 and 1.9 ± 0.2 eV were observed for the GaN/SiO₂, GaN/Si₃N₄, and GaN/HfO₂ interfaces, respectively. The existence of Ga-O bonding at the heterojunction significantly increases the interface dipole, which raises the dielectric bands in relation to the GaN.

**PHOTOEMISSION INVESTIGATION OF THE
ELECTRONIC PROPERTIES OF Ga-FACE
GaN (0001)-DIELECTRIC INTERFACES**

by

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DEDICATION

For my Family

In memory of William H. Roy, Sr.

Biography

Ted Edwin Cook, Jr. was born July 19, 1976 to Ted and Debbie Cook in Wilmington, North Carolina. He is an only child, with his closest resemblance to a sibling being his cousin, Trey Roy. During his years at Laney High School, he lived with and received significant guidance from his grandparents, Bill and Edna Roy. During this time, his interest and love for science continued to grow. Upon finishing high school, Ted attended the University of North Carolina at Wilmington to pursue a double major in Physics and Applied Mathematics. While at UNCW, he had the privilege and honor of participating in four years of Track and Field, winning the school's first ever Colonial Athletic Association title in 1997. Another significant event happened in 1997, when he met his future wife, Mandy. They met in a Physics lab, proving that in some instances, Physics can be fun. During the summer of his sophomore/junior year at UNCW, he participated in a research experience for undergraduates at North Carolina State University under the direction of Dr. Robert Nemanich. This experience was so moving that he chose to enroll at NC State upon graduating in 1998. After deciding to study electronic materials, he switched to the Materials Science and Engineering program in the fall of 1999. While in graduate school, he coached track and field at Cardinal Gibbons High School, winning the state championship three times. He received a non-thesis master's degree in the fall of 2002. The focus of his research in the Surface Science Laboratory was the processing and characterization of GaN/dielectric interfaces. He received his Ph.D. May 5th, 2003.

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Table of Contents

List of Tables.....	xi
----------------------------	-----------

List of Figures.....	xii
-----------------------------	------------

1. Introduction to GaN: Growth, Properties, and Application..	1
1.1 Introduction.....	2
1.2 Properties of Gallium Nitride	5
1.2.1 Growth.....	5
1.2.2 Substrates.....	6
1.2.3 Physical and electronic properties of GaN.....	7
1.3 <i>Ex situ</i> and <i>in situ</i> surface preparation methods of GaN.....	8
1.4 Outline of dissertation.....	12
1.5 References.....	14
2. <i>Band Discontinuities:</i> Formation, Modeling and	
Characterization Techniques.....	19
2.1 Introduction.....	20
2.2 Basic electrical properties of semiconductors and insulators.....	21
2.3 Theoretical models of interfaces.....	24
2.3.1 Electron affinity model.....	24
2.3.2 Charge neutrality model.....	26
2.4 <i>In situ</i> characterization techniques.....	29
2.4.1 Introduction to photoemission.....	29
2.4.2 X-ray photoelectron spectroscopy.....	30
2.4.3 Ultraviolet photoemission spectroscopy.....	31
2.4.4 Measuring band discontinuities via photoemission.....	31
2.5 Conclusions.....	33
2.6 References.....	34

3.	Measurement of the band offsets of SiO₂ on clean n- and p-type GaN(0001).....	42
3.1	Abstract.....	43
3.2	Introduction.....	44
3.3	Experimental.....	47
3.4	Results.....	49
3.5	Discussion.....	55
3.6	Conclusions.....	60
3.7	Acknowledgments.....	60
3.8	References.....	62
4.	Band offset measurements of the Si₃N₄/GaN(0001) interface.	83
4.1	Abstract.....	84
4.2	Introduction.....	85
4.3	Experimental.....	86
4.4	Results.....	88
4.5	Discussion.....	91
4.6	Conclusions.....	95
4.7	Acknowledgments.....	96
4.8	References.....	97
5.	Band offset measurements of the n-type GaN (0001)/HfO₂ interface.....	109
5.1	Abstract.....	110
5.2	Introduction.....	111
5.3	Experimental.....	113
5.4	Results.....	116
5.5	Discussion.....	119
5.6	Conclusions.....	124
5.7	Acknowledgments.....	125

5.8	References.....	126
6.	Electrical characteristics of the SiO₂ and Si₃N₄ on GaN.....	140
6.1	Introduction.....	141
6.2	Experimental Procedure	143
6.3	Results and Discussion.....	145
6.4	Conclusions and Future Work.....	147
6.5	References.....	149
7.	Summary.....	160
8.	Recommended Future Research.....	166

List of Tables

Table 1.1	Physical properties of GaN compared to other semiconductors. Values listed are compiled from refs ^{1-3, 8-10}	17
Table 1.2	Electronic properties of GaN compared to other semiconductors. Values listed are compiled from refs ^{1-3, 8-10}	18
Table 2.1	Bandgap energies and electron affinities of common semiconductors. Values are compiled from refs ¹⁹⁻²²	36
Table 2.2	Experimental bandgaps, charge neutrality level above the valence band edge (CNL), dielectric constant ϵ_{∞} , calculated Schottky barrier slopes S on Si, and electron affinity for each dielectric. Values with an asterisk (*) are estimated values. Values are tabulated from Robertson. ⁷	37
Table 3.1	XPS core level curve fitting results for the n-type GaN/SiO ₂ experiment. (Oxygen plasma is represented as O-Pl)	67
Table 3.2	XPS core level curve fitting results for the p-type GaN/SiO ₂ experiment	68
Table 5.1	XPS core level curve fitting results for the Ga 3p _{3/2} , Hf 4f, O 1s, Ga 3d, and N 1s energy levels for the n-type GaN/HfO ₂ experiment	129
Table 7.1	BB and EA are defined as band bending and electron affinity, respectively. The positive or negative sign on the band bending represents upward or downward band bending, respectively. The negative values for the VBO for the GaN/Si ₃ N ₄ interface represents type II band alignment, where the valence band of the GaN lies below the valence band of the Si ₃ N ₄ . For the GaN/SiO ₂ and GaN/HfO ₂ interfaces, type I band alignment is observed	164

List of Figures

Figure 2.1	Heterojunction band lineups for materials A and B, with type I and type II band alignment represented.....	39
Figure 2.2	Heterojunction band lineups representing the electron affinity model (a) and the interface dipole model (b). The interface dipole, Δ , is shown in Figure 2.2b.....	40
Figure 2.3	Schematic of the 3-step photoemission model with: initial state, b) excitation, c) transport, and d) emission of electrons from a surface	41
Figure 3.1	UPS spectra of a) CVC clean n-type GaN, b) 2Å Si, c) 4Å Si and O ₂ plasma, d) 6Å Si, O ₂ plasma and 650°C anneal, e) 9Å Si and O ₂ plasma, f) 650°C anneal.....	72
Figure 3.2	UPS spectra of the valence band maximum of: a) CVC clean n-type GaN, b) 2Å Si, c) 4Å Si and O ₂ plasma, d) 6Å Si, O ₂ plasma and 650°C anneal, e) 9Å Si and O ₂ plasma, f) 650°C anneal.....	73
Figure 3.3	UPS spectra of the valence band maximum of: a) CVC clean p-type GaN, b) 4Å Si and O ₂ plasma, c) 6Å Si and O ₂ plasma, d) 6Å Si, O ₂ plasma and 650°C anneal, e) 9Å Si and O ₂ plasma, f) 650°C final anneal.....	74
Figure 3.4	UPS spectra of the valence band maximum of CVC clean p-type GaN, with valence band maximum indicated by a dashed line.....	75
Figure 3.5	Gallium 3d XPS spectra for: a) CVC Clean n-type GaN, b) 2Å Si deposition, c) 4Å Si deposition, d) 4Å Si and O ₂ plasma, e) 6Å Si, O ₂ plasma, f) 6Å Si, O ₂ plasma and 650°C anneal, g) 9Å Si and O ₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.....	76
Figure 3.6	Oxygen 1s XPS spectra for: a) CVC Clean n-type GaN, b) 2Å Si deposition, c) 4Å Si deposition, d) 4Å Si and O ₂ plasma, e) 6Å Si, O ₂ plasma, f) 6Å Si, O ₂ plasma and 650°C anneal, g) 9Å Si and O ₂ plasma, h) 650°C final anneal. The peak positions after the initial oxidation, as well as the final surface are indicated with dashed lines.....	77
Figure 3.7	Oxygen 1s XPS spectra for: a) CVC Clean p-GaN, b) O ₂ Plasma, and c) the final SiO ₂ surface. Dashed lines indicate the peak positions for the oxidized GaN, as well as the final SiO ₂ surface.....	78
Figure 3.8	Gallium 3d XPS spectra for: a) CVC Clean p-type GaN, b) 4Å Si deposition, c) 4Å Si and O ₂ plasma, d) 6Å Si, O ₂ plasma, e) 6Å Si, O ₂ plasma and 650°C	

anneal, f) 9Å Si and O₂ plasma, g) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.....79

Figure 3.9 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and SiO₂. The valence band offset, conduction band offset, band bending, and interface dipole are represented.80

Figure 3.10 Deduced bands for the clean p-type GaN surface (left) and the interface between p-type GaN and SiO₂. The valence band offset, conduction band offset, band bending, and interface dipole are represented.....81

Figure 3.11 Band alignment of Si/SiO₂, SiC/SiO₂, and GaN/SiO₂ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the SiO₂ surface, which is common in all three interfaces. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap. The VBO are determined from the measurements.....82

Figure 4.1 UPS Spectra of the valence band maximum of: a) CVC clean n-GaN, b) 4Å Si, c) 4Å Si and N₂ plasma, d) 6Å Si and N₂ plasma, e) 6Å Si, N₂ plasma and 650°C anneal, f) 9Å Si and N₂ plasma, g) 650°C anneal.....102

Figure 4.2 UPS spectra of the valence band maximum of CVC clean n-type GaN and the Si₃N₄ final surface, with the valence band maximum indicated by dashed lines.....103

Figure 4.3 XPS Ga 3d core level spectra of : a) CVC clean n-GaN, b) 4Å Si, c) 4Å Si and N₂ plasma, d) 6Å Si and N₂ plasma, e) 6Å Si, N₂ plasma and 650°C anneal, f) 9Å Si and N₂ plasma, g) 650°C anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.....104

Figure 4.4 XPS Ga 3p and Si 2p core level spectra of : a) CVC clean n-GaN, b) 4Å Si, c) 4Å Si and N₂ plasma, d) 6Å Si and N₂ plasma, e) 6Å Si, N₂ plasma and 650°C anneal, f) 9Å Si and N₂ plasma, g) 650°C anneal. The peak position of the Si 2p core level after silicon deposition, as well as the final surface are indicated with dashed lines.....105

Figure 4.5 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and SiO₂. The valence band offset, E_v , conduction band offset, E_c , band bending, and interface dipole, Δ , are represented.....106

Figure 4.6 Deduced bands for the clean p-type GaN surface (left) and the interface between p-type GaN and SiO₂. The valence band offset, E_v , conduction band offset, E_c , band bending, and interface dipole, Δ , are represented.....107

Figure 4.7 Band alignment of Si/Si₃N₄ and GaN/Si₃N₄ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the Si₃N₄ surface, which is

common in both interfaces. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap. The VBO are determined from the measurements.....108

Figure 5.1 UPS spectra of: a) CVC clean n-GaN, b) 4Å Hf, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma and 650°C anneal, e) 12Å Hf and O₂ plasma, f) 650°C anneal....132

Figure 5.2 UPS spectra of the valence band maximum of: a) CVC clean n-GaN, b) 4Å Hf, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma and 650°C anneal, e) 12Å Hf and O₂ plasma, f) 650°C anneal.....133

Figure 5.3 Gallium 3d and hafnium 4f XPS spectra for: a) CVC Clean n-GaN, b) 4Å Hf deposition, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma, and 650°C anneal, e) 12Å Hf and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.....134

Figure 5.4 Nitrogen 1s XPS spectra for: a) CVC Clean n-GaN, b) 4Å Hf deposition, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma, and 650°C anneal, e) 12Å Hf and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.....135

Figure 5.5 Oxygen 1s XPS spectra for: a) CVC Clean n-GaN, b) 4Å Hf deposition, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma, and 650°C anneal, e) 12Å Hf and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.....136

Figure 5.6 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and HfO₂ before annealing. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented...137

Figure 5.7 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and HfO₂ after annealing at 650 °C. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented...138

Figure 5.8 Band alignment of Si/HfO₂ and GaN/HfO₂ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the HfO₂ surface, which is common in all three interfaces. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap. The VBO are determined from the measurements.....139

Figure 6.1 Schematic representation of the equilibrium state for the following measured interfaces: a) n-GaN/SiO₂, b) p-GaN/SiO₂, c) p-GaN/Si₃N₄.....151

Figure 6.2 Schematic representation of the electrically biased interfaces: a) n-GaN/SiO₂, b) p-GaN/SiO₂, c) p-GaN/Si₃N₄.....152

Figure 6.3 I-V curve for typical n-type GaN/SiO₂ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 1×10^{17} and 1×10^{18} ($N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.....153

Figure 6.4 I-V curve showing intrinsic hard breakdown for typical n-type GaN/SiO₂ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 1×10^{17} and 1×10^{18} ($N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.....154

Figure 6.5 Statistical analysis of the voltage at which intrinsic hard breakdown occurs in SiO₂ deposited on n-type GaN. The oxide thickness was 80 Å. Fifty-two 6×10^{-4} cm² contacts were measured, with the voltage varied from 0-110 V in 0.5 V increments....155

Figure 6.6 I-V curve showing intrinsic hard breakdown for typical p-type GaN/SiO₂ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 2×10^{18} and 1×10^{18} ($N_a - N_d$, $N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.....156

Figure 6.7 Statistical analysis of the voltage at which intrinsic hard breakdown occurs in SiO₂ deposited on p-type GaN. The oxide thickness was 80 Å. Forty-one 6×10^{-4} cm² contacts were measured, with the voltage varied from 0-110 V in 0.5 V increments....157

Figure 6.8 I-V curve for typical p-type GaN/Si₃N₄ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 2×10^{18} and 1×10^{18} ($N_a - N_d$, $N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.....158

Figure 6.9 Statistical analysis of the voltage at which intrinsic hard breakdown occurs in Si₃N₄ deposited on p-type GaN. The nitride thickness was 40 Å. Thirty-five 6×10^{-4} cm² contacts were measured, with the voltage varied from 0-110 V in 0.5 V increments.....159

Figure 7.1 Experimental summary of the band alignment of GaN/SiO₂, GaN/Si₃N₄ and GaN/HfO₂ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the dielectric surfaces, which is common in each interface. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap.....165

1. Introduction to GaN: Growth, Properties, and Surface Preparation

1. Introduction to GaN: Growth, Properties, and Surface Preparation

1.1 Introduction

During the past 50 years, development of microelectronic technology has been a driving force in many aspects of human advancement. Evolution from the simple transistor to complex semiconductor devices created today has allowed the realization of advances and discoveries in essentially every other discipline. The pursuit of research in this field has developed a worldwide industry that drives economies and has revolutionized how we live. Silicon-based devices have been the major thrust of research over the years and are the most developed, but there are many more semiconductor systems that are worthwhile to explore.

During the past several years, a new group of materials has emerged, which has enabled applications from optoelectronics devices to high-power, high-frequency, and high-temperature microelectronic devices. This group is known as the wide bandgap semiconductors, and is lead by silicon carbide (SiC) and the III-Nitride semiconductors (AlN, GaN, InN) and their alloys. These materials have attracted considerable interest in electronic devices for applications in high temperature (above 200 °C) with power conditions. These large bandgap materials allow commercialization in environments such as pressure vessels, combustion engines, and near nuclear reactors, where Si and GaAs cannot be used. This is because the probability of thermal excitation of carriers from the valence band to the conduction is reduced significantly by the large bandgap.

In particular, the GaN-based heterostructures have shown promise in the fabrication of light emitting diodes (LEDs). For example, alloying InN and GaN to form $\text{In}_x\text{Ga}_{1-x}\text{N}$ allows the bandgap to be engineered and potentially produce light from of infrared, visible, and ultraviolet wavelengths. LED's fabricated from these materials would be able to emit light in any color in the visible spectrum, resulting in applicability of these materials in many systems.

The GaN-AlN system is being studied extensively for applications in high-temperature, high-frequency, and high-power microelectronic devices. Similar to the InN-GaN system, the bandgap of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ can be engineered from 3.4 to 6.2 eV by varying the Ga to Al ratio in the material.

A material that is the foundation of the III-Nitride semiconductors material group is gallium nitride (GaN), and is being extensively and collaboratively investigated by industry and universities to address the challenges of developing GaN-based devices. Specific material issues that are being addressed range from growth of GaN thin films, including growth properties, to actual device fabrication and characterization.

One area of significant research for any microelectronic device is the band alignment at a heterojunction interface. As the complexity of devices continues to increase, understanding the basic properties of the semiconductor surface as well as its interfacial reaction with another material are required. In particular, the semiconductor-insulator (dielectric) interface is of significant interest for passivation and field effect transistor (FET) devices. The band alignments at a heterojunction define the carrier transport or confinement properties of the potential device. As with all gate dielectrics, it

is imperative that the barrier heights for electron and hole injection are large to have sufficiently low leakage currents.

For the great potential of GaN-based semiconductors to be realized, some important research must be conducted regarding the properties of its surface and the properties of GaN-dielectric interfaces. In this study, electronic properties of atomically clean GaN surface and nitride-dielectric interfaces for both n- and p-type clean GaN have been extensively investigated. The following section summarizes the properties of GaN that are particularly relevant to this research.

1.2 Properties of Gallium Nitride

1.2.1 Growth

The growth of GaN dates back to the early 1940's, when ammonia was passed over hot gallium, resulting in GaN needles.² In the 1960's small poly-crystals of GaN were produced that were useful for basic studies of the physical and electronic properties. In 1969 single crystal GaN thin films were obtained by vapor phase growth as reported by Maruska and Tietjen.⁴ The authors used HCl as a transport gas to carry the gallium in to the system and ammonia as the nitrogen source. The growth was on sapphire substrates and resulted in highly n-type GaN films. Their approach for growth was modeled after growth techniques used to fabricate other III-V semiconductors such as GaAs and GaP. As a result, GaN was first grown as thin crystalline films on various substrates using vapor phase epitaxy. A major advance regarding GaN growth occurred when Yoshida *et al*⁵ and Amano *et al*^{6,7} introduced an AlN buffer layer using molecular beam epitaxy (MBE) and metal organic vapor phase epitaxy (MOVPE), respectively. The availability of thin films led to a increase in GaN related research in film growth and device development. In 1988, Amano and Akasaki⁶ established a technique for growing p-type GaN, using Mg as the acceptor impurity.

At present date, there are several established techniques for synthesizing both n- and p-type GaN films. The methods most commonly used are metal-organic chemical vapor deposition (MOCVD), hydride vapor phase epitaxy (HVPE), and molecular beam epitaxy (MBE). While each technique has its strong and weak points, all of these methods lead to high quality GaN films for use in research and device applications.

1.2.2 Substrates

At the present date, large area bulk single crystal nitride growth is not yet available, requiring GaN and other related nitrides to be grown on foreign substrates. For effective film growth, the physical properties of the substrate, including crystal structure, lattice spacing, thermal expansion, and electrical conductivity, should be as close as possible to that of the film being grown. Hexagonal, wurtzite GaN is most commonly grown on sapphire (Al_2O_3) and silicon carbide (SiC) substrates.

The most common substrate for GaN growth is sapphire, because of its availability in large quantities. Though sapphire is hexagonal, the atomic spacing in the (0001) plane is not close to that of GaN. The lattice mismatch is very large for the GaN- Al_2O_3 system, with a 15% difference at the closest distance, which leads to strain in the film. Another important factor in device fabrication is the material cost of the substrate. The ease of production of sapphire lends to it costing significantly less than silicon carbide.

Silicon carbide is a hexagonal semiconductor that has several stacking arrangements along the c-axis, with 6H being the most common. The arrangement of atoms in the (0001) plane is very similar to that of the III-nitrides and is the plane on which GaN is grown. The lattice mismatch between the GaN/6H-SiC system is about 3%, which is relatively small compared to the mismatch with sapphire. Unlike the case for sapphire, SiC can be doped n- and p-type, potentially allowing vertical device fabrication for GaN grown on SiC. Additionally, the thermal conductivity of silicon carbide is ~6-8 times greater (3.0-3.8 vs. .46 W/cmK) than that of sapphire, allowing heat transfer during processing and device operation. These advantages suggest the use of SiC

as a substrate for GaN growth, allowing high-power, high-frequency, and high-temperature devices to be created.

1.2.3 Physical and Electronic Properties of GaN

Tables 1.1 and 1.2 list some of the basic physical and electronic properties of semiconductors, allowing comparison between GaN and other materials. Physical properties such as lattice constants, thermal conductivity, thermal expansion, and others are listed in Table 1.1. Electronic properties such as bandgap, dielectric constant, mobility, and others, are listed in Table 1.2.

1.3 *Ex situ and in situ surface preparation methods of GaN*

Currently, GaN-based heterostructure devices are based on GaN thin films grown on sapphire or silicon carbide substrates. Selected GaN wafer technologies require the removal of the substrate from the GaN for device fabrication. This commercially available technique is accomplished via a laser lift-off of thick films grown on sapphire substrates.¹¹ The extensive processing of the wafers required to achieve this result leaves the surfaces contaminated with hydroxides, hydrocarbons, and other chemical species. Experience gained from silicon and gallium arsenide technologies has shown that surface chemistry of the wafers greatly affects device performance. Effectively cleaning the wafers significantly reduces the concentrations of point, line, and two-dimensional defects that affect in uncontrollable ways the electrical properties of films and device structures deposited on these structures. These effects include increased resistance of Ohmic contacts, increased leakage currents at Schottky barriers and p-n junctions, reduced dielectric breakdown, and reduced threshold voltages. As such, removal of surface contaminants has been and remains a subject of considerable research.

Smith *et al*¹² and Prabhakaran *et al*¹³ report as-grown GaN films removed from vacuum have a significant contamination layer, with oxygen and carbon being the major source. Therefore, in order for commercialization of GaN-based devices to be realized, development of a technique to remove those contaminants, while preserving the as-grown electronic structure and microstructure is needed.

Ex situ cleaning of GaN grown by both MOVPE and gas source molecular beam epitaxy (GSMBE) was investigated using HCl, HF, ultraviolet/ozone, BHF, BHF vapor, NH₄OH, NH₄OH:H₂O₂, NH₄F, H₂SO₄:H₂O₂:DI, H₃PO₄, RCA SC1 and RCA SC2

chemistries.^{12,14-16} While most processes showed a reduction in the concentrations of carbon and oxygen, each of the above treatments did not provide a surface free of both C and O contamination, as determined by subsequent *in situ* (in vacuum) x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) investigations. The *ex situ* (out of vacuum) cleaning that shows the most promise is HCl-based, producing the lowest carbon and oxygen coverages.¹⁴

In situ cleaning studies involving annealing in vacuum have been explored by several authors. King *et al*¹⁴ and Smith *et al*¹² found that *ex situ* HF processing and subsequent annealing of the GaN (0001) surfaces resulted in the most efficient contamination removal, although complete desorption of contaminants was only obtained at 950°C. King *et al*¹⁴ presented desorption results that indicate Ga evaporation occurs above ~800°C when heating in vacuum. The researchers found that annealing in an ammonia atmosphere (5×10^{-6} Torr) at 800°C resulted in the removal of the carbon, and a reduction of the oxygen to $\sim 1/10^{\text{th}}$ of a monolayer for both MOVPE and GSMBE grown films.

Additional studies have examined *in situ* cleaning of GaN films by exposure to reactive ion plasmas. Plasmas of Ar, Xe, and Ne have been found to be ineffective at completely removing contamination from GaN (0001) surfaces grown by various methods.¹⁷⁻¹⁹ Additionally, it was shown that both Ar and Ne ions generated surfaces that were gallium rich after the treatment. The use of nitrogen sputter and anneal techniques have produced GaN (0001) films that are free of carbon and oxygen contamination.¹⁹⁻²³ Berlitto *et al*¹⁹ found that while the carbon and oxygen contamination was removed,

surface damage was caused, as indicated by (1x1) low energy electron diffraction (LEED) images that showed evidence of faceting.

Wu and Kahn²⁰ investigated nitrogen sputtering (500eV for 10 min) and annealing at 900°C for 10 minutes for both n- and p-type GaN films grown via MOVPE on SiC substrates. The sputter and anneal technique produced ordered (1x1) LEED images with a Ga/N ratio that approached unity.

An alternative to reactive ion processing to clean GaN (0001) films is the deposition and subsequent desorption of Ga metal.. Khan *et al*²⁴ formed 3.5 micron thick MOVPE GaN (0001) films that were cleaned via an anneal (600-900°C) in a Ga flux or by sequentially depositing several monolayers of Ga at room temperature and flashing the metal from the surface at 900°C. The oxygen signal was reduced to the detection limit in AES, and a (1x1) LEED pattern was observed.

Bermudez²³ conducted a study that compared the cleaning efficiency of a Ga deposition and desorption technique with a N_2^+ ion sputter process followed by a vacuum anneal at 900°C on MOVPE GaN surfaces grown on a-plane and c-plane sapphire.²⁵ He found that both cleaning techniques were equivalent in reducing the oxygen surface concentration with sharp (1x1) LEED patterns with ~0.9 eV upward band bending. In a separate report, Bermudez *et al*²⁶ investigated the following cleaning techniques: vacuum annealing at temperatures ranging from 200-1000°C, ammonia dosing the surface during annealing between 750 and 900°C, Ga deposition, and N_2^+ sputter/anneal process routes. It was proposed that while the UHV annealing and ammonia flux techniques were not effective in cleaning, annealing an ion-bombarded surface in ammonia impeded the formation of N vacancies that can occur when annealing in vacuum.²⁶

GaN films used in studies presented in this dissertation were prepared with a combination of *ex situ* and *in situ* methods. *Ex situ* preparation consisted of a process where the films were cleaned sequentially in trichloroethylene, acetone, and methanol baths for 1 minute each, followed by immersion into 49% HCl for 10 minutes. *In situ* preparation consisted of annealing at 860°C for 15 minutes in an NH₃ atmosphere. Surface characterization after this cleaning process revealed a surface with carbon and oxygen below the XPS and AES detection limits, with a sharp (1x1) LEED pattern. Specific information about the cleaning process can be found in the chapter 3, and also in the literature.^{14,27,28}

1.4 *Outline of dissertation*

Chapter 2 contains discussions of various GaN-dielectric formation and characterization techniques. The electron affinity model, charge neutrality model, and other models used to explain heterojunction band alignments are presented. Photoemission techniques such as x-ray photoelectron spectroscopy and ultraviolet photoemission spectroscopy are also discussed.

Chapter 3 describes in detail the experiments, results, and analysis of the n- and p-type GaN-SiO₂ interfaces. The chemical and electronic properties of this interface are reported, as well as observation of a change in the interface dipole as the heterojunction is formed.

Chapter 4 details the experimental investigation of the n- and p-type GaN-Si₃N₄ interfaces. Photoemission analysis of the nitride layer is presented in an attempt to determine the nitride chemistry, as well as chemical and electronic properties of the interface. Observation of a change in the interface dipole as the interface is formed is also reported.

Chapter 5 details the experimental investigation of the n-type GaN-HfO₂ interface, where Hf is deposited and subsequently oxidized on atomically clean GaN surfaces. The chemical and electronic properties of this interface are reported, as well as a change in the interface dipole as the heterojunction is formed.

Chapter 6 presents limited electrical characterization of the GaN/SiO₂ and GaN/Si₃N₄ interfaces. Integrity of the dielectric is examined via electric field breakdown measurements.

Chapter 7 summarizes the results presented in chapters 3-5 and discusses paths for future research efforts.

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Table 1.1 Physical properties of GaN compared to other semiconductors. Values listed are compiled from refs^{1-3, 8-10}

	GaN	AlN	InN	6H-SiC	Si	GaAs	Sapphire
Crystal Structure	Wurtzite	Wurtzite	Wurtzite	Wurtzite	Diamond	Zinc blende	Corundum
Lattice Constants a (Å)	3.189	3.112	3.548	3.081	5.431	5.653	4.758
Lattice Constants c (Å)	5.185	4.982	5.760	15.117	-	-	12.99
Thermal Conductivity (W/cmK)	1.3-1.7	2.0	0.45-0.8	3.0-3.8	1.5	0.46	0.46
Thermal Expansion $\Delta a/a$ ($10^{-6}/K$)	5.59	4.2	3.6	4.2	2.6	6.9	9.2
Thermal Expansion $\Delta c/c$ ($10^{-6}/K$)	3.17	5.3	2.6	4	-	-	9.3
Melting Temp (°C)	>1700	3000	1100	2830	1414	1238	2050
Density (g/cm ³)	6.15	3.23	6.81	3.21	2.33	5.32	3.98

Table 1.2 Electronic properties of GaN compared to other semiconductors. Values listed are compiled from refs^{1-3, 8-10}

	GaN	AlN	InN	6H-SiC	Si	GaAs
Bandgap Energy (eV)	3.4	6.2	1.89	3.03	1.12	1.42
Bandgap Transition	Direct	Direct	Direct	Indirect	Indirect	Indirect
Dielectric Constant ϵ_r	9.5	8.5	15.3	9.66	11.9	13.1
Dielectric Constant ϵ_∞	5.35	4.77	8.4	6.7	-	-
Electron Mobility μ_e (cm ² /Vs)	900	300	4400	500	1500	8500
Hole Mobility μ_h (cm ² /Vs)	15	14	-	50	450	400
Breakdown Field (MV/cm)	>3	-	-	3	0.3	0.4

2. *Band Discontinuities:* Formation, Modeling, and Characterization Techniques

2. *Band Discontinuities: Formation, Modeling and Characterization Techniques*

2.1 *Introduction*

Heterojunction band alignment between two materials determines the properties of the interface, therefore controlling device functionality. There are three types of energy band alignments, type I, type II, and type III. Type I and type II are the most common, and reviewed in this chapter. The band alignment at the heterojunction interface controls the dynamics of how charge carriers flow. Apart from the obvious possibility of making insulated gate field effect transistors, this work has relevance to almost all semiconductor devices, electronic and optoelectronic. This is particularly so as devices are reduced in size and the active regions where carriers flow are closer and closer to the surfaces of the device.

This chapter is concerned with the formation of the heterojunction interface when a semiconductor (GaN) and an insulator (various dielectrics) are placed in intimate contact. Basic electrical properties of semiconductors and insulators are discussed. Theoretical models are presented in this chapter in an attempt to explain the behavior of the semiconductor-dielectric interface. Photoemission characterization techniques necessary to determine this behavior are discussed.

2.2 *Basic electrical properties of semiconductors and insulators*

Before a detailed discussion of the electronic structure of the semiconductor-insulator interfaces can be initiated, the basic electronic properties of semiconductors and insulators must be addressed individually. Topics such as conduction band, bandgap, valence band, Fermi level, and electron affinity will be addressed for both semiconductors and insulators. The following discussions regarding semiconductors will be intrinsic in nature; i.e. there are no impurities or lattice defects. The extension of these statements to n- or p-type doping is straightforward.

The electronic structure of materials can be explained from the band theory of solids.¹⁻³ In general, when atoms are brought together, the outermost energy levels of the individual atoms are split into discrete, quantized energy levels. The levels from neighboring atoms overlap, causing the respective atomic spacing to decrease and the split levels to recombine to form an energy band. This energy band defines the electronic states the electrons can occupy. As the atoms are brought closer to their equilibrium atomic spacing distance, the energy band splits to form separate bands, the conduction and valence bands. In the case of the semiconductor, the conduction and valence bands are separated by an energy gap, usually referred to as the bandgap. The bandgap in a perfectly intrinsic crystal cannot have any states for electrons to occupy. In intrinsic semiconductors, there are no free charge carriers at 0K, since the valence band is filled with electrons and the conduction band is empty. By contrast, at room temperature (~300K) the conduction band of an intrinsic semiconductor usually contains some electrons (10^{10} EHP/cm³) that occupy conduction band states. Consequently, filling empty states leads to valence band states that are no longer completely filled. This gives

rise to the term, “semi” conductor, as some electrons reside near the conduction band and conductivity can be achieved by reasonable amounts of thermal or optical energy.

Insulators are defined similarly to semiconductors, with a valance and conduction band of allowable energies. The bandgap of insulators is typically larger than that of semiconductors. In contrast to semiconductors, energy states in the valence band of insulators are completely filled at room temperature, and require a substantial amount of energy to excite the electrons to the conduction band. This allows a significant amount of charge to build up in an insulator without conduction for an applied bias. Thus, an important difference between semiconductors and insulators is that the number of electrons available for conduction can be increased greatly in semiconductors by thermal or optical energy.

Another difference that separates semiconductors from insulators is the susceptibility to doping. The conductivity of a semiconductor can be greatly influenced by introducing impurities into the lattice. The Fermi level of the semiconductor can be moved in the bandgap by the introduction of impurities into the lattice. For example, GaN can be doped n-type (Si impurities) to move the Fermi level closer to the conduction band minimum and p-type (Mg impurities) to move the Fermi level closer to the valence band maximum.

The Fermi level is defined as the energy at which there is a probability of $\frac{1}{2}$ for a state at that level to be occupied by an electron. In the case of the n-type semiconductor, the Fermi level is situated between the middle of the bandgap and the conduction band minimum. If the doping concentration is known, the location of the Fermi level relative to the conduction band minimum can be found by the relation:

$$E_c - E_f = kT \ln\left(\frac{N_c}{n}\right) \quad (2.1)$$

where k is Boltzman's constant, T is the temperature, n is the concentration of donors, and effective density of states at the conduction band edge, N_c , is given by the relation:

$$N_c = 2\left(\frac{2\pi m_e kT}{h^2}\right)^{\frac{3}{2}} \quad (2.2)$$

where m_e is the effective mass of an electron and h is Plank's constant. The doping concentration of the n-type GaN used in the experiments that comprise this dissertation was measured $1 \times 10^{17} \text{ cm}^{-3}$, giving rise to the Fermi level location of 0.1 eV below the conduction band minimum.

The semiconductor work function (ϕ) can be defined as the difference in energy from the Fermi level at the surface to the vacuum level. In the case of semiconductors, the Fermi level is dependent on the doping of the material, which in turn means the work function for a semiconductor will not have a unique value. As such, the work function of a semiconductor does not accurately describe the energy relations of the bands to the vacuum energy, which can lead to erroneous definitions of the electronic properties of the material.

A more appropriate quantity to represent the relation of the semiconductor bands to the vacuum level is the electron affinity (χ). The electron affinity of a material is defined as the energy difference between the conduction band minimum and the vacuum level; therefore, the energy difference is independent of the doping level. The electron affinities for some common semiconductors are given in Table 2.1.

2.3 *Theoretical models of interface formation*

2.3.1 *Electron affinity model*

The modeling of interface formation dates back to 1938, when Schottky and Mott independently introduced a model for determining the band lineup for metal-semiconductor heterostructures. The Schottky-Mott model was the first to quantify the rectifying behavior at the junction, which is now termed the Schottky barrier. The theory by Schottky and Mott suggested a region of the semiconductor interface will be depleted of carriers, and consequently have a higher resistivity. The origin of the depleted region is dependent on the relative locations of the semiconductor's conduction and valence bands to the Fermi level of the metal at the interface. For example, for a metal/p-type semiconductor interface where the difference between the valence band maximum of the semiconductor and the metal Fermi level is large, a degree of band bending is needed to align the Fermi level in the bulk of the semiconductor to the Fermi level of the metal. The band bending is due to an internal electric field, which results in a depletion of the carrier concentration near the heterojunction interface.

The Schottky-Mott model for the formation of a metal-semiconductor heterojunction is based on the work function of the metal and the electron affinity of the semiconductor. The work function of the metal is the difference in energy from the Fermi level to the vacuum level, while the electron affinity is defined as the energy difference between the conduction band minimum and the vacuum level. This allows the Schottky barrier for metals on n- and p-type semiconductors to be defined by the following relations:

$$\phi_{Bn} = (\phi_m - \chi) \quad (2.3)$$

$$\phi_{Bp} = E_g - \phi_m + \chi_s \quad (2.4)$$

where ϕ_m , χ , and E_g are the work function of the metal, electron affinity of the semiconductor, and bandgap of the semiconductor, respectively. According to the Schottky-Mott model, as the metal and semiconductor are brought into intimate contact, the relative positions of the metal Fermi level and the energy bands of the semiconductor remain the same at the interface. Since the metal and semiconductor are in electrical contact, charge will flow to align the Fermi level of the metal with the Fermi level of the semiconductor. The flow of charge results in band bending, and an internal electric field that is the basis for the rectifying nature of the contact.

Most models for metal-semiconductor interfaces can be extended to semiconductor-semiconductor or semiconductor-insulator heterojunctions. The electron affinity model (EAM), put forth by Anderson,⁴ describes the band discontinuities that form when two materials are placed in intimate contact. According to the model, the energy levels of the respective materials align at the vacuum level, resulting in a conduction band offset, which is equal to the difference in the electron affinities of the materials represented in the following relation:

$$\phi_{CBO} = (\chi_1 - \chi_2) \quad (2.5)$$

where χ_1 and χ_2 represent the electron affinity of each material. This result, along with knowledge of the respective bandgap of each material allows calculation of the valence band offset to be calculated by the relation:

$$\phi_{VBO} = (E_{g,2} - E_{g,1}) - (\chi_1 - \chi_2) \quad (2.6)$$

where E_{g1} and E_{g2} are the respective bandgaps of each material. By examining Eq. 2.6, two cases may arise as the interface is formed. The first case, type I, arises when the value of ϕ_{VBO} is *positive*, where the valence band of material A is closer to the Fermi level and therefore above the valence band of material B. This case leads to carrier confinement in semiconductor-insulator systems. The second case arises when the value of ϕ_{VBO} is *negative*, meaning the valence band of the semiconductor lies below the valence band of the insulator with respect to the Fermi level. This band alignment predicts holes will not be confined to the semiconductor, and will move freely in the insulator resulting in significant leakage current. This case is not desirable in semiconductor-insulator systems, as the role of the insulator is to isolate the charge in the semiconductor for efficient device operation. Type I and type II are expressed in a schematic in Figure 2.1 a, b, with the assumption the electron affinity model describes the heterojunction.

2.3.2 Charge Neutrality Model

A first approach to describing a heterostructure interface is to apply the electron affinity model (EAM). This model holds in the ideal case, assuming there is no potential created as the heterostructure is formed. A model described by Tersoff^{5,6} based on metal induced gap states draws a connection between the metal-semiconductor junction and the semiconductor-semiconductor interface. The basic idea behind Tersoff's model is the wave functions of the electrons in the metal have tails that extend across the interface that generate states in the gap. The effect of gap states at the interface is to screen any deviation from the canonical lineup by a characteristic dielectric constant, therefore

pinning the Fermi level to maintain local charge neutrality. The charge neutrality condition at the interface suggests the Fermi level of the interface is near the middle of the bandgap. Furthermore, in application of Tersoff's model of semiconductor-semiconductor heterojunctions, the misalignment of the neutrality levels corresponds to a "restoring" dipole at the interface.

The charge neutrality level (CNL) model has been used to describe the band alignment of a heterojunction interface between two semiconductors. Tersoff⁵ suggested that the band alignment between two semiconductors is controlled by the charge transfer across the interface and the resulting interface dipoles in a fashion similar to Schottky barrier models. Recently, Robertson⁷ employed the S parameter, which reflects the dielectric screening to relate the relative contribution of the electron affinity model and the dipole from the charge neutrality levels. Empirically, Monch^{8,9} found that S obeys the following relation:

$$S = \frac{1}{1 + 0.1(\epsilon_{\infty} - 1)^2} \quad (2.7)$$

where ϵ_{∞} is the dielectric constant of a given material. A list of S parameters, dielectric constants, charge neutrality levels, and other useful properties is compiled in Table 2.2.

As an alternative to the EAM, it has been proposed that heterojunction band alignments are determined by alignment of the charge neutrality levels (CNL) of the two materials. The charge neutrality levels represent the branch point of the surface or interface states related to the valence or conduction band. Thus a neutral interface would have a Fermi level at the branch point. The presumption is that charge can transfer between the interface states of the two materials, which will cause an interface dipole. If the density of states is high or if the CNL of the two semiconductors are at similar

relative energies, then the band offset will be determined by the relative position of the CNL of the two materials.

Recently, Robertson⁷ adapted the interface defect model presented by Cowley and Sze¹⁰ to employ the CNL as the pinning levels. The model was applied to analyze the band alignment of a range of oxides on silicon, and the model seems consistent with most experimental results. In this model, charge transfer across the interface creates a dipole, which modifies the band lineup given by the electron affinity rule and is described by the relation:

$$\phi_{CBO} = (\phi_{CNL,a} - \phi_{CNL,b}) - (E_{g,a} - E_{g,b}) + S\{(\chi_a - \chi_b) + (E_{g,a} - E_{g,b}) - (\phi_{CNL,a} - \phi_{CNL,b})\}$$

(2.8)

where ϕ_{CBO} is the CBO, χ and ϕ_{CNL} are the electron affinities and charge neutrality levels for each semiconductor (a and b), and S is a pinning factor based on the dielectric properties of the materials. Here, the ϕ_{CNL} is defined relative to the VBM of each semiconductor. A value of S=1 represents the EAM while a value of 0 represents pinning at the CNL levels. Figure 2.2 presents a heterojunction lineup with and without a change in the interface dipole, corresponding to the electron affinity model and to the charge neutrality model, respectively. The focus of our research is to use photoemission to measure the band offsets and to observe a change in the interface dipole at the interface as this heterostructure is formed.

2.4 *In situ characterization techniques*

2.4.1 *Introduction to photoemission*

During the past 30 years, advances in technologies have allowed ultra-high vacuum (10^{-8} to 10^{-10} Torr). Many advancements in surface science are now possible due to this advancement in vacuum technology. As such, photoemission has evolved into a very useful and indispensable technique for thin film characterization. X-ray photoelectron spectroscopy and ultraviolet photoemission spectroscopy are used to characterize surfaces and heterostructure interfaces to obtain information about their electronic and chemical properties.

The basic physics of photoemission is the photoelectric effect. There are three essential components required for photoemission measurements: a photon source, an electron energy analyzer, and an electron detector. The basic process involves incident photons that strike the sample and excite electrons, some of which are emitted. The emitted electrons are collected and analyzed according to their kinetic energy.

While the photoemission process is complex, it can be explained using a three-step conceptual model by Berglund and Spicer.¹¹ There are three steps in their model: excitation of electrons into states in the conduction band, propagation of the electrons to the surface and generation of secondary electrons, and emission of electrons into vacuum. These steps are represented schematically in Figure 2.4. Figure 2.4a shows the density of filled and unoccupied states as they relate to the conduction and valence bands of a material. As photons strike the sample, as shown in Figure 2.4b, electrons from occupied states are excited into unoccupied states by an energy difference equal to that of the photon energy. The excited electrons move toward the surface of the material, but some

recombine, and some are scattered. Figure 2.4c represents electrons that have sufficient energy to overcome the work function of the material and are emitted into vacuum.

2.4.2 *X-ray photoelectron spectroscopy*

X-ray photoelectron spectroscopy employs x-rays as the photon source, with the most common being Mg k_{α} (1253.6 eV) and Al k_{α} (1486.6 eV). The purpose of the high energy x-rays is to excite core level electrons from deep within the atom. This technique is surface sensitive due to the escape depth of the electrons that are not scattered. Theoretical calculations and measurements show the escape depth for electrons excited by XPS is approximately 25 to 35 Å.¹² The emitted electrons have energies representative of the elements they originated from while the scattered electrons originate from deeper in the sample and represent the broad background normally observed in photoemission spectra.

The data obtained in XPS is typically represented in a plot of electron count vs. binding energy. The binding energy of an electron can be related to the kinetic energy of the emitted electron by the relation:

$$BE = h\nu - KE \quad (2.9)$$

where $h\nu$ is the photon energy, and KE is the kinetic energy of the electron. Binding energy is defined as the difference between the initial and final state of an atom after photoemission, implying a binding energy of zero is the Fermi level.¹³ Electron energy levels are different for each element, implying each core level of each element will have a series of transition energies associated with it. This fact makes XPS an ideal technique

for investigation of the chemical properties of surface and interfaces by analysis of the core levels of each material.

2.4.3 *Ultraviolet photoemission spectroscopy*

While high energy photons are necessary to excite core level electrons, the use of a low energy photon source allows information about valence band electrons to be obtained. UPS employs ultraviolet light generated from a gas discharge lamp. While several gases can be used, helium is the most common. The helium plasma generated creates two useful discharge energies: He I (21.2 eV) and He II (40.8 eV). The relatively low mean free path generated by the low photon energy allows valence band information to be obtained. Similar to XPS, UPS spectra is represented as intensity vs. binding energy, with the zero value usually set to that of the Fermi level. In addition to measuring the valence band states, UPS can also be useful for measuring the electron affinity of a material by tracking the low-energy cut-off (vacuum level). The electron affinity can be deduced from the relation:

$$\chi = h\nu - W - E_g \quad (2.10)$$

where $h\nu$ is the photon energy, W is the spectral width measured from the valence band turn on the low energy cut-off, and E_g is the bandgap of the material. UPS, in tandem with XPS, provide a substantial amount of information regarding the electronic properties of a given surface or interface.

2.4.4 *Measuring electronic properties via photoemission*

The use of photoemission to discern band discontinuities is a well-established method that has been reported in the literature.¹⁴⁻¹⁶ The method for determining the valence band discontinuity is similar to that of Waldrop and Grant¹⁷ and Kraut et al.,¹⁸ which is represented in the following relation for the valence band offset:

$$\Delta E_{VBO} = \Delta E_{CL} + (E_{core}^a - E_v^a) - (E_{core}^b - E_v^b) \quad (2.11)$$

where $E_{core}^{a,b}$ is the core level energy of each material, $E_v^{a,b}$ is the valence band energy of each material, and $\Delta E_{CL} = (E_{core}^b - E_{core}^a)$ is the difference in energy between the core levels of the two materials. Their basic approach is to reference the VBM to a core level in the XPS spectra for each semiconductor and to use the measured difference between the core level energies to discern the band discontinuities. In our studies, we have employed UPS to measure the energy of the VBM from the Fermi level, and XPS is used to measure core level energies relative to the Fermi level.

Specifically, XPS and UPS were employed after cleaning to measure initial core level positions and the valence band turn-on position, respectively. These measurements serve as a baseline with which to compare successive measurements. A sequential process involving the careful formation of a thin dielectric on the surface of the clean GaN is conducted until emission from the substrate can no longer be measured. XPS and UPS measurements are obtained after each step of the process, and the band bending is deduced from the shifts of the gallium and nitrogen core levels. The band offsets and electron affinities are determined from the UPS spectra, and the formation of the oxide and the value of the interfacial dipole are determined from the XPS and UPS measurements.

2.5 *Conclusions*

The concept of band discontinuities has been discussed, with theoretical models presented in an attempt to understand semiconductor-insulator interfaces. While there is not an all-encompassing predictive model that is valid for each heterojunction formation, the charge neutrality model gives predictions for band discontinuities that are consistent with experimental results for GaN-dielectric interfaces. Fortunately, the theoretical model does not have to be completely defined to reap the benefit of these interfaces in device applications. The charge neutrality model can be used as a guide for new heterostructure information, but should not be taken as the final word on the subject. Interface characterization used to determine the electronic properties of the heterostructure are much more defined, and allow the use of said interfaces in electronic device fabrication.

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Table 2.1 Bandgap energies and electron affinities of common semiconductors.

Values are compiled from refs¹⁹⁻²²

<u>Semiconductor</u>	<u>Bandgap (eV)</u>	<u>Electron Affinity (eV)</u>
Si	1.12	4.05
GaAs	1.42	4.07
Ge	0.66	4.0
GaN	3.45	3.0-4.1
AlN	6.2	0-2.1
InN	1.89	4.5
ZnO	3.4	4.1
SiC	3.03	3.5

Table 2.2 Experimental bandgaps, charge neutrality level above the valence band edge (CNL), dielectric constant ϵ_{∞} , calculated Schottky barrier slopes S on Si, and electron affinity for each dielectric. Values with an asterisk (*) are estimated values. Values are tabulated from Robertson.⁷

	Bandgap (eV)	CNL (eV)	Dielectric Constant (ϵ_{∞})	S calculated	Electron Affinity (eV)
Si	1.1	0.2	12	0.05	4.0
SiO ₂	9	-	2.25	0.86	0.9
Si ₃ N ₄	5.3	-	3.8	0.51	2.1
SrTiO ₃	3.3	2.60	6.1	0.28	3.9
Ta ₂ O ₅	4.4	3.3	4.84	0.40	3.2
TiO ₂	3.05	2.2	7.8	0.18	3.9*
ZrO ₂	5.8	3.6	4.8	0.41	2.5*
HfO ₂	6	3.7	4	0.53	2.5*
ZrSiO ₄	6*	3.6	3.8	0.56	2.5*
HfSiO ₄	6*	3.6	3.8	0.56	2.5*
GaN	3.4	2.37	8.9	0.14	3.1

FIGURE CAPTIONS

Figure 2.1 Heterojunction band lineups for materials A and B, with type I and type II band alignment represented.

Figure 2.2 Heterojunction band lineups representing the electron affinity model (a) and the interface dipole model (b). The interface dipole, Δ , is shown in Figure 2.2b.

Figure 2.3 Schematic of the 3-step photoemission model with: initial state, b) excitation, c) transport, and d) emission of electrons from a surface

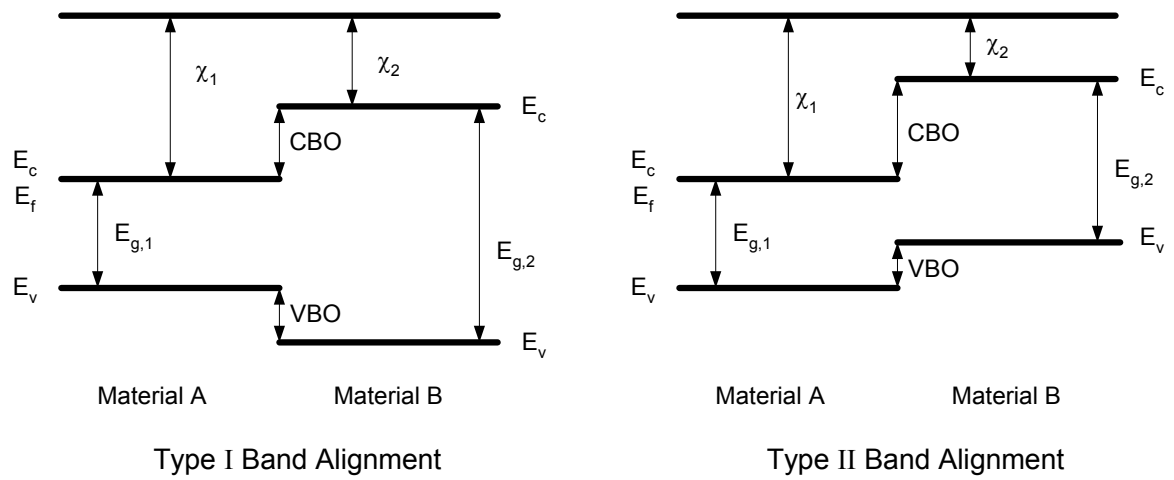
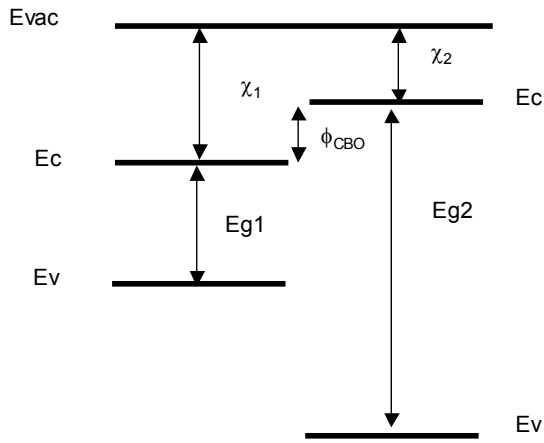


Figure 2.1 Heterojunction band lineups for materials A and B, with type I and type II band alignment represented.

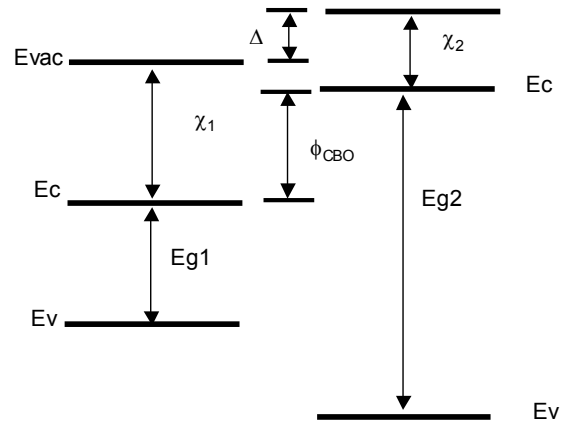


Electron Affinity Model (EAM)

The vacuum levels of the two materials line up

$$\phi_{CBO} = \chi_1 - \chi_2$$

(a)



Interface Dipole Model

The vacuum levels are offset by a factor Δ from the EAM

$$\phi_{CBO} = (\chi_1 - \chi_2) + \Delta$$

(b)

Figure 2.2 Heterojunction band lineups representing the electron affinity model (a) and the interface dipole model (b). The interface dipole, Δ , is shown in Figure 2.2b.

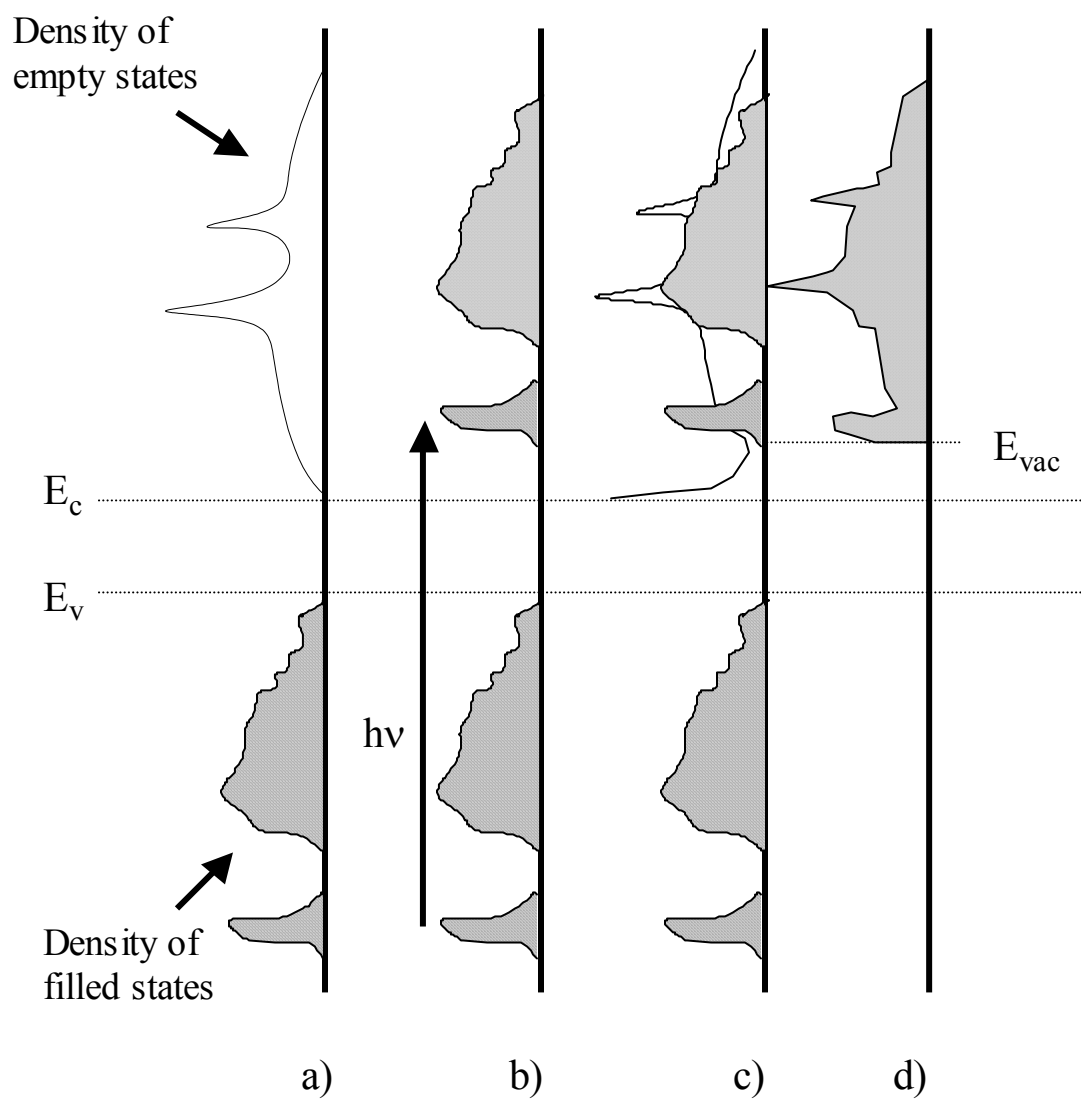


Figure 2.3 Schematic of the 3-step photoemission model with: initial state, b) excitation, c) transport, and d) emission of electrons from a surface

3. Measurement of the band offsets of SiO₂ on clean n- and p-type GaN (0001)

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3.1 *Abstract*

The band alignment at the SiO₂-GaN interface is important for passivation of high voltage devices and for gate insulator applications. X-ray photoelectron spectroscopy and ultraviolet photoemission spectroscopy have been used to observe the interface electronic states as SiO₂ was deposited on clean GaN (0001) surfaces. The substrates, grown by metallorganic chemical vapor deposition, were n-type (1×10^{17}) and p-type (2×10^{18}) GaN on 6H-SiC (0001) with an AlN (0001) buffer layer. The GaN surfaces were atomically cleaned via an 860 °C anneal in an NH₃ atmosphere. For the clean surfaces, n-type GaN showed upward band bending of 0.3 ± 0.1 eV, while the p-type GaN showed downward band bending of 1.3 ± 0.1 eV. The electron affinity for n-type and p-type GaN was measured to be 2.9 ± 0.1 eV and 3.2 ± 0.1 eV, respectively. To avoid oxidizing the GaN, layers of Si were deposited on the clean GaN surface via ultrahigh vacuum e-beam deposition, and the Si was oxidized at 300 °C by a remote O₂ plasma. The substrates were annealed at 650 °C for densification of the SiO₂ films. Surface analysis techniques were performed after each step in the process, and yielded a valence band offset (VBO) of 2.0 ± 0.2 eV and a conduction band offset (CBO) of 3.6 ± 0.2 eV for the GaN-SiO₂ interface for both p- and n-type samples. Interface dipoles of 1.8 eV and 1.5 eV were deduced for the n- and p-type GaN-SiO₂ interfaces, respectively.

3.2 Introduction

Gallium nitride is being investigated for a wide range of electronic and optoelectronic applications. In particular, the interfacial band alignment is of significant interest in the fabrication of devices based on heterostructures. The heterojunction band discontinuities are key parameters of device design because the valence and conduction band offsets determine the transport and confinement properties at the interface. A fundamental objective for technology and basic research would be the control of the band discontinuities¹. The deposition of SiO₂ on GaN could be important for passivation of high voltage devices and for the gate insulator in field effect transistor (FET) devices.² While the Si-SiO₂ interface has been studied extensively,³⁻⁷ little research has been reported and large uncertainties exist on the band offsets at nitride interfaces.⁸⁻¹²

Surface preparation is a critical step to controlled heterostructure formation. In prior studies Bermudez¹³ compared GaN surfaces prepared by sputtering with nitrogen ions followed by annealing in ultrahigh vacuum (UHV) and surfaces prepared by *in situ* deposition of Ga metal followed by thermal desorption. For the two processes, no significant differences of the values of work function, band bending and Ga 3d binding energy were found, which suggests that nitrogen-ion sputtering and annealing are equivalent for preparation of ordered GaN surfaces. However, surfaces prepared by these methods show additional emission at energies above the valence band maximum (VBM) in photoemission data that has been attributed to surface states. In our study, GaN is prepared by an *in situ* ammonia exposure at an elevated temperature,¹⁴ producing atomically clean surfaces without observable emission above the VB turn-on.

Several groups have reported the electrical characteristics of the SiO₂-GaN interface grown by plasma enhanced chemical vapor deposition (PECVD). Casey *et al*¹⁵ found no observable hysteresis in room temperature C-V measurements, as well as an increase of capacitance with incident ultraviolet light while in deep depletion. These observations are consistent with a low concentration of interface traps. M. Sawada *et al*¹⁶ and Arulkumaran *et al*¹⁷ support this observation, measuring $1-2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ and $2.5 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$, respectively for the minimum interface state density at the SiO₂-GaN interface. T. Sawada *et al*¹⁸ investigated the effect of thermal annealing of the interface. The interface state density was reduced 33 % to $2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ after annealing in H₂ at 500 °C. Also noted was that the Fermi level was not pinned and could move within the upper band gap. The as-deposited sample had a Fermi level 0.2 eV from the conduction band edge under thermal equilibrium conditions, and the value increased to 0.5 eV after annealing. The relatively low interface trap density suggests the promise of applications for this interface. While several studies¹⁹⁻²¹ have employed photoemission techniques to explore metal/GaN interfaces, there has been, to our knowledge, no similar report for the SiO₂-GaN interface.

A first approach to describing a heterostructure interface is to apply the electron affinity model (EAM). This model holds in the ideal case, assuming there is no potential created as the heterostructure is formed. The alternative model is the interface dipole model, where the structure of the interface causes a shift in the entire band lineup relative to the predictions of the EAM. The well-known occurrence of reconstructions, chemical reactions, dislocations and strain at the interface may result in contributions to the so-

called “structural interface dipole”.²² The focus of our experiment is to measure the band offsets and to compare the results to this dipole at the heterostructure interface.

The charge neutrality level (CNL) model has been used to describe the band alignment of a heterojunction interface between two semiconductors. Tersoff²³ suggested that the band alignment between two semiconductors is controlled by the charge transfer across the interface and the resulting interface dipoles in a fashion similar to Schottky barrier models. Recently, Robertson²⁴ employed the S parameter, which reflects the dielectric screening, to relate the relative contribution of the electron affinity model and the dipole from the charge neutrality levels. In this study, correlation between the CNL model and experimental data will be presented.

In this study, *in situ* x-ray photoelectron spectroscopy (XPS) and ultra violet photoemission spectroscopy (UPS) measurements are used to determine the band discontinuities, or band offsets, at the GaN-SiO₂ interface. This process is a well-established method that has been reported in the literature.^{22,25,26} After achieving an atomically clean GaN (0001) surface, care is taken to avoid oxidation during the process. Our basic approach in this study is to obtain a clean GaN surface through an ammonia exposure at an elevated temperature and to form an SiO₂ layer by depositing silicon and to employ low temperature oxidation to minimize disruption of the interface. XPS and UPS measurements are obtained after each step of the process, and the band bending is deduced from the shifts of the gallium and nitrogen core levels. The band offsets and electron affinities are determined from the UPS spectra, and the formation of the oxide and the value of the interfacial dipole are determined from the XPS and UPS measurements.

3.3 *Experimental Procedures*

The GaN films used in this study were grown via metallorganic chemical vapor deposition (MOCVD) on 50 mm diameter on-axis Si-face, 6H-SiC (0001) substrates with a conducting AlN (0001) buffer layer. The thickness of the GaN epilayer and the AlN buffer were 1.1 μm and 0.1 μm , respectively. Prior research has established that MOCVD growth of GaN on Si face SiC(0001) results in Ga face GaN(0001).^{27,28} Silicon was used as the n-dopant, and magnesium was used as the p-dopant. Doping concentrations (N_d-N_a) of 1×10^{17} and (N_a-N_d) of $2 \times 10^{18} \text{ cm}^{-3}$ were measured for the n- and p-type samples using capacitance-voltage measurements with a mercury probe.

Raman spectroscopy was employed to characterize the residual strain in the GaN film. The E_2 mode, which is employed to characterize the biaxial strain,²⁹ was found at 564.4 cm^{-1} . The E_2 mode is found at 567.2 cm^{-1} for a free standing film, and this value is used as the reference. Therefore, we deduce a residual tensile strain of 1.4×10^{-3} and a residual tensile stress of 0.6 GPa.³⁰

Ex situ preparation of the GaN consisted of a process where the films were cleaned sequentially in trichloroethylene, acetone, and methanol baths for 1 minute each, followed by immersion into 49% HCl for 10 minutes. The samples were then rinsed for 10 seconds in deionized water, and blown dry using nitrogen. The samples were mounted to molybdenum plates, secured by tantalum wires, and then placed in the load lock for entry into the transfer line that interconnects several analysis and processing chambers. The total time between the completion of *ex situ* cleaning and inserting into the system was about 10 minutes.

Initial surface analysis was performed, and the sample was moved to the gas source molecular beam epitaxy (GSMBE) chamber for *in situ* cleaning. The cleaning process consists of annealing at 860 °C for 15 minutes in an NH₃ atmosphere. Ammonia was introduced into the chamber when the temperature reached 500 °C via a needle valve and a chamber pressure of 1×10^{-4} torr was obtained. The distance between the ammonia doser and sample was ~5 cm, and the partial pressure of ammonia at the sample surface is expected to be as much as an order of magnitude higher than the system pressure. After allowing 5 minutes for the pressure to stabilize, the heater was ramped to 860 °C at a rate of 30 °C per minute. The temperature and ammonia flow was maintained for 15 minutes. Subsequently, a ramp rate of -40 °C per minute was used to achieve a heater temperature of 500 °C; the sample was held at this temperature while the needle valve was closed. The pressure decreased to the low 10^{-8} torr range, during which the sample cooled to ~200 °C, and was transferred out of the system.

After cleaning and other process steps, the samples were transferred in UHV for surface analysis. For XPS, a dual anode X-ray source was used to generate magnesium (1253.6 eV) or aluminum (1486.6 eV) X-rays, and the photoemitted electrons were analyzed with a Fisons Clam II. The resolution of the analyzer was determined from the full width at half maximum (FWHM) of a gold $4f_{7/2}$ spectral peak to be ~1.0 eV; however through curve fitting, spectral peak positions could be determined to 0.1 eV. UPS with He I (21.2 eV) radiation was employed to measure the electronic states near the valence band and to determine the electron affinity. The photoemitted electrons were analyzed with a VSW 50 mm mean radius hemispherical analyzer operated with a resolution of 0.1

eV. A negative 4 V bias was applied to the sample to overcome the work function of the analyzer.

The XPS and UPS spectra were obtained after each process step in a sequence of experiments to follow the shifts of the XPS peaks and the evolution of the valence band spectra. The spectra were measured to track the peak shifts and discern the band bending and band offsets after each of the following steps: 2 Å Si deposition, a second 2 Å Si deposition (4 Å total), O₂ plasma at 300 °C, 2 Å Si (6 Å total Si) and O₂ plasma at 300 °C, 650 °C anneal for 15 minutes, a final 3 Å Si deposition (9 Å Si total) and O₂ plasma at 300 °C, and a 15 minute 650 °C final anneal. Throughout the manuscript, references to the Si thickness in the processing steps refer to the total amount of Si deposited up to that particular step. The ultimate thickness of the oxide film was calculated to be ~18 Å using a density comparison method. This thickness was measured experimentally to be ~17 Å by examining the XPS core level intensities for the clean and final process steps.

3.4 Results

The evolution of the UPS spectra from the clean GaN through oxidation and anneal of the deposited 9 Å Si for the n-type experiment is shown in Figures 1 and 2. The VBM of the clean GaN surface was determined from an extrapolation of a line fit to the leading edge of the spectrum. A turn-on of the GaN signal was measured at 3.0 ± 0.1 eV (referenced to the Fermi level). From the doping concentration of 1×10^{17} in the GaN, the bulk Fermi level was determined to be ~100 meV below the conduction band minimum. Because the deposited layers obscure the valence band maximum, in order to follow the position of the VBM, it is necessary to detect a more intense bulk GaN

spectral feature to reference the position of the VBM. A feature at 13.4 eV in the spectra shown in Figure 1 has been attributed to a GaN bulk excitation.³¹ Note that this feature shifts to a higher binding energy by 0.3 ± 0.1 eV with the deposition of 4 Å of Si and the oxidation that followed. This shift is an indication of a reduction of the band bending by 0.3 eV and is consistent with essentially flat band conditions after the oxidation. Tracking the peak movement is only possible when the substrate emission is observable, therefore when the layer thickness obscures this emission, no further information can be obtained. In our UPS measurements, emission from the substrate was not detected for the 9 Å silicon deposition and oxidation. With increased thickness, the turn-on and signature peaks for SiO₂ remained unchanged.

The spectra shown in Figure 1 were used to determine the electron affinity of GaN, as well as the deposited SiO₂. The electron affinity can be determined by the relation:

$$\chi = h\nu - W - E_g \quad (3.1)$$

where W is the spectral width from the VBM to the low energy cut-off, $h\nu$ is the photon energy (21.2 eV), and E_g is the bandgap of the material. For different cleaning procedures the VBM is sometimes obscured by surface states,^{13,32} but for this study we will employ the method noted above assuming it is representative of the VBM. For the clean GaN surface, the width of the spectrum was measured to be 14.9 eV and 14.7 eV for the n- and p-type, respectively. Using the generally accepted bandgap of GaN, 3.4 eV, the electron affinity was determined to be 2.9 eV and 3.1 eV for the n- and p-type, respectively. While the electron affinity differs by 0.2 eV between the two samples, this is within the experimental error and in agreement with prior reports of 3.0 eV for GaN.^{13,20,33}

We employ the same approach to determine the electron affinity of the SiO₂ layer. The turn-on for the SiO₂ is observed at ~5.1 eV below the Fermi level, and the spectral width is measured to be 11.1 eV. Assuming a bandgap of 9.0 eV, we obtain an electron affinity of 1.1 eV, which is consistent with prior reports.²⁴

The scans shown in Figure 3 represent the evolution of the UPS spectra from the clean GaN through the final surface for the p-type substrate. Figure 4 presents an expanded scan of the clean surface, which indicates a VBM at 1.6 eV (referenced to the Fermi level). Based on the $2 \times 10^{18} \text{ cm}^{-3}$ doping of the Mg, the bulk Fermi level is calculated to be ~300 meV above the VBM. The GaN bulk feature observed at 12.2 eV is in agreement with values reported elsewhere.¹⁹ This feature shifts to a higher binding energy by $0.9 \pm 0.1 \text{ eV}$ with the formation of the SiO₂ layer.

The evolution of the gallium 3d peak during the n-type GaN experiment is shown in Figure 5. The initial peak position and width of the peak for the clean surface was determined to be $20.4 \pm 0.1 \text{ eV}$ and $1.35 \pm 0.1 \text{ eV}$, respectively. This peak position minus the VB turn-on is 17.4 eV, and is close to the value of 17.7 eV reported by Waldrop and Grant³⁴. In some data sets we have found values consistent with the 17.7 eV found by Waldrop and Grant.³⁴ In our case the core level and valence band measurements are made with two separate instruments and variations in calibration are likely responsible for the small differences. The primary considerations of our measurements are on relative peak shifts, so these small variations do not affect our analysis.

Spectra observed after the first and second 2 Å Si depositions showed shifts that were smaller than 0.1 eV. After an anneal following the third 2 Å Si deposition (6 Å

total) and oxidation, the peak shifted to 20.65 ± 0.1 eV, while the width increased to 1.4 ± 0.1 eV. For the final surface, which consisted of a 9 Å Si layer that was oxidized, the peak was observed at 20.76 ± 0.1 eV, indicating a shift of 0.36 ± 0.1 eV for the entire experiment. There are no indications of a reaction between the GaN and the SiO₂, therefore suggesting that this shift is due to a change in the band bending.³⁵

Similar behavior was observed for the evolution of the nitrogen 1s core level. The N 1s peak position for the clean n-type GaN surface was observed at 397.9 ± 0.1 eV, and the width was measured to be 1.1 ± 0.1 eV. As in the case of the Ga 3d, the N 1s shifted a discernable amount after the third 2 Å Si deposition (6 Å total) and oxidation, to 398.2 ± 0.1 eV, with a width of 1.2 ± 0.1 eV. For the final surface, the peak shifted to 398.3 ± 0.1 eV, with a width of 1.1 ± 0.1 eV. This difference of 0.37 ± 0.1 eV is again consistent with values obtained for the gallium core level peaks.

Figure 6 displays the evolution of the oxygen 1s core level. As measured by XPS, the as-loaded GaN sample contains ~14 and 8 atomic percent of oxygen and carbon, respectively. The chemical vapor clean (CVC) clean reduces the oxygen and carbon below the XPS detection limits (< 1 atomic percent).

The surface termination of the GaN after the CVC clean has not been determined. The Si 2p and N 1s core levels were examined for evidence of Si-N bonding immediately after the first silicon deposition. For the Si 2p, the nearby location of the Ga 3p core level, as well as the subtle difference in peak location for Si-O and Si-N bonding limited the ability to detect Si-N bonding. Similarly, we found that the N 1s core level in GaN and in Si₃N₄ deposited on GaN essentially overlap. With these considerations, we cannot

exclude the possibility of Si-N at the surface even though no direct evidence was found in our measurements.

After deposition of 4Å Si and the O₂ plasma, the initial peak position was observed at 532.2 ± 0.1 eV. Through the course of the experiment, the peak shifted to 533.1 eV, for a total of 0.9 ± 0.1 eV. This peak only slightly deviates by 0.2 eV from the 533.3 eV value reported in the literature for SiO₂ on silicon substrates.^{36,37} The final peak position for the O 1s core level of the SiO₂ on p-type GaN is at 532.5 eV, which is also generally consistent with the prior value.

The oxide quality is an important issue because it affects the bandgap of the material. Careful comparisons were made of the oxide grown on the GaN surface to SiO₂ grown on silicon. The difference in energy between the O 1s and Si 2p core levels was found to be 429.5 eV in the oxide grown in our experiment, which is equivalent with the value found in the literature.³⁸ This finding suggests that the quality of our film is consistent with SiO₂ grown on Si.

Figure 7 shows the O 1s core level for p-type GaN CVC cleaned, oxidized and SiO₂ surfaces. The oxidized GaN surface has a peak position of 530.2 eV. The SiO₂ surface shown is that of the final surface of the p-type experiment, and has a peak position of 532.5 eV. The Ga-O bond found in the oxidized case could not be resolved in the SiO₂ spectra. The Ga 3p core level has a higher surface sensitivity than the Ga 3d core level, and is shown in Tables I and II for the n- and p-type experiments. The Ga 3p core level displays shifts that are consistent with those of the Ga 3d and N 1s core levels, without indication of a chemical shift due to Ga₂O₃ formation. As mentioned previously,

the SiO₂ formed on the surface is shown to have a limited reaction with the GaN and is below the detection limits in XPS.

Further evidence of SiO₂ formation can be detected in the silicon 2p peak spectra. After Si deposition, the initial peak position was observed at 101.59 ± 0.1 eV. This peak shifted to 103.61 ± 0.1 eV after oxidation and subsequent annealing of the substrate. This peak position, as well as the shift of 2 eV, is consistent with SiO₂ on Si substrates,³⁹ which we attribute to a chemical shift due to the formation of SiO₂.

The evolution of the gallium 3d peak for the p-type GaN experiment is shown in Figure 8. The initial peak position for the clean surface was observed at 19.18 ± 0.1 eV. After the 4 Å Si deposition and oxidation, the peak shifted to a value of 19.4 ± 0.1 eV. While the peak shifted ~ 0.2 eV during the oxidation, the largest shift occurred after each anneal of the sample, as evidenced by the peak positions of the 6 Å total Si/O₂ plasma/650 °C anneal and the 9 Å total Si/O₂ plasma/650 °C anneal treatments shown at 19.95 ± 0.1 eV and 20.05 ± 0.1 eV, respectively. Annealing is a well-documented process for densification of the deposited oxide, which enhances the quality of the film.⁴⁰⁻⁴² During the course of the experiment we observed a shift in the spectra of 0.87 ± 0.1 eV. The lack of a Ga-O peak in the spectra once again suggests a very limited reaction between the GaN and the SiO₂, implying that this shift is due to a change in the band bending.

The peak position of the nitrogen 1s core level on the clean p-type GaN surface was observed at 396.65 ± 0.1 eV, while the final position was 397.5 ± 0.1 eV. This difference of 0.85 ± 0.1 eV is in excellent agreement with values for the Ga 3d levels.

The spectral peak positions and the full width-half maximum (FWHM) of the Ga 3p_{3/2}, Si 2p, O 1s, Ga 3d, and N 1s have been summarized in Tables I and II for both n and p-type GaN, respectively. From the results, two important properties of the interface can be stated. First, there does not appear to be a significant reaction at the GaN-SiO₂ interface. If this reaction were significant, there would be additional peaks reflecting the reacted environment, and/or changes in the widths of the peaks. Second, the observed shift for the Ga 3p_{3/2}, Ga 3d, and N 1s core levels are essentially the same, allowing the inference that the shifts are a result of band bending.

3.5 Discussion

The method for determining the valence band discontinuity is similar to that of Waldrop and Grant³⁴ and Kraut *et al.*⁴³ Their basic approach is to reference the VBM to a core level in the XPS spectra for each semiconductor and to use the measured difference between the core level energies to discern the band discontinuities. In our study, we have employed UPS to measure the energy of the VBM from the Fermi level, and XPS is used to measure core level energies relative to the Fermi level.

Care was taken to avoid oxidation of the clean GaN surface after the CVC clean. A significant Ga₂O₃ layer at the interface can be a source of deep acceptors and interface states that can be detrimental to device fabrication.⁴⁴ Although gallium oxide was not observed within our detection limits, we expect that Ga-O bonding exists at the SiO₂-GaN interface. Therrien *et al.*⁴⁵ reported the significance of an ultra-thin Ga₂O₃ layer formation, which allowed a redistribution of electronic charge and reduction of the interfacial defect density.

The Ga face GaN (0001) is a polar surface, and the spontaneous polarization will lead to a negative bound charge at the GaN film surface and a positive bound charge at the back substrate interface. The GaN is also piezoelectric, but because the films are grown above the critical thickness there is only a small residual strain, and the piezoelectric induced polarization ($P_{pz}=0.002 \text{ C/m}^2$) is small in comparison to the spontaneous polarization ($P_{sp}=0.033 \text{ C/m}^2$).⁴⁶ The piezoelectric polarization for biaxial tensile strain contributes in the same direction as the spontaneous polarization. The negative surface bound charge is compensated by surface states and screened by ionized donors while the positive bound charge at the substrate interface is screened by the free carriers. The polarization bound charge screened by the ionized donors would lead to upward band bending at the GaN surface. We note that the XPS measurements of the Ga and N core levels would be shifted by the polarization fields, but all measurements of the band offsets are made relative to these values, and thus the measured band offsets should not be affected by polarization induced band bending. Moreover, since the strain is relatively small, the effect of strain on the band offsets is anticipated to be less than the experimental uncertainties in our measurements.⁴⁷

Figure 9 shows the proposed band lineups for the n-type GaN-SiO₂ interface. The decrease of 0.3 eV band bending from the clean surface indicates essentially flat band conditions are achieved. The valence band offset determination is the measured UPS turn-on for SiO₂ (5.3 eV), minus the GaN turn-on (3.0 eV), minus the band bending (0.3 eV). With this value and the knowledge of the bandgap of the material, the conduction band offset is obtained. The bandgap of SiO₂ has been widely reported to be 9.0 eV⁴⁸⁻⁵⁰, and this value was used for the conduction band offset and electron affinity calculations.

From our experiment, the valence band offset is deduced to be 2.0 eV, and the conduction band offset is 3.6 eV.

The p-type GaN-SiO₂ band lineup is represented in Figure 10. For the clean surface, the measured downward band bending and electron affinity were calculated to be 1.3 ± 0.1 eV and 3.2 ± 0.1 eV, respectively, assuming the Mg acceptor level lies ~300 meV above the VBM and a room temperature bandgap of 3.4 eV.⁵¹ Using the considerations mentioned above, the valence band offset was calculated to be 2.0 eV, and the conduction band offset of 3.6 eV.

The electron affinity levels for GaN and SiO₂ are represented in Figures 9 and 10. The electron affinity model of heterojunction formation predicts these levels to align at the interface. Our results show a deviation from the electron affinity model of 1.8 eV for the n-type GaN substrate and 1.5 eV for the p-type GaN substrate.

The electron affinity model is based on the premise that the interface is formed without disruption of the surface electronic states of either of the two materials. All reference is to the vacuum levels of the two materials. The measured difference between the prediction of the electron affinity model and the experimentally observed band offset represents a change in the interface dipole. In general, it is not possible to assign a specific interface dipole to the heterostructure, but it is reasonable to consider the change in interface dipole from that deduced by the electron affinity model. However, the relation to the vacuum level in the first place is somewhat arbitrary. While the electron affinity of a surface can be determined following the approach employed in this study, it is dependent on the details of the surface structure where surface reconstruction, steps, and adsorbates can cause changes of the electron affinity by several eV. Moreover, after

interface formation, the vacuum level of the materials at the interface is not defined or measurable, and the interface structure may have little relation to the specific bonding of the free surface that was responsible for the value of the electron affinity.

As an alternative to the electron affinity model, it has been proposed that heterojunction band alignments are determined by alignment of the charge neutrality levels (CNL) of the two materials. The charge neutrality levels represent the branch point of the surface or interface states related to the valence or conduction band. Thus a neutral interface would have a Fermi level at the branch point. The presumption is that charge can transfer between the interface states of the two materials, which will cause an interface dipole. If the density of states is high or if the CNL of the two semiconductors are at similar relative energies, then the band offset will be determined by the relative position of the CNL of the two materials.

Recently, Robertson²⁴ adapted the interface defect model presented by Cowley and Sze⁵² to employ the CNL as the pinning levels. The model was applied to analyze the band alignment of a range of oxides on silicon, and the model seems consistent with most experimental results. In this model, charge transfer across the interface creates a dipole, which modifies the band lineup given by the electron affinity rule and is described by the relation:

$$\varphi_{CBO} = (\varphi_{CNL,a} - \varphi_{CNL,b}) - (E_{g,a} - E_{g,b}) + S\{(\chi_a - \chi_b) + (E_{g,a} - E_{g,b}) - (\varphi_{CNL,a} - \varphi_{CNL,b})\} \quad (3.2)$$

Where φ_{CBO} is the CBO, χ and φ_{CNL} are the electron affinities and charge neutrality levels for each semiconductor (a and b), and S is a pinning factor based on the dielectric properties of the materials. Here, the φ_{CNL} are defined relative to the VBM of each semiconductor. A value of $S=1$ represents the EAM while a value of 0 represents pinning

at the CNL levels. To our knowledge, the CNL of SiO₂ has not been reported, and because of the high value of S for the SiO₂-Si interface (0.86),²⁴ we cannot use the experimental results of the Si/SiO₂ interface to reliably place the SiO₂ CNL.

In an attempt to understand the relation of our measured band alignment and the different models for heterostructure band alignment, we have compared our measured interface alignments to experimental results for SiO₂ on Si and SiO₂ on SiC in Figure 11. In each case the diagrams are aligned to the vacuum level at the SiO₂, which has been measured to be at the same energy relative to the oxide bands. The bandgap of each material is indicated, as is the VBO. The position of the vacuum level of the clean surface of the semiconductor is indicated, and the difference between these values and the surface vacuum level is the deviation from the EAM. This difference represents the change in the interface dipole, and was found to be 0.5, 1.1, and 1.6 eV for SiO₂ on Si, SiC and GaN, respectively.

Also indicated in Figure 11 is the CNL of the semiconductors based on prior reports.^{24,53} We find that the CNL of the Si and the GaN are in relative alignment with respect to the SiO₂ band gap, but the CNL of the SiC falls substantially below these values. The variation of the CNL model for these three interfaces may be anticipated by the wide bandgap and the high value of S of the SiO₂.

The progression of the interface dipole deduced from the deviation from the EAM is most likely related to the changes at the semiconductor surface since the oxide is the same in all cases. For the SiO₂/Si interface, the surface reconstruction of the Si is not expected to survive the bonding and this effect alone could account for the change in the interface dipole. The same might be true for the SiO₂/SiC interface where the increased

interface dipole could also represent the charge transfer from the Si to the nearest neighbor C atoms. For both Si and SiC, the oxide interface layer is expected to contain Si-O bonding. For the SiO₂/GaN interface, Ga-O bonding is expected at the interface. With the Ga atomic layer more positive and the O layer more negative, the interface dipole would be expected to lower the GaN electronic levels with respect to the SiO₂ levels, which is consistent with our observations.

3.6 Conclusions

The band alignment of a SiO₂ layer on $1 \times 10^{17} \text{ cm}^{-3}$ n-type and $2 \times 10^{18} \text{ cm}^{-3}$ p-type GaN has been investigated. Annealing in ammonia at 860 °C provided atomically clean, stoichiometric GaN surfaces with $0.3 \pm 0.1 \text{ eV}$ upward band bending and $1.3 \pm 0.1 \text{ eV}$ downward band bending for the n-type and p-type surfaces, respectively. The electron affinity for the clean n-type and p-type GaN surfaces was measured to be 2.9 eV and 3.2 eV, respectively. After careful formation of the GaN-SiO₂ interface, flat bands were observed in the n-type experiment, while an additional 0.9 eV downward band bending was observed for the p-type experiment. For both measurements, a valence band offset of $2.0 \pm 0.1 \text{ eV}$ was obtained, while the conduction band offset was determined to be $3.6 \pm 0.1 \text{ eV}$ (assuming $E_{\text{g SiO}_2} = 9.0 \text{ eV}$). The interface dipole deduced from comparison with the electron affinity model was 1.8 eV and 1.5 eV for the n-type and p-type surfaces, respectively.

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Table 3.1 XPS core level curve fitting results for the n-type GaN/SiO₂ experiment.

(Oxygen plasma is represented as O-Pl)

Process Step	Ga 3p _{3/2}		Si 2p		O 1s		Ga 3d		N 1s	
	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)
CVC	105.71	2.69	-	-	-	-	20.41	1.35	397.90	1.10
2Å Si	105.71	2.67	101.59	3.72	-	-	20.48	1.35	398.02	1.12
4Å Si	105.71	2.68	100.90	2.87	-	-	20.46	1.35	398.01	1.13
O-Pl	105.73	2.66	102.71	2.26	532.19	1.94	20.45	1.40	398.01	1.29
6Å Si, O-Pl	105.89	2.68	102.95	2.06	532.37	1.85	20.56	1.44	398.05	1.26
Anneal	106.01	2.65	103.54	2.15	532.81	1.76	20.65	1.41	398.16	1.14
9Å Si, O-Pl	106.03	2.68	103.59	1.92	533.10	1.77	20.74	1.37	398.25	1.11
Final	106.10	2.54	103.61	1.98	533.10	1.77	20.76	1.37	398.27	1.14
Difference	0.39		2.02		0.91		0.35		0.37	

Table 3.2 XPS core level curve fitting results for the p-type GaN/SiO₂ experiment.

	Ga 3p _{3/2}		Si 2p		O 1s		Ga 3d		N 1s	
Process Step	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)
CVC	104.53	2.81	-	-	-	-	19.18	1.64	396.65	1.34
4Å Si	104.8	2.91	99.8	3.81	531.34	2.57	19.55	1.66	396.93	1.31
O-PI	104.74	2.51	102.42	2.45	531.83	2.02	19.4	1.61	396.8	1.33
6Å Si, O-PI	104.86	2.70	102.84	2.46	531.94	1.92	19.42	1.63	396.82	1.36
Anneal	105.37	2.77	103.3	1.74	532.36	1.58	19.95	1.66	397.35	1.37
9Å Si, O-PI	104.72	2.98	102.68	1.90	532.0	1.80	19.48	1.61	396.9	1.27
Final	105.41	2.85	103.34	1.95	532.53	1.52	20.05	1.72	397.5	1.36
Difference	0.88		3.54		1.19		0.87		0.85	

FIGURE CAPTIONS

Figure 3.1 UPS spectra of a) CVC clean n-type GaN, b) 2Å Si, c) 4Å Si and O₂ plasma, d) 6Å Si, O₂ plasma and 650°C anneal, e) 9Å Si and O₂ plasma, f) 650°C anneal.

Figure 3.2 UPS spectra of the valence band maximum of: a) CVC clean n-type GaN, b) 2Å Si, c) 4Å Si and O₂ plasma, d) 6Å Si, O₂ plasma and 650°C anneal, e) 9Å Si and O₂ plasma, f) 650°C anneal.

Figure 3.3 UPS spectra of the valence band maximum of: a) CVC clean p-type GaN, b) 4Å Si and O₂ plasma, c) 6Å Si and O₂ plasma, d) 6Å Si, O₂ plasma and 650°C anneal, e) 9Å Si and O₂ plasma, f) 650°C final anneal.

Figure 3.4 UPS spectra of the valence band maximum of CVC clean p-type GaN, with valence band maximum indicated by a dashed line.

Figure 3.5 Gallium 3d XPS spectra for: a) CVC Clean n-type GaN, b) 2Å Si deposition, c) 4Å Si deposition, d) 4Å Si and O₂ plasma, e) 6Å Si, O₂ plasma, f) 6Å Si, O₂ plasma and 650°C anneal, g) 9Å Si and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

Figure 3.6 Oxygen 1s XPS spectra for: a) CVC Clean n-type GaN, b) 2Å Si deposition, c) 4Å Si deposition, d) 4Å Si and O₂ plasma, e) 6Å Si, O₂ plasma, f) 6Å Si, O₂ plasma and 650°C anneal, g) 9Å Si and O₂ plasma, h) 650°C final anneal. The peak

positions after the initial oxidation, as well as the final surface are indicated with dashed lines.

Figure 3.7 Oxygen 1s XPS spectra for: a) CVC Clean p-GaN, b) O₂ Plasma, and c) the final SiO₂ surface. Dashed lines indicate the peak positions for the oxidized GaN, as well as the final SiO₂ surface.

Figure 3.8 Gallium 3d XPS spectra for: a) CVC Clean p-type GaN, b) 4Å Si deposition, c) 4Å Si and O₂ plasma, d) 6Å Si, O₂ plasma, e) 6Å Si, O₂ plasma and 650°C anneal, f) 9Å Si and O₂ plasma, g) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

Figure 3.9 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and SiO₂. The valence band offset, conduction band offset, band bending, and interface dipole are represented.

Figure 3.10 Deduced bands for the clean p-type GaN surface (left) and the interface between p-type GaN and SiO₂. The valence band offset, conduction band offset, band bending, and interface dipole are represented.

Figure 3.11 Band alignment of Si/SiO₂, SiC/SiO₂, and GaN/SiO₂ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the SiO₂ surface, which is common in all three interfaces. The deviation from the electron affinity

model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap. The VBO are determined from the measurements.

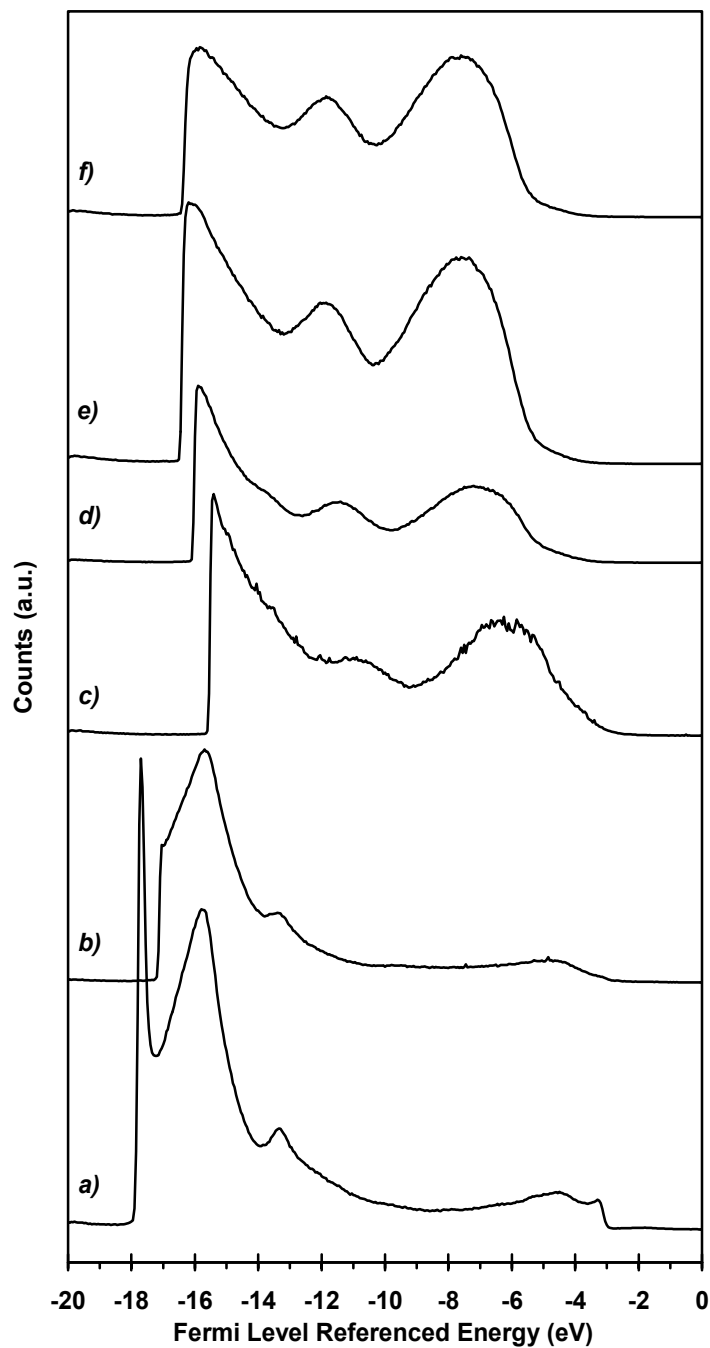


Figure 3.1 UPS spectra of a) CVC clean n-GaN, b) 2 Å Si, c) 4 Å Si and O₂ plasma, d) 6 Å Si, O₂ plasma and 650°C anneal, e) 9 Å Si and O₂ plasma, f) 650°C anneal.

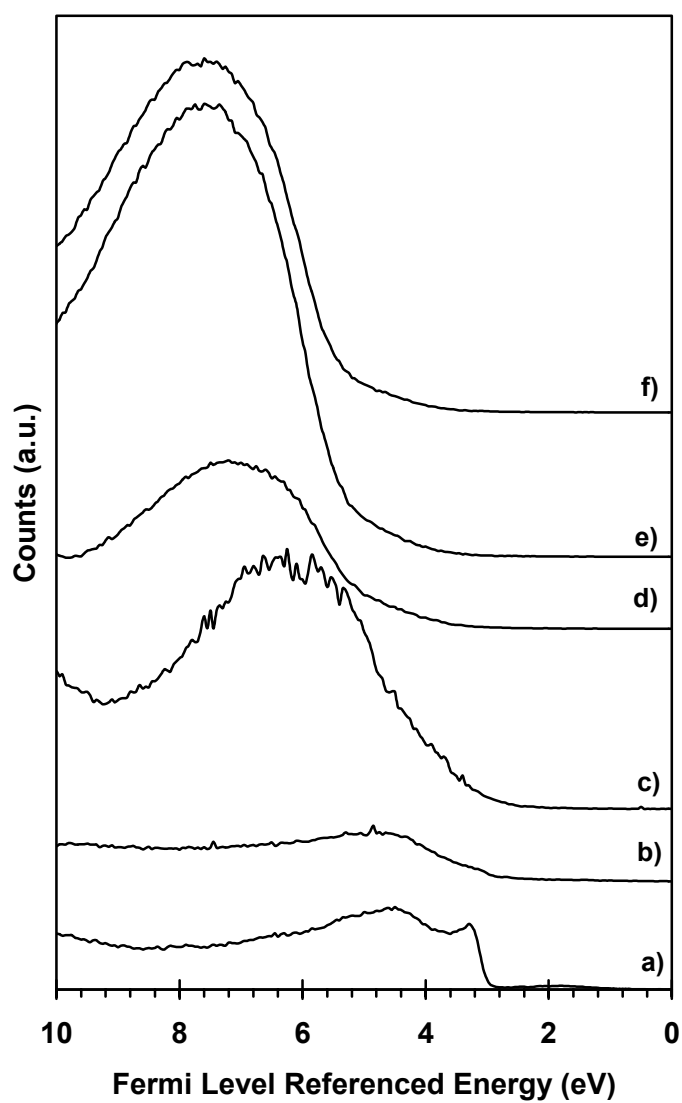


Figure 3.2 UPS spectra of the valence band maximum of: a) CVC clean n-GaN, b) 2 Å Si, c) 4 Å Si and O₂ plasma, d) 6 Å Si, O₂ plasma and 650°C anneal, e) 9 Å Si and O₂ plasma, f) 650°C anneal.

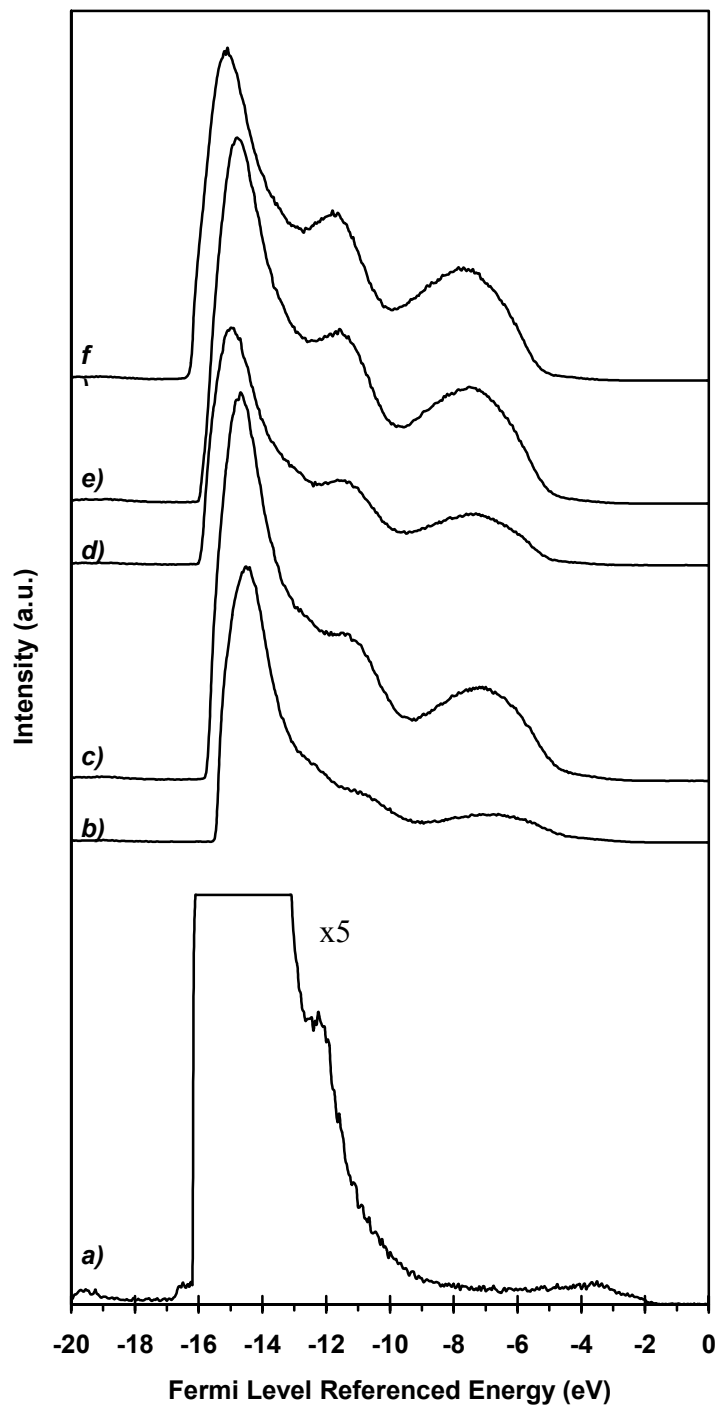


Figure 3.3 UPS spectra of the valence band maximum of: a) CVC clean p-GaN, b) 4Å Si and O₂ plasma, c) 6Å Si and O₂ plasma, d) 6Å Si, O₂ plasma and 650°C anneal, e) 9Å Si and O₂ plasma, f) 650°C final anneal.

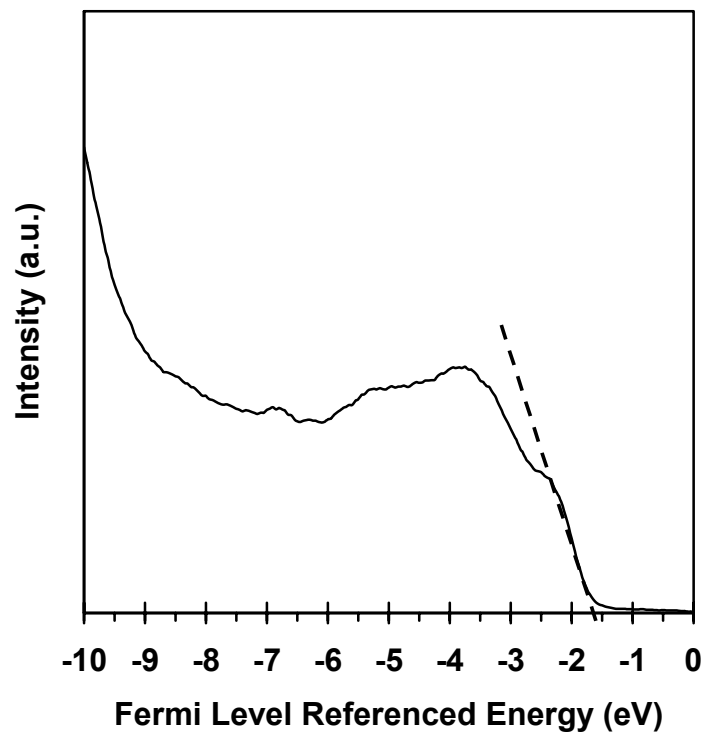


Figure 3.4 UPS spectra of the valence band maximum of CVC clean p-GaN, with valence band maximum indicated by a dashed line.

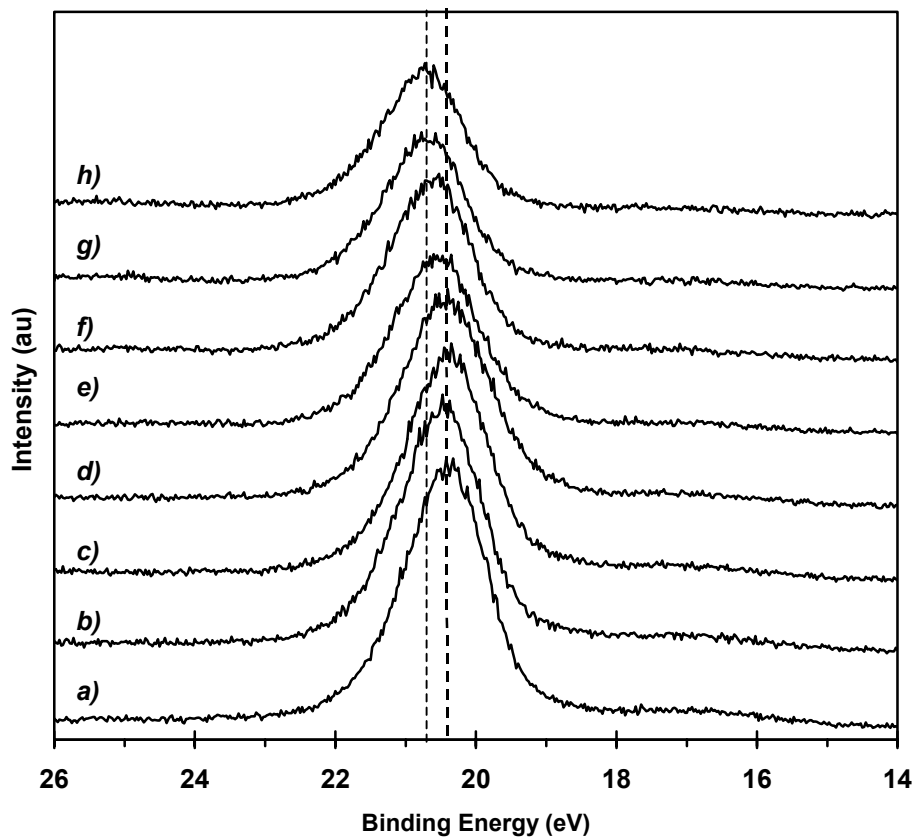


Figure 3.5 Gallium 3d XPS spectra for: a) CVC Clean n-GaN, b) 2 Å Si deposition, c) 4 Å Si deposition, d) 4 Å Si and O₂ plasma, e) 6 Å Si, O₂ plasma, f) 6 Å Si, O₂ plasma and 650°C anneal, g) 9 Å Si and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

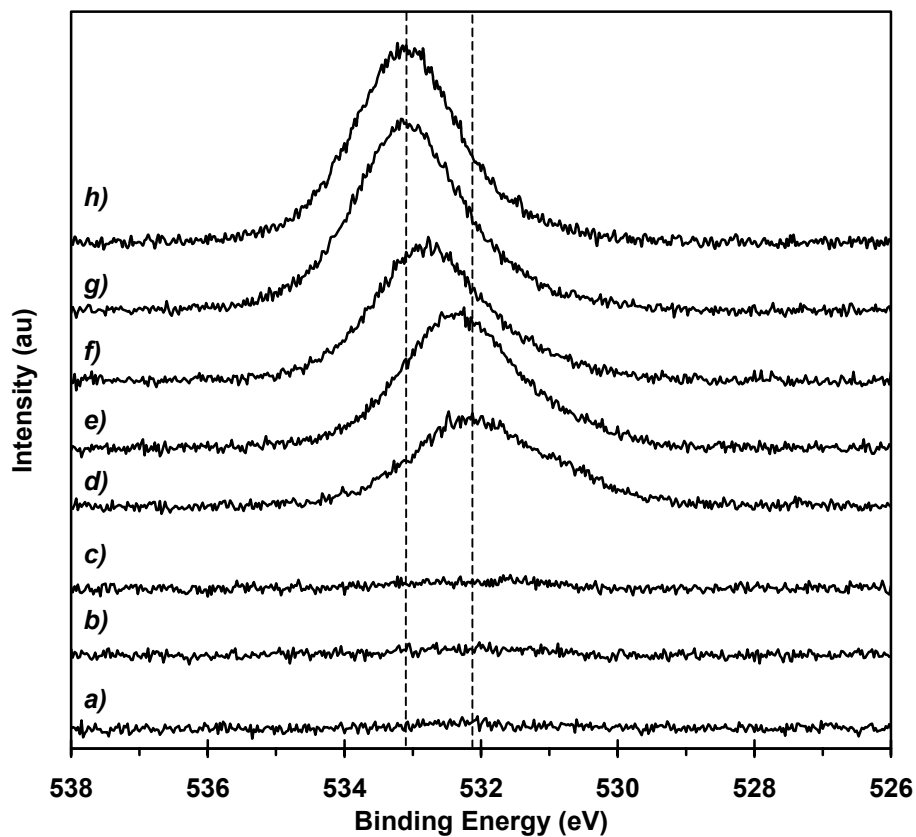


Figure 3.6 Oxygen 1s XPS spectra for: a) CVC Clean n-GaN, b) 2 Å Si deposition, c) 4 Å Si deposition, d) 4 Å Si and O₂ plasma, e) 6 Å Si, O₂ plasma, f) 6 Å Si, O₂ plasma and 650°C anneal, g) 9 Å Si and O₂ plasma, h) 650°C final anneal. The peak positions after the initial oxidation, as well as the final surface are indicated with dashed lines.

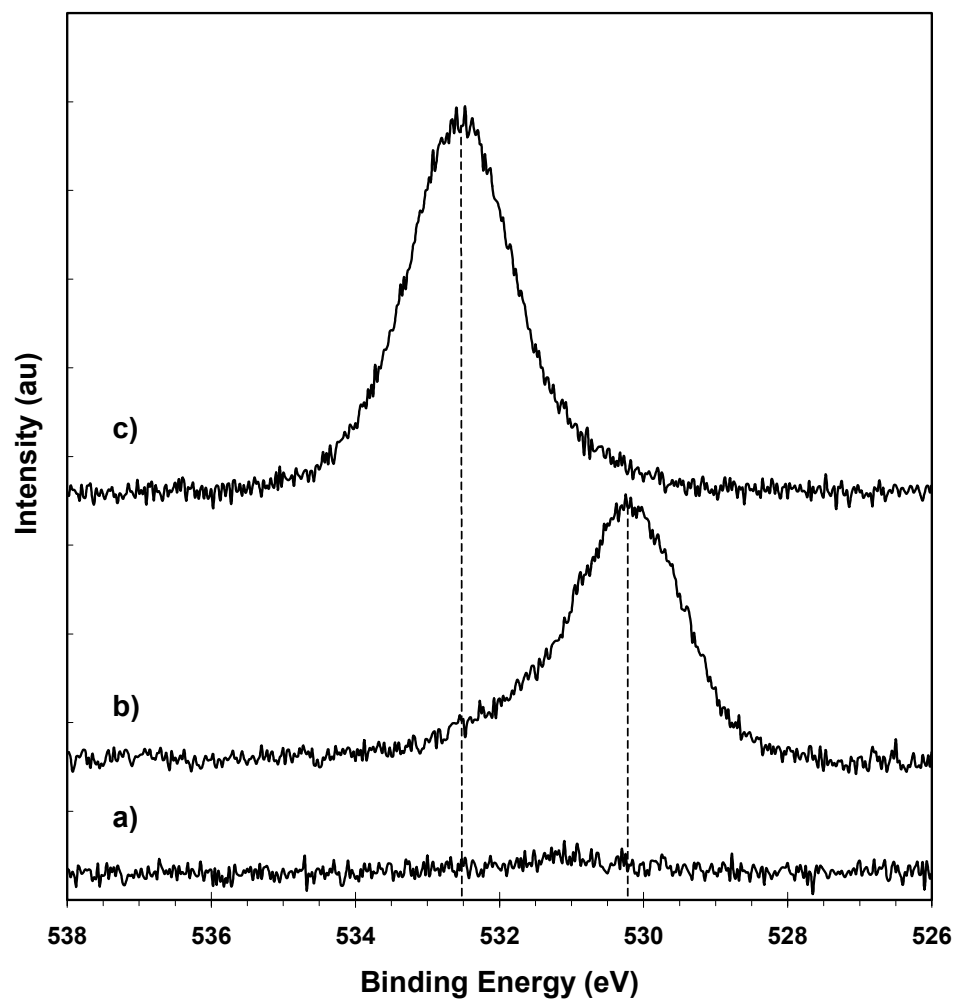


Figure 3.7 Oxygen 1s XPS spectra for: a) CVC Clean p-GaN, b) O₂ plasma, and c) the final SiO₂ surface. Dashed lines indicate the peak positions for the oxidized GaN, as well as the final SiO₂ surface.

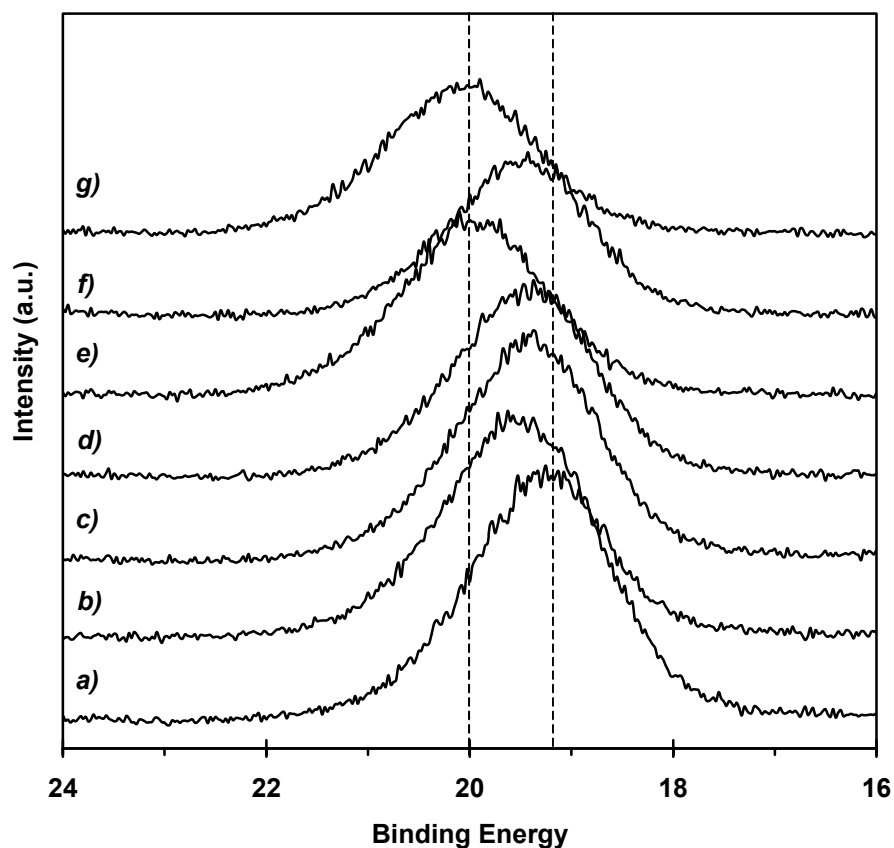


Figure 3.8 Gallium 3d XPS spectra for: a) CVC Clean p-GaN, b) 4Å Si deposition, , c) 4Å Si and O₂ plasma, d) 6Å Si, O₂ plasma, e) 6Å Si, O₂ plasma and 650°C anneal, f) 9Å Si and O₂ plasma, g) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

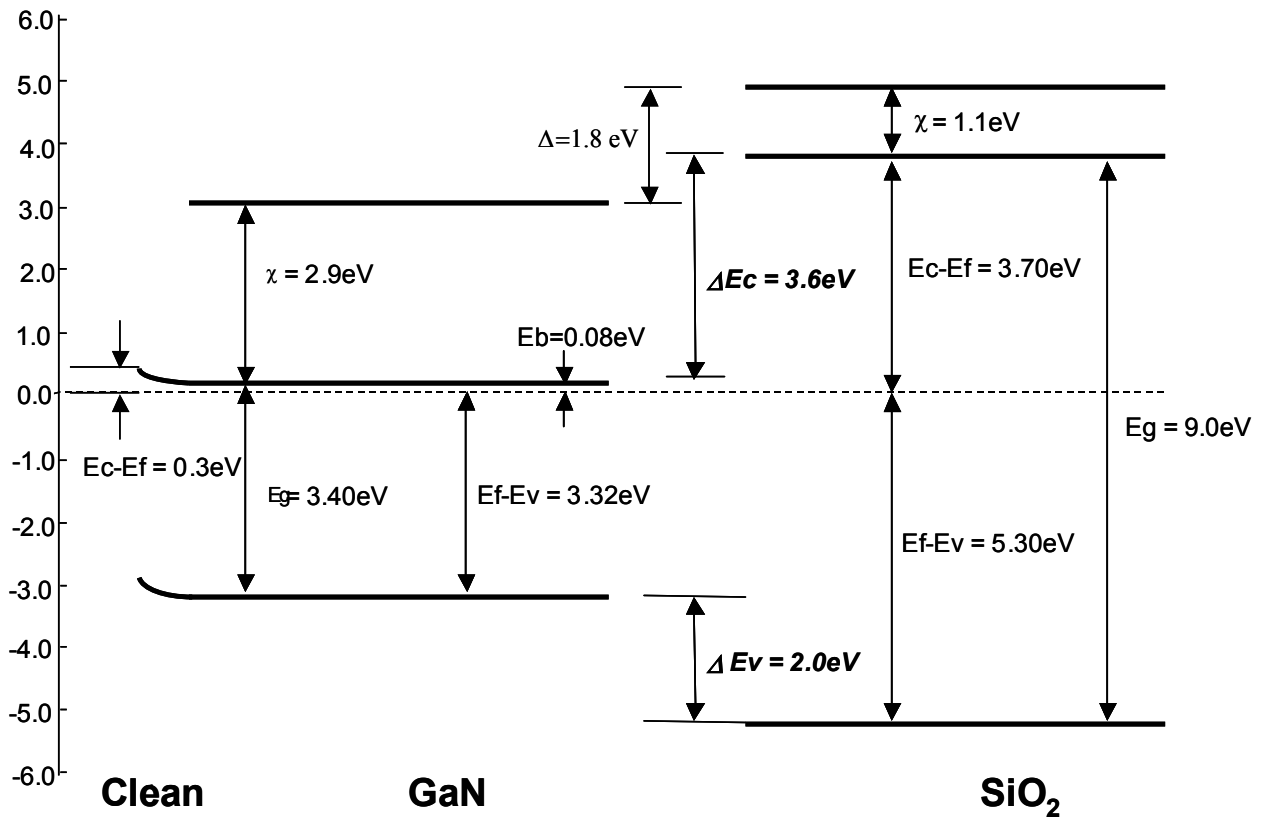


Figure 3.9 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and SiO₂. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented.

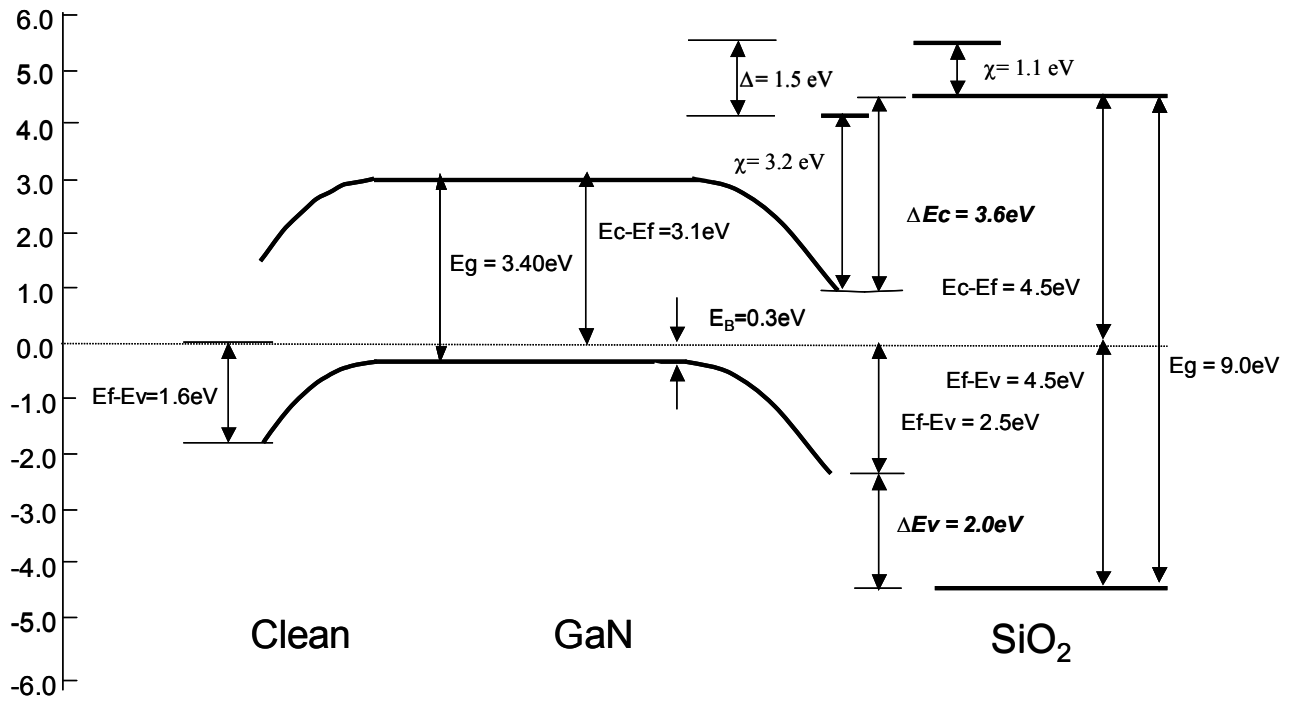


Figure 3.10 Deduced bands for the clean p-type GaN surface (left) and the interface between p-type GaN and SiO₂. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented.

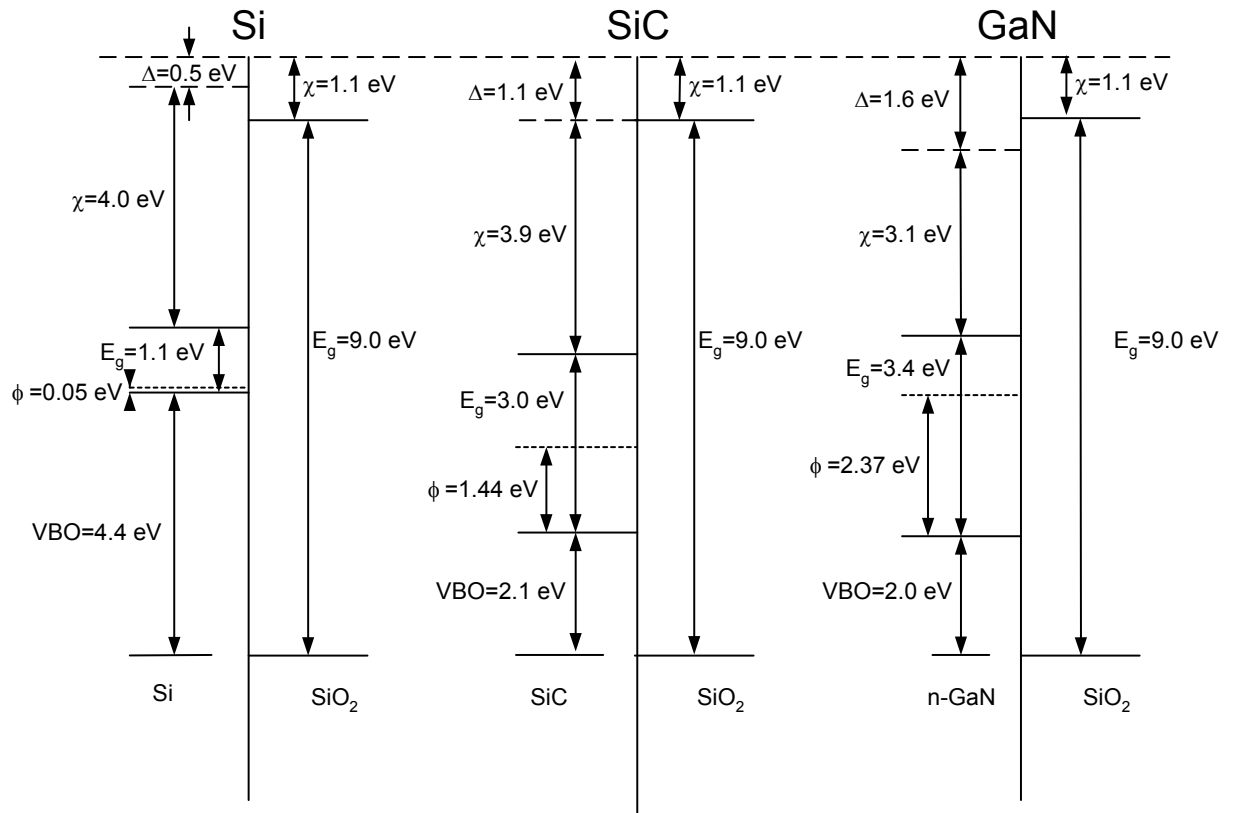


Figure 3.11 Band alignment of Si/SiO₂, SiC/SiO₂, and GaN/SiO₂ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the SiO₂ surface, which is common in all three interfaces. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap. The VBO are determined from the measurements.

4. Band Offset measurements of the $\text{Si}_3\text{N}_4/\text{GaN}$ (0001) interface

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4.1 Abstract

X-ray photoelectron spectroscopy (XPS) and UV photoelectron spectroscopy (UPS) were used to measure the electronic states as Si_3N_4 was deposited on clean GaN (0001) surfaces. The n-type (2×10^{18}) and p-type (1×10^{17}) GaN surfaces were atomically cleaned in NH_3 at 860°C , and the n- and p-type surfaces showed upward band bending of $\sim 0.2 \pm 0.1$ eV and downward band bending of 1.1 ± 0.1 eV, respectively, both with an electron affinity of 3.1 ± 0.1 eV. Layers of Si (~ 0.2 nm) were deposited on the clean GaN and nitrided using an electron cyclotron resonance (ECR) N_2 plasma at 300°C and subsequently annealed at 650°C for densification into a Si_3N_4 film. Surface analysis was performed after each step in the process, and yielded a valence band offset (VBO) of 0.5 ± 0.1 eV. Both interfaces exhibited type II band alignment where the valence band maximum of the GaN lies below that of Si_3N_4 valence band. The deduced conduction band offset (CBO) is found to be 2.4 ± 0.1 eV, and a change of the interface dipole of 1.1 ± 0.1 eV was observed for the $\text{Si}_3\text{N}_4/\text{GaN}$ interface formation.

4.2 Introduction

Gallium nitride has been established as a material of choice for high frequency electronic and optoelectronic applications. In the fabrication of devices based on heterostructures, the interfacial band alignment is of significant interest. Investigation of heterojunction band discontinuities is important for device design because the valence and conduction band offsets determine the transport and confinement properties at the interface. A fundamental objective for technology and basic research would be the control of the band discontinuities.¹ The use of Si₃N₄ as a passivation layer on GaN-based high voltage devices and as a gate insulator in field effect transistor (FET) devices are potential applications that require knowledge of the band alignment of this interface.

Recent studies of the electrical properties of the Si₃N₄/GaN interface by Arulkumaran *et al*² and Nakasaki *et al*³ have reported interface trap densities of $6.5 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ and $5.0 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ with clear deep depletion behavior. Chang *et al*⁴ found that silicon nitride passivation enhances light output and increases the reliability of GaN-based light emitting diodes by reducing the leakage current. Electrical data in the literature indicates the promise of advanced GaN metal-insulator-semiconductor (MIS) devices.²⁻⁴ While several groups have employed photoemission techniques to study GaN/metal interfaces,⁵⁻⁷ only Nakasaki *et al*³ report band offsets for GaN/Si₃N₄ interfaces. They report type I band alignment with a valence band offset of 1.0-1.2 eV for the Si₃N₄/GaN(0001) interface.

Application of the electron affinity model (EAM) is a first approach to characterizing the electronic properties of a heterostructure. This model holds in the case when there is no change in the potential at each surface as the interface is formed. An

alternative approach is the interface dipole model, where the structure of the interface causes a shift in the entire band lineup relative to the predictions of the EAM.

The main focus of our experiment is to measure the band offsets and to explore the interface dipole at the heterostructure interface. The combination of XPS and UPS measurements is a well-established method of determining band discontinuities at heterojunction interfaces.^{8,9} Our basic approach in this study is to obtain clean GaN surfaces through an ammonia exposure at elevated temperatures and to form an Si₃N₄ layer by depositing silicon on the clean surface followed by a low temperature ECR plasma nitridation. The XPS and UPS measurements are obtained after each step in the process, yielding the band bending from the shifts in the gallium 3d and 3p core levels. The band offsets and electron affinities are deduced from the UPS spectra, and the contribution of the interface dipole is determined from the XPS and UPS measurements.

4.3 Experimental Procedures

The GaN films used in this study were grown via metallorganic vapor phase epitaxy (MOVPE) on 50 mm diameter on-axis 6H (0001) substrates with a conducting AlN (0001) buffer layer. The thickness of the GaN epilayer and the AlN buffer were 1.1 μ m and 0.1 μ m, respectively. Silicon was used as the n-dopant, and magnesium was used as the p-dopant. Dopant concentrations (N_d-N_a) of $1 \times 10^{17} \text{ cm}^{-3}$ and (N_a-N_d) of $2 \times 10^{18} \text{ cm}^{-3}$ were measured for the n-type and p-type samples using capacitance-voltage measurements with a mercury probe.

Ex situ surface preparation consisted of a series of three sequential dips of 1 minute in trichloroethylene, acetone, and methanol, followed by an immersion in 49%

HCl for 10 minutes. The samples were then placed in the load lock for entry into the transfer line that interconnects several analysis and processing chambers. After the initial surface analysis, the sample was moved to the gas source molecular beam epitaxy chamber (GSMBE) for *in situ* cleaning. The *in situ* cleaning process consisted of annealing at 860°C for 15 minutes in an NH₃ atmosphere, where the details have been previously reported.^{5,10,11}

After cleaning and other process steps, the samples were transferred in UHV to the surface analysis chambers. For XPS, a dual anode source was used to generate magnesium (1253.6 eV) or aluminum (1486.6 eV) X-rays. The resolution of the analyzer was determined from the full width half maximum (FWHM) of a gold 4f_{7/2} spectral peak to be approximately 1.0 eV; however through curve fitting, spectral peak positions could be resolved to ±0.1 eV.

UPS with He I (21.2 eV) radiation was employed to measure the electronic states near the valence band and to determine the electron affinity. A negative 4 V bias was applied to the sample to overcome the work function of the analyzer.

To form the silicon nitride layer, silicon was deposited via molecular beam epitaxy (MBE), and nitrided by an electron cyclotron resonance (ECR) N₂ plasma. The plasma conditions were 300 W of microwave power for 30 seconds, pressure of 7.5x10⁻⁴ Torr, and a sample temperature of 300°C.

The XPS and UPS spectra were measured to obtain information about the core levels and valence band after each of the following steps: 4Å Si deposition, N₂ plasma of the Si layer at 300°C, a 2Å Si deposition (6Å total) and N₂ plasma at 300°C, 650°C anneal for 15 minutes, a final 3Å Si deposition (9Å total) and N₂ plasma at 300°C, and a

15 minute 650°C final anneal. XPS allows chemical bonding and band bending to be discerned by following the relative peak position shift during the evolution of the experiment. Valence band information, as well as the electron affinity of each material, are determined from the UPS spectra. A combination of XPS and UPS provides information about the band discontinuities at the interface, as well as allows an observation of a change in the interfacial dipole.

4.4 Results

The evolution of the UPS spectra from the clean GaN through nitridation and final anneal of the deposited 9Å Si for the n-type experiment is shown in Figure 1. The valence band maximum (VBM) of the clean GaN surface was determined from an extrapolation of a line fit to the leading edge of the spectrum. The VBM of the GaN and the Si₃N₄ signal were measured at 3.1 ± 0.1 eV and 2.3 ± 0.1 eV (referenced to the Fermi level), respectively. Because the deposited layers obscure the VBM, it is necessary to detect a more intense bulk GaN spectral feature to reference the position of the VBM. A feature at 13.4 eV in the spectra shown in Figure 1 has been attributed to a GaN bulk excitation.¹² This feature shifts to a lower binding energy by 0.2 ± 0.1 eV with the deposition of 4Å of Si and the nitridation that followed, and is ascribed to an increase of the band bending by 0.2 eV. Following the peak movement is only possible when the substrate emission is observable, therefore when the layer thickness obscures this emission, further information about band bending cannot be obtained. In our UPS measurements, emission from the substrate was not detected for the final 3Å (9Å total)

silicon deposition and nitridation. With increased thickness, the valence band turn-on and signature peaks for Si₃N₄ remained unchanged.

The valence band turn-on was measured to be 1.4 ± 0.1 eV for the p-type GaN material. From the doping concentration of 2×10^{18} in the p-type GaN, the bulk Fermi level was determined to be ~ 300 meV above the valence band maximum. This indicates significant downward band bending of 1.1 eV for the clean p-type GaN surface.

The electron affinity can be obtained from the UPS by determining the width of the spectra, using the relation:

$$\chi = h\nu - W - E_g \quad (4.1)$$

where W is the spectral width from the VBM to the low energy cut-off, $h\nu$ is the photon energy (21.2 eV), and E_g is the bandgap of the material. Using 3.4 eV as the bandgap, the electron affinity was determined to be 3.1 ± 0.1 eV for both the n- and p-type GaN. As a verification that our measured turn-on is indeed the VBM, we note that our results indicate that the Ga 3d is 17.7 eV below the VBM, which is consistent with Waldrop and Grant.¹³

The same approach is used to determine the electron affinity of the Si₃N₄ layer. Though the bandgap of Si₃N₄ has a range of reported values,^{14,15} we will use the value of 5.3 eV and consequently obtain an electron affinity of 1.8 ± 0.1 eV. While this value is similar to prior reports^{16,17} of 2.1 eV, the uncertainty of the bandgap of the material, as well as the ± 0.1 eV measurement uncertainty can account for the 0.3 eV deviation.

The evolution of the gallium 3d peak during the n-type GaN experiment is shown in Figure 3. The initial peak position for the clean surface was determined to be

20.63 ± 0.1 eV. Spectra observed after the Si deposition showed shifts that were smaller than 0.1 eV. For the final surface, which consisted of an accumulated 9 Å of Si, which was nitrided, the peak was observed at 20.43 ± 0.1 eV, indicating a shift of 0.2 ± 0.1 eV for the entire experiment. This shift is consistent with the movement of the bulk peak located at ~ 13.4 eV in the UPS spectra shown in Figure 1.

Figure 4 represents the evolution of the gallium 3p and silicon 2p core levels during the n-type experiment. The Ga 3p core levels are consistent with the Ga 3d core levels, shifting to a lower binding energy by 0.2 eV during the course of the experiment. This shift to a lower binding energy is ascribed to an increase in the band bending by 0.2 eV during interface formation. The Si 2p peak position after the initial deposition of Si is found to be 100.03 ± 0.1 eV. After nitridation, this core level shifts to a peak position of 102.44 ± 0.1 eV, remaining essentially constant throughout the remainder of the experiment. This large 2.44 eV shift of the Si 2p core level is indicative of a chemical shift due to the Si-N bonding, and is consistent with reported values for Si_3N_4 .^{18,19} In an additional approach to explore the composition of our films, we measured the energy difference between the N 1s and Si 2p core levels. For the thin films in this study the N 1s core level was obtained, but the Si-N peak was not resolvable due to the dominance of the nearby Ga-N peak. We prepared thicker films of Si_3N_4 on GaN using the same techniques, as well as thin films on silicon. In both cases, the energy difference between the N 1s and Si 2p core levels was found to be 295.65 ± 0.1 eV. Literature values for this difference are found to be 295.7 eV for Si_3N_4 films, while for SiN_x ($x < 1.33$) films a value of 295.4 eV is observed.¹⁹⁻²¹ Moreover, analysis of the integrated areas for the N 1s

and Si 2p core level peak yielded a N/Si ratio of 1.32 ± 0.01 . These results are consistent with the formation of stoichiometric Si_3N_4 .

The evolution of the gallium 3d peak for the p-type GaN experiment was also measured. The initial peak position for the clean surface was observed at 18.88 ± 0.1 eV. After the 4 Å Si deposition and nitridation, the peak shifted to a value of 19.38 ± 0.1 eV, a difference of ~ 0.5 eV. After each process with a 650 °C, the Ga 3d core level shifted from the value of the as deposited film by an additional ~ 0.2 eV, as evidenced by the peak positions of the Si_3N_4 formed from 6 Å total Si and plasma/650 °C anneal and the 9 Å total Si and plasma/650 °C anneal treatments shown at 19.61 ± 0.1 eV and 19.58 ± 0.1 eV, respectively. The purpose of the anneal is to allow reconstruction and densification of the nitride film after deposition, therefore, improving the quality of the film for device fabrication.^{22,23} During the course of the experiment we observed a shift in the Ga 3d peak of 0.70 ± 0.1 eV. This shift is consistent with the gallium 3p core level, suggesting that the change in the core level is due to a change in the band bending.

4.5 Discussion

The method used for determining the valence band offset is similar to that of Waldrop and Grant and Kraut *et al.*²⁴ Their basic approach is to reference the VBM to a core level in the XPS spectra for each semiconductor and to use the measured difference between the core level energies to discern the band discontinuities. In our study, we use UPS to measure the energy of the VBM relative to the Fermi level, and XPS is used to obtain band bending information by measuring the shift in the core level energies relative

to the Fermi level. A combination of these two photoemission techniques provides the band alignment at the heterojunction interface.

Figure 5 shows the proposed band lineups for the n-type GaN/Si₃N₄ interface. The VBO determination is the measured UPS turn-on for GaN (3.1 eV), minus the Si₃N₄ turn-on (2.3 eV), minus the band bending (0.2 eV). This value, along with knowledge of the bandgap of the material, allows the CBO to be deduced. The VBO is found to be type II band alignment, where the valence band of the Si₃N₄ is 0.6 ± 0.1 eV above the GaN VBM, and the CBO is 2.5 eV. Figure 6 shows the proposed band lineups for the p-type GaN/Si₃N₄ interface. The UPS turn-on for the clean GaN and the Si₃N₄ was observed at 1.4 eV and 2.2 eV, respectively. XPS spectra showed downward band bending of ~ 0.8 eV during formation of the interface. The VBO is again found to be type II band alignment 0.4 ± 0.1 eV above the GaN VBM, and the CBO is 2.3 eV.

The measured electron affinities for GaN and Si₃N₄ are represented in Figures 5 and 6. The electron affinity model of heterojunction formation assumes that the vacuum levels would align at the interface. Our results show a deviation from the EAM of 1.2 eV and 1.0 eV for the n-type GaN and p-type GaN substrates, respectively. The EAM model is based on the premise that the interface is formed without disruption of the surface electronic states of either of the two materials. The measured difference between the prediction of the EAM and the experimentally observed band offset represents a change in the interface dipole.

As an alternative to the electron affinity model, it may be considered that the heterojunction band offsets are determined by alignment of the charge neutrality levels (CNL) of the two materials. The charge neutrality levels represent the branch point of the

surface (or interface) states as they are related to the valence or conduction band. Charge can transfer between the interface states of the two materials, which will cause an interface dipole. The band offset will be determined by the relative position of the CNL of the two materials if the density of states is high or if the CNL of the two semiconductors are similar in relative energy.

Robertson¹⁶ adapted the Schottky barrier interface defect model presented by Cowley and Sze²⁵ to employ the CNL as the pinning levels at a heterojunction interface. This model was used to analyze silicon/oxide interfaces, and the model seems consistent with most experimental results. This model is given by the relation:

$$\varphi_{CBO} = (\varphi_{CNL,a} - \varphi_{CNL,b}) - (E_{g,a} - E_{g,b}) + S\{(\chi_a - \chi_b) + (E_{g,a} - E_{g,b}) - (\varphi_{CNL,a} - \varphi_{CNL,b})\} \quad (4.2)$$

Where φ_{CBO} is the CBO, χ and φ_{CNL} are the electron affinities and charge neutrality levels for each semiconductor (a and b), and S is a pinning factor based on the dielectric properties of the materials. Here, the φ_{CNL} are defined relative to the VBM of each semiconductor. A value of $S=1$ represents the EAM while a value of 0 represents pinning at the CNL levels. To our knowledge, the CNL of Si_3N_4 has not been reported. Using the value of S for the Si_3N_4 -Si interface (0.51) and the measured band offset from previous work,^{16, 23} we can deduce the CNL of Si_3N_4 to be 1.5eV above the valence band maximum. While more research is necessary to assign a CNL value for Si_3N_4 , it is reasonable to consider this prediction of the valence band offset for comparison to our experimental results. Monch²⁶ has reported the CNL of GaN to be 2.37 eV above the valence band maximum. Though the dielectric screening parameter S has not been determined for the GaN/ Si_3N_4 interface, in the limits of $S=0$ and $S=1$ the valence band types and offsets would be type II 0.9 eV and type I 0.9eV, respectively. If the

assumption is made that the parameter S is similar to that for the Si/Si₃N₄ interface (0.51), the CNL relation given in Eq. 2 predicts the valence band offset to be ~ 0.1 eV (essentially no offset) for the GaN/Si₃N₄ interface. Conversely, the dielectric screening parameter can be deduced for the interface using our results and the CNL of GaN and Si₃N₄. A value of $S=0.26$ is obtained for the GaN/Si₃N₄ interface.

This prediction, as well as our results, are significantly different from the results by Nakasaki *et al.*,³ who report type I band alignment with an offset of 1.0-1.2 eV for the GaN/Si₃N₄ interface. A factor that could play a major role in this difference is the cleaning method used for the GaN. Their studies used an NH₄OH etch and a combination of H₂ and N₂ plasmas for *in situ* surface preparation. While the oxygen content was greatly reduced from the as-loaded case, a significant amount remained after surface preparation, suggesting Ga-O bonding.³ In a previous study¹⁰, the GaN/SiO₂ interface was examined via photoemission, showing a type I alignment and a VBO ~ 2 eV. We suggested that Ga-O bonding exists at the GaN/SiO₂ interface and contributes to the large offset and interfacial dipole change. Our study begins with a clean GaN surface (contamination levels of $<1\%$ for oxygen and carbon) that allows the GaN/Si₃N₄ interface to be measured more precisely.

In an attempt to understand the relation of our measured band alignment and the different models for heterostructure band alignment, in Figure 7 we have compared our measured interface alignments to experimental results for Si₃N₄ on Si.^{16,22,23} In both cases the diagrams are aligned to the vacuum level at the Si₃N₄, which has been measured to be at the same energy relative to the silicon nitride bands. The bandgap of each material is indicated, as is the VBO. The position of the vacuum level of the clean

semiconductor surface is indicated, and the difference between these values and the surface vacuum level is the deviation from the EAM. This difference represents the change in the interface dipole, and was found to be 0.5 and 1.2 eV for Si₃N₄ on Si and GaN, respectively.

Also indicated in Figure 7 is the CNL of the semiconductors.^{16,26} Additionally, the predicted CNL of Si₃N₄ (1.5 eV) deduced as described above is also represented. We observe that the CNL's nearly align for the GaN/Si₃N₄ interface, suggesting the correlation of this interface with the CNL model with a low dielectric screening parameter S . The progression of the interface dipole deduced from the deviation from the EAM is most likely related to the changes at the semiconductor surface since the silicon nitride is the same in both cases. For the Si/Si₃N₄ interface, the Si surface reconstruction is expected to change during the formation of the nitride layer. This effect alone could account for the small change in the interface dipole, and the same could be true for the GaN/Si₃N₄ interface. For GaN/Si₃N₄, we expect Ga-N-Si bonding to exist within the first few monolayers at the heterojunction interface. Because of the similarity in bonding at the interface we may expect a smaller interface dipole than that of the GaN/SiO₂ interface. Indeed, this is the case where we find an 1.1 ± 0.1 eV interface dipole for GaN/Si₃N₄ and a 1.7 ± 0.1 eV for the GaN/SiO₂ interface.

4.6 Conclusions

The surface and interface properties of n- and p-type GaN/Si₃N₄ were systematically investigated by photoemission techniques and band alignment information was obtained. Annealing in ammonia at 860°C provided clean stoichiometric GaN

surfaces with ~ 0.2 eV upward band bending and ~ 1.1 eV downward band bending for the n-type and p-type surfaces, both with an electron affinity of 3.1 eV. For GaN/Si₃N₄, type II band alignment was observed and valence band offsets were measured to be ~ 0.5 eV for both the n-type and p-type cases. The interface dipole deduced from comparison with the electron affinity model was 1.1 ± 0.1 eV. The charge neutrality model provided a reasonable description of the band alignment of the GaN/Si₃N₄ interface. It is suggested that the presence of oxygen at the interface could substantially change the band offsets. These results indicate that Si₃N₄ should passivate n-type surfaces, but may not be appropriate for passivation of p-type surfaces.

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FIGURE CAPTIONS

Figure 4.1 UPS Spectra of the valence band maximum of: a) CVC clean n-GaN, b) 4Å Si, c) 4Å Si and N₂ plasma, d) 6Å Si and N₂ plasma, e) 6Å Si, N₂ plasma and 650°C anneal, f) 9Å Si and N₂ plasma, g) 650°C anneal.

Figure 4.2 UPS spectra of the valence band maximum of CVC clean n-type GaN and the Si₃N₄ final surface, with the valence band maximum indicated by dashed lines.

Figure 4.3 XPS Ga 3d core level spectra of : a) CVC clean n-GaN, b) 4Å Si, c) 4Å Si and N₂ plasma, d) 6Å Si and N₂ plasma, e) 6Å Si, N₂ plasma and 650°C anneal, f) 9Å Si and N₂ plasma, g) 650°C anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

Figure 4.4 XPS Ga 3p and Si 2p core level spectra of : a) CVC clean n-GaN, b) 4Å Si, c) 4Å Si and N₂ plasma, d) 6Å Si and N₂ plasma, e) 6Å Si, N₂ plasma and 650°C anneal, f) 9Å Si and N₂ plasma, g) 650°C anneal. The peak position of the Si 2p core level after silicon deposition, as well as the final surface are indicated with dashed lines.

Figure 4.5 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and SiO₂. The valence band offset, E_v , conduction band offset, E_c , band bending, and interface dipole, Δ , are represented.

Figure 4.6 Deduced bands for the clean p-type GaN surface (left) and the interface between p-type GaN and SiO₂. The valence band offset, E_v , conduction band offset, E_c , band bending, and interface dipole, Δ , are represented.

Figure 4.7 Band alignment of Si/Si₃N₄ and GaN/Si₃N₄ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the Si₃N₄ surface, which is common in both interfaces. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap. The VBO are determined from the measurements.

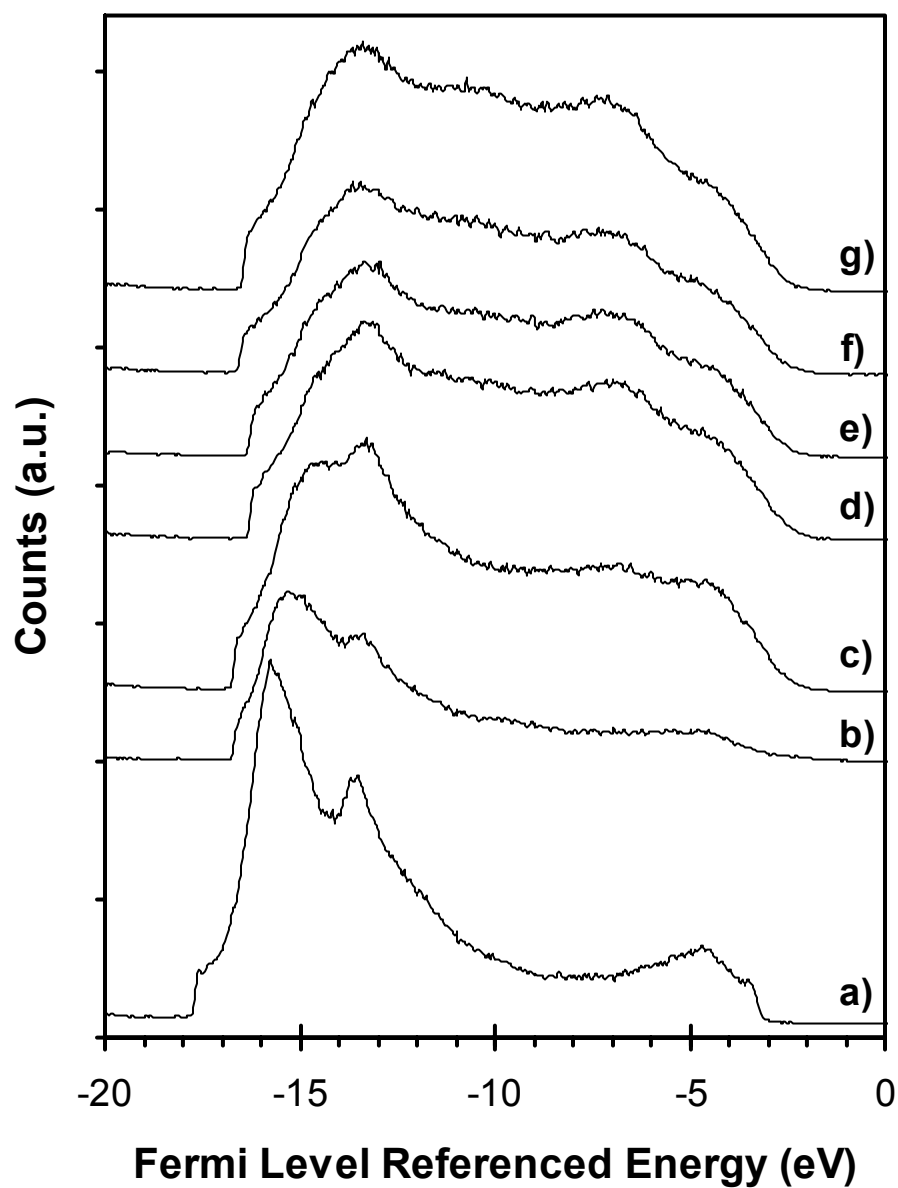


Figure 4.1 UPS Spectra of the valence band maximum of: a) CVC clean n-GaN, b) 4Å Si, c) 4Å Si and N₂ plasma, d) 6Å Si and N₂ plasma, e) 6Å Si, N₂ plasma and 650°C anneal, f) 9Å Si and N₂ plasma, g) 650°C anneal.

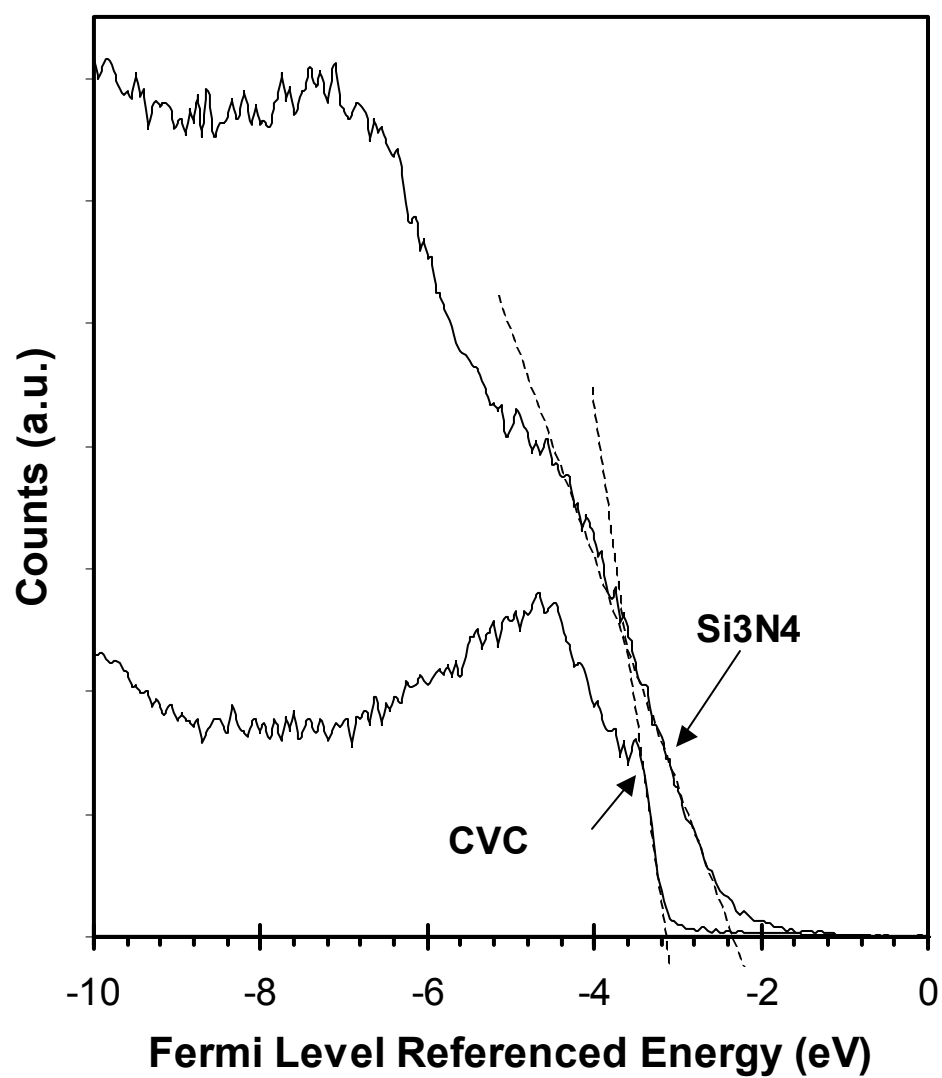


Figure 4.2 UPS spectra of the Valence Band turn-on of clean GaN and the Si₃N₄ final surface

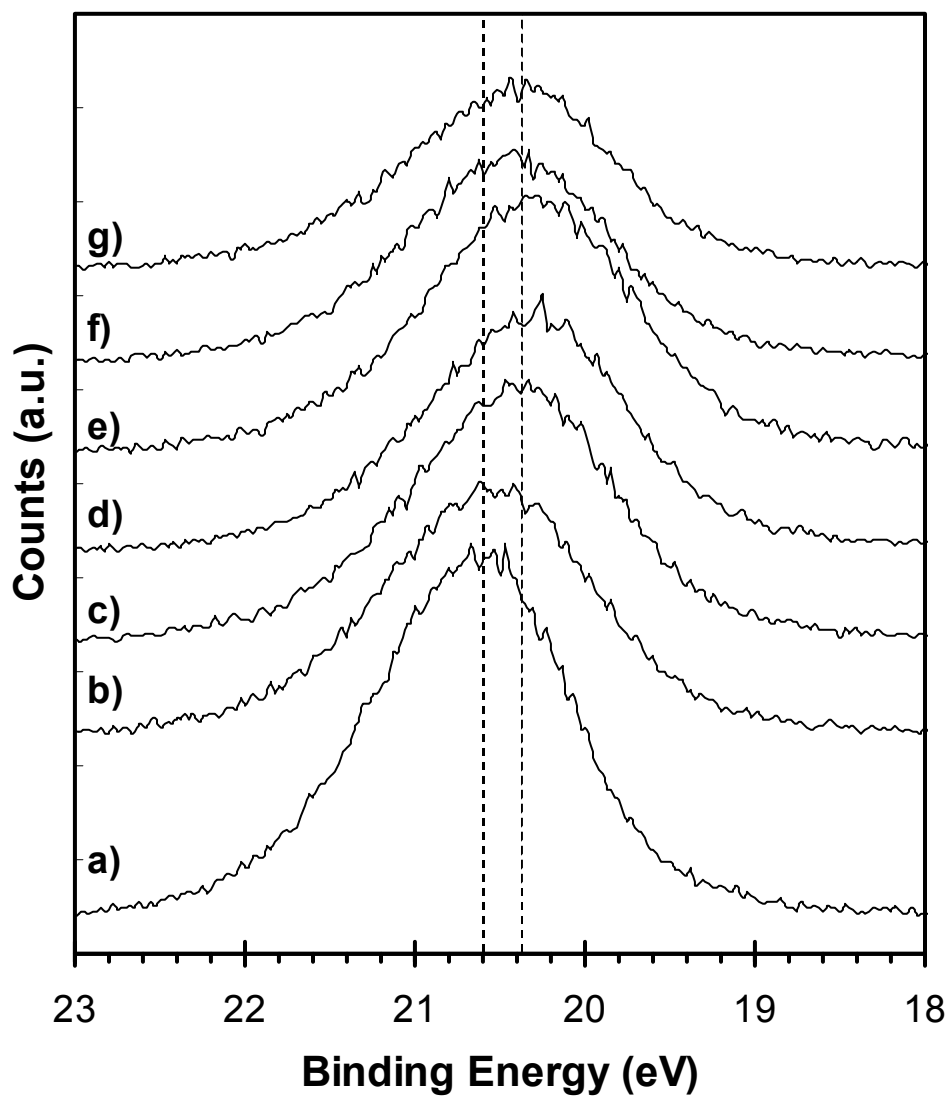


Figure 4.3 XPS Ga 3d core level spectra of : a) CVC clean n-GaN, b) 4 Å Si, c) 4 Å Si and N₂ plasma, d) 6 Å Si and N₂ plasma, e) 6 Å Si, N₂ plasma and 650°C anneal, f) 9 Å Si and N₂ plasma, g) 650°C anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

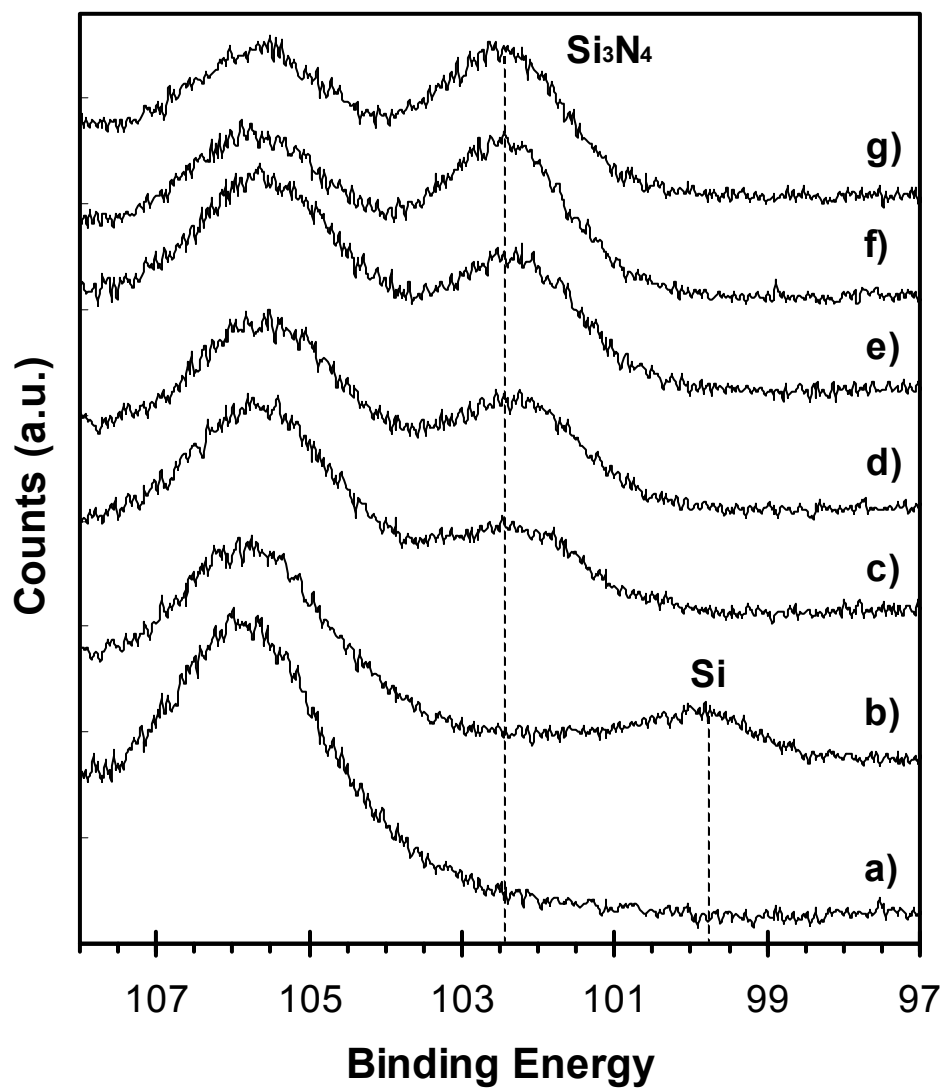


Figure 4.4 XPS Ga 3p and Si 2p core level spectra of : a) CVC clean n-GaN, b) 4 Å Si, c) 4 Å Si and N₂ plasma, d) 6 Å Si and N₂ plasma, e) 6 Å Si, N₂ plasma and 650°C anneal, f) 9 Å Si and N₂ plasma, g) 650°C anneal. The peak position of the Si 2p core level after silicon deposition, as well as the final surface are indicated with dashed lines.

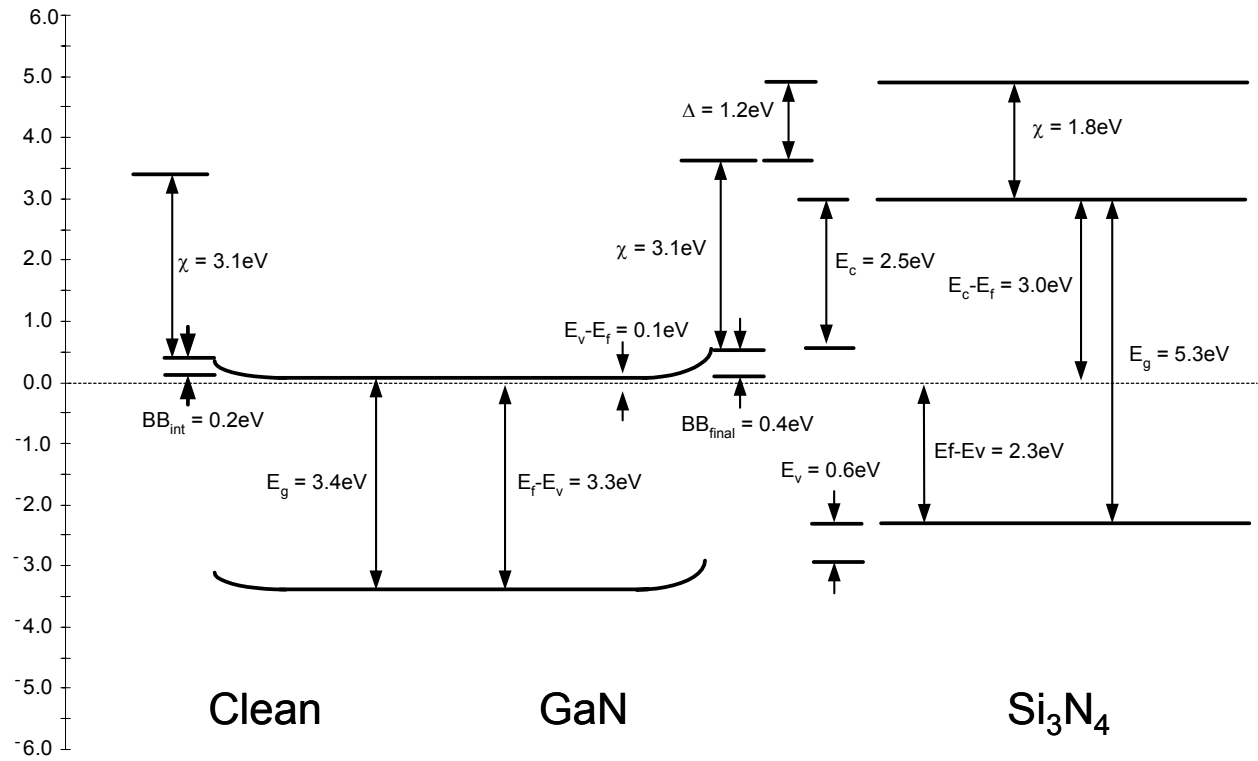


Figure 4.5 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and SiO₂. The valence band offset, E_v , conduction band offset, E_c , band bending, and interface dipole, Δ , are represented.

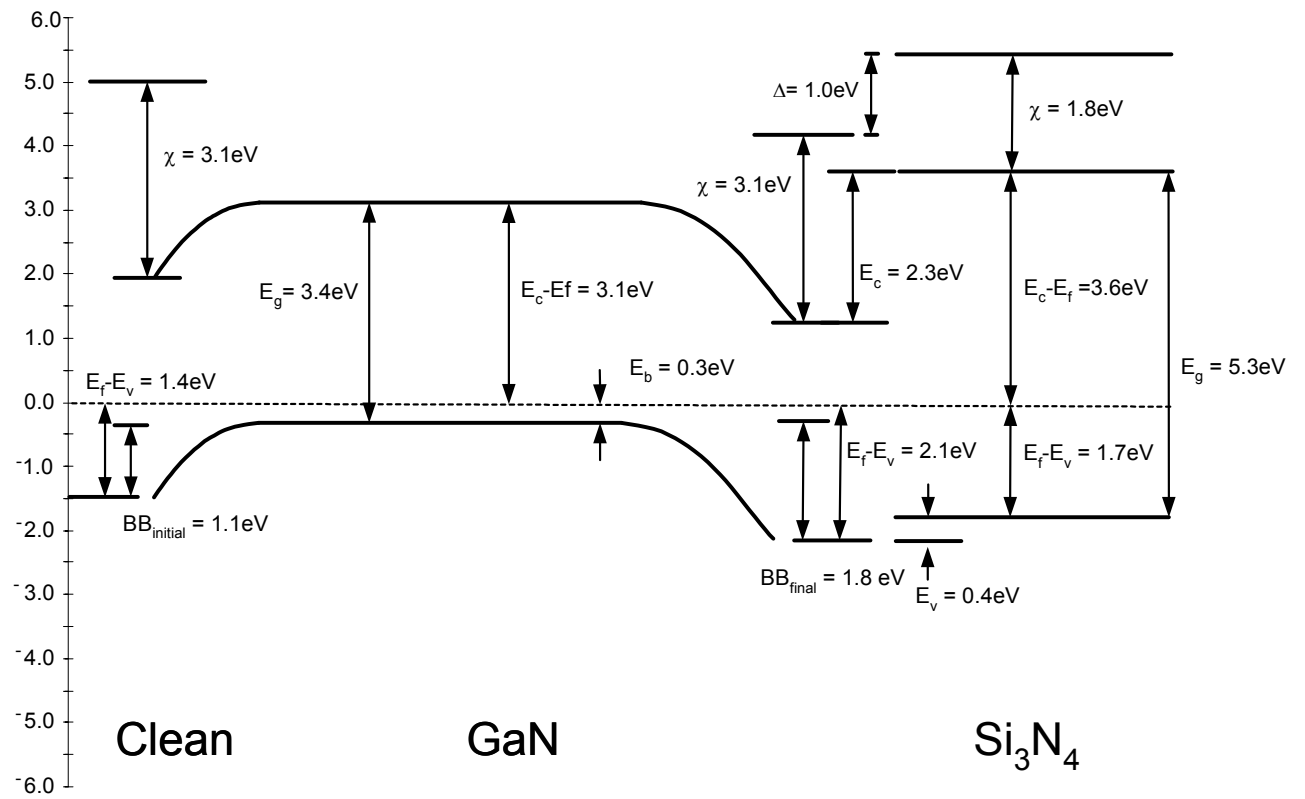


Figure 4.6 Deduced bands for the clean p-type GaN surface (left) and the interface between p-type GaN and SiO₂. The valence band offset, E_v , conduction band offset, E_c , band bending, and interface dipole, Δ , are represented.

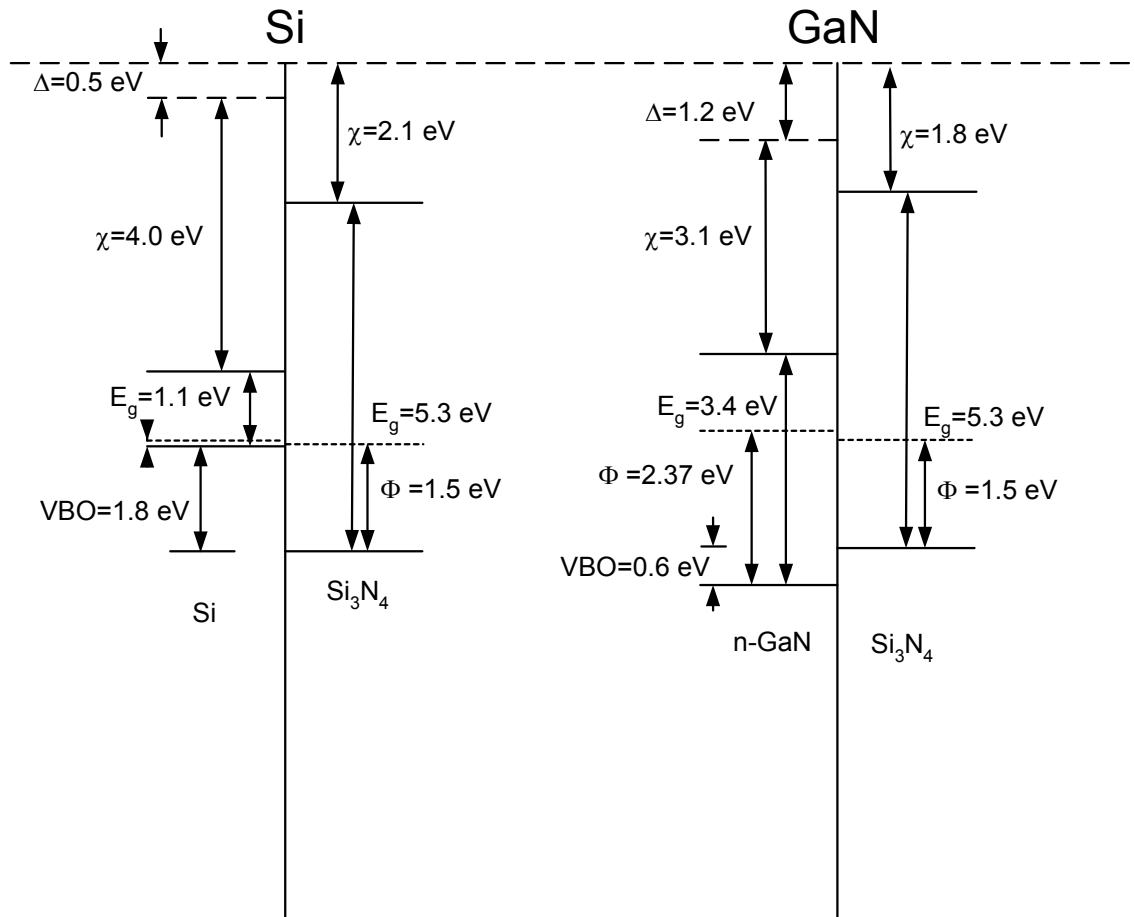


Figure 4.7 Band alignment of Si/Si₃N₄ and GaN/Si₃N₄ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the Si₃N₄ surface, which is common in both interfaces. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap. The VBO are determined from the measurements.

5. Band Offset measurements of the n-type GaN(0001)/HfO₂ interface

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5.1 *Abstract*

In this study, X-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) have been used to observe the interface electronic states as HfO_2 was deposited on clean Ga face GaN (0001) surfaces. The substrates were metallorganic chemical vapor deposition (MOCVD) grown n-type (1×10^{17}) GaN on 6H-SiC (0001) with an AlN (0001) buffer layer. The GaN surfaces were atomically cleaned via an 860°C anneal in a NH_3 atmosphere. For the GaN surface, upward band bending and electron affinity were measured to be 0.3 ± 0.1 eV and 3.0 ± 0.1 eV, respectively. In an attempt to limit oxidation of the GaN, a thin layer (0.4 nm) of Hf was deposited on the clean GaN surface via UHV e-beam deposition, and the Hf was oxidized at 300 °C by a remote plasma. The substrates were annealed at 650 °C for densification of the HfO_2 films. Photoemission techniques were performed after each step in the process, and yielded a valence band offset (VBO) of 0.4 eV and a conduction band offset (CBO) of 2.0 eV for the final annealed GaN- HfO_2 interface. An interface dipole of 1.9 eV was deduced for the GaN- HfO_2 interface. Annealing the HfO_2 film revealed thermodynamic instability that caused the band offsets to shift by ~ 0.5 eV.

5.2 Introduction

Gallium nitride is being investigated for a wide range of electronic and optoelectronic applications. The band alignment for GaN-dielectric systems is of significant interest, as it defines carrier confinement or transport at the interface. A fundamental objective for technology and basic research would be the control of the band discontinuities.¹ The use of HfO₂ and other high- κ dielectrics as a passivation layer on GaN-based high voltage devices and as a gate insulator in field effect transistor (FET) devices are potential applications that require knowledge of the band alignment of this interface. Although insufficient thermodynamic data exists for high- κ dielectrics (HfO₂, ZrO₂), ZrO₂ has been projected to be stable when in contact with underlying films.² Because the Gibbs energy of formation for HfO₂ is more negative than ZrO₂ (-1088 kJ/mol vs. -1040 kJ/mol), HfO₂ could be stable as well.³

Surface preparation is a critical step to controlled heterostructure formation. In prior studies Bermudez⁴ compared GaN surfaces prepared by sputtering with nitrogen ions followed by annealing in ultrahigh vacuum (UHV) and surfaces prepared by *in situ* deposition of Ga metal followed by thermal desorption. For the two processes, no significant differences of the values of work function, band bending and Ga 3d binding energy were found, which suggests that nitrogen-ion sputtering and annealing are equivalent for preparation of ordered GaN surfaces. However, surfaces prepared by these methods show additional emission at energies above the valence band maximum (VBM) in photoemission data that has been attributed to surface states. In our study, GaN is prepared by an *in situ* ammonia exposure at an elevated temperature,⁵ producing atomically clean surfaces without observable emission above the VB turn-on.

The exploration of HfO₂ dielectric films began in the 1970's for optical coatings and DRAM applications. Balog *et al*⁶ performed C-V measurements on CVD grown HfO₂ films on Si (100) and found no observable hysteresis and a minimum interface state density of $\sim 1-6 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$. Additionally, the dielectric constant was measured to be $\kappa=22-25$ at 1 MHz, with a breakdown field of $\sim 4 \text{ MV/cm}$. Lee *et al*⁷ found leakage currents $< 3 \times 10^{-2} \text{ A/cm}^2$ at -1.5 V for HfO₂ films on Si (100) with a capacitance equivalent oxide thickness of $\sim 10 \text{ \AA}$. Kirsch *et al*⁸ investigated the effect of a nitride layer at the HfO₂/Si interface. At 1 V, leakage currents of 4×10^{-5} and $4 \times 10^{-3} \text{ A/cm}^2$ were measured for $\sim 50 \text{ \AA}$ HfO₂ capacitors fabricated with and without SiN_x, respectively. Properties such as high dielectric constant, low leakage current, and relatively low interface density suggest the promise of HfO₂ in electronic device fabrication. While several studies⁹⁻¹⁴ have employed photoemission techniques to explore Si-HfO₂ interfaces, there has been, to our knowledge, no similar report for the GaN-HfO₂ interface.

A first approach to describing a heterostructure interface is to apply the electron affinity model (EAM). This model holds in the ideal case, assuming there is no potential created as the heterostructure is formed. The alternative model is the interface dipole model, where the structure of the interface causes a shift in the entire band lineup relative to the predictions of the EAM. The focus of our experiment is to measure the band offsets and to compare the results to this dipole at the heterostructure interface.

The charge neutrality level (CNL) model has been used to describe the band alignment of a heterojunction interface between two semiconductors. Tersoff¹⁵ suggested that the band alignment between two semiconductors is controlled by the charge transfer

across the interface and the resulting interface dipoles in a fashion similar to Schottky barrier models. Recently, Robertson¹⁶ employed the S parameter, which reflects the dielectric screening to relate the relative contribution of the electron affinity model and the dipole from the charge neutrality levels. This work presents a correlation between the CNL model and experimental data.

In this study, *in situ* XPS and UPS measurements are used to determine the band discontinuities, or band offsets, at the GaN-SiO₂ interface. This process is a well-established method that has been reported in the literature.¹⁷⁻¹⁹ After achieving an atomically clean GaN (0001) surface, care is taken to avoid oxidation during the process. Our basic approach is to obtain a clean GaN surface through an ammonia exposure at an elevated temperature and to form an HfO₂ layer by depositing hafnium and to employ low temperature oxidation to minimize disruption of the interface. XPS and UPS measurements are obtained after each step of the process, and the band bending is deduced from the shifts of the gallium and nitrogen core levels. The band offsets and electron affinities are determined from the UPS spectra, and the formation of the oxide and the value of the interfacial dipole are determined from the XPS and UPS measurements.

5.3 *Experimental Procedures*

The GaN films used in this study were grown via metallorganic chemical vapor deposition (MOCVD) on 50 mm diameter on-axis Si-face, 6H SiC (0001) substrates with a conducting AlN (0001) buffer layer. The thickness of the GaN epilayer and the AlN buffer were 1.1 μm and 0.1 μm , respectively. Prior research has established that MOCVD

growth of GaN on Si face SiC (0001) results in Ga face GaN (0001).^{20,21} Silicon was used as the n-dopant with a net ionized donor concentration ($N_d - N_a$) of $1 \times 10^{17} \text{ cm}^{-3}$ determined by mercury probe capacitance-voltage measurements.

Ex situ preparation of the GaN consisted of a process where the films were cleaned sequentially in trichloroethylene, acetone, and methanol baths for 1 minute each, followed by immersion into 49 % HCl for 10 minutes. The samples were then rinsed for 10 seconds in deionized water, and blown dry using nitrogen. The samples were mounted to molybdenum plates, secured by tantalum wires, and then placed in the load lock for entry into the transfer line that interconnects several analysis and processing chambers. The total time between the completion of *ex situ* cleaning and inserting into the system was about 10 minutes.

Initial surface analysis was performed, and the sample was moved to the gas source molecular beam epitaxy (GSMBE) for *in situ* cleaning. The cleaning process consists of annealing at 860 °C for 15 minutes in an NH₃ atmosphere. Ammonia was introduced into the chamber when the temperature reached 500 °C via a needle valve and a chamber pressure of 1×10^{-4} torr was obtained. After allowing 5 minutes for the pressure to stabilize, the heater was ramped to 860 °C at a rate of 30 °C per minute. The temperature and ammonia flow was maintained for 15 minutes. Subsequently, a ramp rate of -40 °C per minute was used to achieve a heater temperature of 500 °C; the sample was held at this temperature while the needle valve was closed. The pressure decreased to the low 10^{-8} torr range, during which the sample cooled to ~200 °C, and was transferred out of the system.

After cleaning and other process steps, the samples were transferred in UHV for surface analysis. For XPS, a dual anode source was used to generate magnesium (1253.6 eV) or aluminum (1486.6 eV) X-rays. The resolution of the analyzer was determined from the full width half maximum (FWHM) of a gold $4f_{7/2}$ spectral peak to be approximately 1.0 eV; however through curve fitting, spectral peak positions could be resolved to ± 0.1 eV.

UPS with He I (21.2 eV) radiation was employed to measure the electronic states near the valence band and to determine the electron affinity. The photoemitted electrons were analyzed with a VSW 50 mm mean radius hemispherical analyzer operated with a resolution of 0.1 eV. A negative 4 V bias was applied to the sample to overcome the work function of the analyzer.

The XPS and UPS spectra were obtained after each process step in a sequence of experiments to follow the shifts of the XPS peaks and the evolution of the valence band spectra. The spectra were measured to track the peak shifts and discern the band bending and band offsets after each of the following steps: a 4 Å Hf deposition, O₂ plasma at 300°C, 4 Å Hf (8 Å total Hf) and O₂ plasma at 300 °C, 650 °C anneal for 15 minutes, a final 4 Å Hf deposition (12 Å Hf total) and O₂ plasma at 300 °C, and a 15 minute 650 °C final anneal. Throughout the manuscript, the Hf thickness in the processing steps refers to the total amount of Hf deposited up to that particular step. For the 12 Å Hf total, the ultimate thickness of the HfO₂ film was calculated to be ~20 Å based on bulk densities. This thickness was measured experimentally to be ~20 Å by examining the XPS core level intensities for the clean and final process steps.

5.4 Results

The evolution of the UPS spectra from the clean GaN through the oxidation and anneal of the 12 Å Hf is shown in Figures 1 and 2. The VBM of the clean GaN surface was determined from an extrapolation of a line fit to the leading edge of the spectrum.¹² A turn-on of the GaN signal was measured to be at 3.0 ± 0.1 eV (referenced to the Fermi level). From the doping concentration of 1×10^{17} in the GaN, the bulk Fermi level was determined to be ~ 100 meV below the conduction band minimum. Because the deposited layers obscure the valence band maximum, in order to follow the position of the VBM, it is necessary to detect a more intense bulk GaN spectral feature to reference the position of the VBM. A feature at 13.4 eV in the spectra shown in Figure 1 has been attributed to a GaN bulk excitation.²² Note that this feature shifts to a lower binding energy by 0.6 ± 0.1 eV with the deposition of 4 Å of Hf and the oxidation that followed. After this step, the absolute peak position of the bulk feature cannot be reliably determined in the UPS spectra, so no further band bending information can be obtained by this method.

The spectra shown in Figure 1 were used to determine the electron affinity of GaN, as well as the deposited HfO₂. The electron affinity can be determined by the relation:

$$\chi = h\nu - W - E_g \quad (5.1)$$

where W is the spectral width from the VBM to the low energy cut-off, $h\nu$ is the photon energy (21.2 eV), and E_g is the bandgap of the material. As a verification that our measured turn-on is indeed the VBM, we note that our results indicate that the Ga 3d is 17.7 eV below the VBM, which is consistent with Waldrop and Grant.²³ For the clean

n-type GaN surface, the width of the spectrum was measured to be 14.8 eV. Using the generally accepted bandgap of GaN, 3.4 eV, the electron affinity was determined to be 3.0 eV, which is in agreement with prior reports.²⁴⁻²⁷

We employ the same approach to determine the electron affinity of the HfO₂ layer. The turn-on for the HfO₂ is observed at ~3.3 eV below the Fermi level, and the spectral width is measured to be 12.5 eV. Assuming a bandgap of 5.8 eV, we obtain an electron affinity of 2.9 eV, which is larger than the estimated value reported by Robertson.¹⁶

The evolution of the gallium 3d peak during the n-type GaN experiment is shown in Figure 3. The initial peak position and width of the peak for the clean surface was determined to be 20.6 ± 0.1 eV and 1.6 ± 0.1 eV, respectively. Spectra observed after the 4 Å Hf deposition showed a shift of 0.3 eV to lower binding energy. Oxidation of the Hf layer resulted in the core level shifting an additional 0.2 eV towards the Fermi level. After an anneal following the second 4 Å Hf deposition (8 Å total) and oxidation, the peak shifted to 20.7 ± 0.1 eV, with the width remaining relatively constant at 1.4 ± 0.1 eV. For the final surface, which consisted of a 12 Å Hf layer that was oxidized and annealed to 650 °C, the peak was observed at 20.7 ± 0.1 eV, indicating a shift of 0.1 ± 0.1 eV for the entire experiment. There are no indications of a reaction between the GaN and the HfO₂, therefore suggesting that this small shift is due to a change in the band bending.

Similar behavior was observed for the evolution of the nitrogen 1s core level. The N 1s peak position for the clean n-type GaN surface was observed at 398.0 ± 0.1 eV, and the width was measured to be 1.7 ± 0.1 eV. As in the case of the Ga 3d, the N 1s shifted a discernable amount after the first 4 Å Hf deposition and oxidation, to $397.3 \pm$

0.1 eV, with a width of 2.4 ± 0.1 eV. For the anneal of the second 4 Å Hf deposition (8 Å total) and oxidation, as well as the anneal of the final surface, the peak shifted to 397.9 ± 0.1 eV, with a width of 1.7 ± 0.1 eV. The difference from CVC clean GaN to final surface is 0.1 ± 0.1 eV and again consistent with values obtained for the gallium core level peaks.

Figure 5 displays the evolution of the oxygen 1s core level. As measured by XPS, the as-loaded GaN sample contains ~14 and 8 atomic percent of oxygen and carbon, respectively. The chemical vapor clean (CVC) clean reduces the oxygen and carbon below the XPS detection limits (< 1 atomic percent). After deposition of 4 Å Hf and the O₂ plasma, the initial peak position was observed at 529.9 ± 0.1 eV. Through the course of the experiment, the peak shifted to 530.7 eV, a difference of 0.8 ± 0.1 eV.

The oxide quality is an important issue because it affects the bandgap of the material. Careful comparisons were made of the oxide grown on the GaN surface to HfO₂ grown on silicon. The difference in energy between the O 1s and Hf 4f core levels was found to be 511.6 eV in the oxide grown in our experiment (before and after annealing), which is equivalent with the value found in the literature.^{28,29} This finding suggests that the quality of our film is consistent with HfO₂ grown on Si.

The spectral peak positions and the full width-half maximum (FWHM) of the Ga 3p_{3/2}, Hf 4f, O 1s, Ga 3d, and N 1s have been summarized in Table I for the n-type GaN/HfO₂ interface. From the results, two important properties of the interface can be stated. First, there does not appear to be a significant reaction at the GaN-HfO₂ interface. If this reaction were significant, there would be additional peaks reflecting the reacted environment, and/or changes in the widths of the peaks. Second, the observed shift for

the Ga 3p_{3/2}, Ga 3d, and N 1s core levels are essentially the same, allowing the inference that the shifts are a result of band bending.

5.5 Discussion

The method for determining the valence band discontinuity is similar to that of Waldrop and Grant²³ and Kraut *et al.*³⁰ Their basic approach is to reference the VBM to a core level in the XPS spectra for each semiconductor and to use the measured difference between the core level energies to discern the band discontinuities. In our study, we have employed UPS to measure the energy of the VBM from the Fermi level, and XPS is used to measure core level energies relative to the Fermi level.

Care was taken to avoid oxidation of the clean GaN surface after the CVC clean. A significant Ga₂O₃ layer at the interface can be a source of deep acceptors and interface states that can be detrimental to device fabrication.³¹ Although gallium oxide was not observed within our detection limits, we expect that Ga-O bonding exists at the HfO₂-GaN interface.

The Ga face GaN (0001) is a polar surface, and the spontaneous polarization will lead to a negative bound charge at the GaN film surface and a positive bound charge at the back substrate interface. The GaN is also piezoelectric, but because the films are grown above the critical thickness there is only a small residual strain, and the piezoelectric induced polarization ($P_{pz}=0.002 \text{ C/m}^2$) is small in comparison to the spontaneous polarization ($P_{sp}=0.033 \text{ C/m}^2$).³³ The piezoelectric polarization for biaxial tensile strain contributes in the same direction as the spontaneous polarization. The negative surface bound charge is compensated by surface states and screened by ionized

donors while the positive bound charge at the substrate interface is screened by the free carriers. The polarization bound charge screened by the ionized donors would lead to upward band bending at the GaN surface. We note that the XPS measurements of the Ga and N core levels would be shifted by the polarization fields, but all measurements of the band offsets are made relative to these values, and thus the measured band offsets should not be affected by polarization induced band bending. Moreover, since the strain is relatively small, the effect of strain on the band offsets is anticipated to be less than the experimental uncertainties in our measurements.³⁴

Figure 6 shows the proposed band lineups for the n-type GaN-HfO₂ interface without annealing. The increase of 0.6 eV band bending from the clean surface as the interface is formed is shown. The valence band offset determination is the measured UPS turn-on for the HfO₂ on the GaN (2.3 eV), minus the GaN turn-on (3.0 eV), plus the change of band bending (0.6 eV). With this value and the knowledge of the bandgap of the material, the conduction band offset is obtained. The bandgap of HfO₂ has been reported to be 5.7-6.0 eV.^{11,12,16} A value of 5.8 eV was used for the conduction band offset and electron affinity calculations. The valence band offset is deduced to be 0.1 eV, and the conduction band offset is 2.5 eV for our as deposited GaN/HfO₂ interface.

Figure 7 shows the proposed band lineups for the n-type GaN-HfO₂ interface after annealing at 650 °C. The increase of 0.1 eV band bending from the clean surface is small and near the experimental uncertainty of our experiment and indicates essentially no change in the band bending as the interface is formed. The valence band offset determination is the measured UPS turn-on for the HfO₂ on the GaN (3.3 eV), minus the GaN turn-on (3.0 eV), plus the change of band bending (0.1 eV). From our annealed

interface experiment, the valence band offset is deduced to be 0.4 eV, and the conduction band offset is 2.0 eV.

Annealing above 600 °C is crucial for densification of HfO₂ films.^{8,35} Deposition of HfO₂ on the clean GaN resulted in a Ga 3p core level shift from 105.8 eV to 105.2 eV, indicative of downward band bending as the film was deposited. An anneal to 650 °C shifted the core level to 105.8 eV, bending the energy bands upward. Subsequent HfO₂ film depositions and anneals resulted in a Ga 3p energy levels of 105.2 and 105.8 eV, respectively. Depositing and subsequently annealing the sample could move the Ga 3p core level positions, and therefore the change in band bending, between the two energy positions. This result suggests thermodynamic instability of the hafnium oxide film as the GaN/HfO₂ interface is formed.

The electron affinity levels for GaN and HfO₂ are represented in Figures 6 and 7. The electron affinity model of heterojunction formation predicts these levels to align at the interface. Our results show a deviation from the electron affinity model of 2.0 and 1.9 eV before and after annealing, respectively, for the GaN-HfO₂ interface.

The electron affinity model is based on the premise that the interface is formed without disruption of the surface electronic states of either of the two materials. All energies are referenced to the vacuum levels of the two materials. The measured difference between the prediction of the electron affinity model and the experimentally observed band offset represents a change in the interface dipole. In general, it is not possible to assign a specific interface dipole to the heterostructure, but it is reasonable to consider the change in interface dipole from that deduced by the electron affinity model. However, the relation to the vacuum level in the first place is somewhat arbitrary. While

the electron affinity of a surface can be determined following the approach employed in this study, it is dependent on the details of the surface structure where surface reconstruction, steps, and adsorbates can cause changes of the electron affinity by several eV. Moreover, after interface formation, the vacuum levels of the materials at the interface are not defined or measurable, and the interface structure may have little relation to the specific bonding of the free surface that was responsible for the value of the electron affinity.

As an alternative to the electron affinity model, it has been proposed that heterojunction band alignments are determined by alignment of the charge neutrality levels (CNL) of the two materials. The charge neutrality levels represent the branch point of the surface or interface states related to the valence or conduction band. Thus a neutral interface would have a Fermi level at the branch point. The presumption is that charge can transfer between the interface states of the two materials, which will cause an interface dipole. If the density of states is high or if the CNL of the two semiconductors are at similar relative energies, then the band offset will be determined by the relative position of the CNL of the two materials.

Recently, Robertson¹⁶ adapted the interface defect model presented by Cowley and Sze³⁶ to employ the CNL as the pinning levels. The model was applied to analyze the band alignment of a range of oxides on silicon, and the model seems consistent with most experimental results. In this model, charge transfer across the interface creates a dipole, which modifies the band lineup given by the electron affinity rule and is described by the relation:

$$\varphi_{CBO} = (\varphi_{CNL,a} - \varphi_{CNL,b}) - (E_{g,a} - E_{g,b}) + S\{(\chi_a - \chi_b) + (E_{g,a} - E_{g,b}) - (\varphi_{CNL,a} - \varphi_{CNL,b})\} \quad (5.2)$$

Where ϕ_{CBO} is the CBO, χ and ϕ_{CNL} are the electron affinities and charge neutrality levels for each semiconductor (a and b), and S is a pinning factor based on the dielectric properties of the materials. Here, the ϕ_{CNL} are defined relative to the VBM of each semiconductor. A value of $S=1$ represents the EAM while a value of 0 represents pinning at the CNL levels. Robertson¹⁶ has reported the CNL of HfO₂ to be 3.7 eV above the valence band.

In an attempt to understand the relation of our measured band alignment and the different models for heterostructure band alignment, in Figure 8 we have compared our measured alignments for the annealed interface to experimental results for HfO₂ on Si.¹⁶ In both cases the diagrams are aligned to the vacuum level at the HfO₂, which has been measured to be at the same energy relative to the oxide bands. The bandgap of each material is indicated, as is the VBO. The position of the vacuum level of the clean surface of the semiconductor is indicated, and the difference between these values and the surface vacuum level is the deviation from the EAM. While the Si-HfO₂ interface does not present a deviation from the electron affinity model, the GaN-HfO₂ interface has a change in interface dipole of 1.9 eV. Also indicated in Figure 8 is the CNL of the semiconductors based on prior reports.^{16,37} We find that the CNL of the Si and the GaN are not in relative alignment with respect to the HfO₂ band gap. The S parameter in Eq. 5.2 was deduced from experimental results for the GaN/HfO₂ interface. A value could not be found for the dielectric screening between either extreme (0 to 1) for S , suggesting the EAM and CNL model are not appropriate for describing this interface.

The progression of the interface dipole deduced from the deviation from the EAM is most likely related to the changes at the semiconductor surface since the oxide is the

same in both cases. For the GaN-HfO₂ interface, Ga-O bonding is expected at the interface. With the Ga atomic layer more positive and the O layer more negative, the interface dipole would be expected to lower the GaN electronic levels with respect to the HfO₂ levels, which is consistent with our observations. In support of this explanation, we note that the interface dipole deduced from the GaN/SiO₂ interface is 1.7 eV with Ga-O bonding expected at the interface.³⁸

5.6 Conclusions

The band alignment of an HfO₂ layer on $1 \times 10^{17} \text{ cm}^{-3}$ n-type GaN has been investigated. Annealing in ammonia at 860°C provided atomically clean, stoichiometric GaN surfaces with 0.3 ± 0.1 eV upward band bending. The electron affinities for the clean n-type GaN and HfO₂ were measured to be 3.0 and 2.9 eV, respectively. After careful formation of the GaN-HfO₂ interface, upward band bending of 0.4 and 0.9 ± 0.1 eV existed for the as grown and annealed interface, respectively. A valence band offset of 0.1 ± 0.1 eV was obtained for the as grown interface, with a conduction band offset of 2.5 ± 0.1 eV (assuming $E_{\text{g HfO}_2} = 5.8$ eV). For the annealed interface, a valence band offset of 0.4 ± 0.1 eV was obtained, while the conduction band offset was determined to be 2.0 ± 0.1 eV. This result suggests the thermal stability of the hafnium oxide film greatly affects the electronic properties at the GaN-HfO₂ interface. The interface dipole deduced from comparison with the electron affinity model was 2.0 and 1.9 eV before and after annealing, respectively, for the GaN-HfO₂ interface. The charge neutrality model does not reliably predict the band alignment of the GaN-HfO₂ interface. These results

suggest that HfO_2 may be appropriate for passivation of n-type surfaces, but should not passivate n-type surfaces.

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Table 5.1 XPS core level curve fitting results for the Ga 3p_{3/2}, Hf 4f, O 1s, Ga 3d, and N 1s energy levels for the n-type GaN/HfO₂ experiment.

	Ga 3p _{3/2}		Hf 4f		O 1s		Ga 3d		N 1s	
Process Step	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)	Center (eV)	FWHM (eV)
CVC	105.8	2.7	-	-	-	-	20.6	1.6	398.0	1.7
4Å Hf	105.5	3.2	17.4	2.0	-	-	20.3	2.0	397.5	2.0
O-PI	105.2	3.3	18.4	1.7	529.9	2.1	20.1	1.7	397.3	2.4
8Å Hf, O-PI, anneal	105.8	3.1	19.2	1.5	530.8	1.9	20.7	1.5	397.9	1.6
12Å Si, O-PI	105.2	3.3	18.3	1.6	529.9	2.2	20.1	1.6	397.4	2.4
Final	105.8	3.1	19.1	1.4	530.7	1.9	20.7	1.4	397.9	1.7
Difference	0.0		1.7		-0.3		0.1		0.1	

FIGURE CAPTIONS

Figure 5.1 UPS spectra of: a) CVC clean n-GaN, b) 4Å Hf, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma and 650°C anneal, e) 12Å Hf and O₂ plasma, f) 650°C anneal.

Figure 5.2 UPS spectra of the valence band maximum of: a) CVC clean n-GaN, b) 4Å Hf, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma and 650°C anneal, e) 12Å Hf and O₂ plasma, f) 650°C anneal.

Figure 5.3 Gallium 3d and hafnium 4f XPS spectra for: a) CVC Clean n-GaN, b) 4Å Hf deposition, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma, and 650°C anneal, e) 12Å Hf and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

Figure 5.4 Nitrogen 1s XPS spectra for: a) CVC Clean n-GaN, b) 4Å Hf deposition, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma, and 650°C anneal, e) 12Å Hf and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

Figure 5.5 Oxygen 1s XPS spectra for: a) CVC Clean n-GaN, b) 4Å Hf deposition, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma, and 650°C anneal, e) 12Å Hf and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

Figure 5.6 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and HfO₂ before annealing. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented.

Figure 5.7 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and HfO₂ after annealing at 650 °C. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented.

Figure 5.8 Band alignment of Si/HfO₂ and GaN/HfO₂ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the HfO₂ surface, which is common in all three interfaces. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap. The VBO are determined from the measurements.

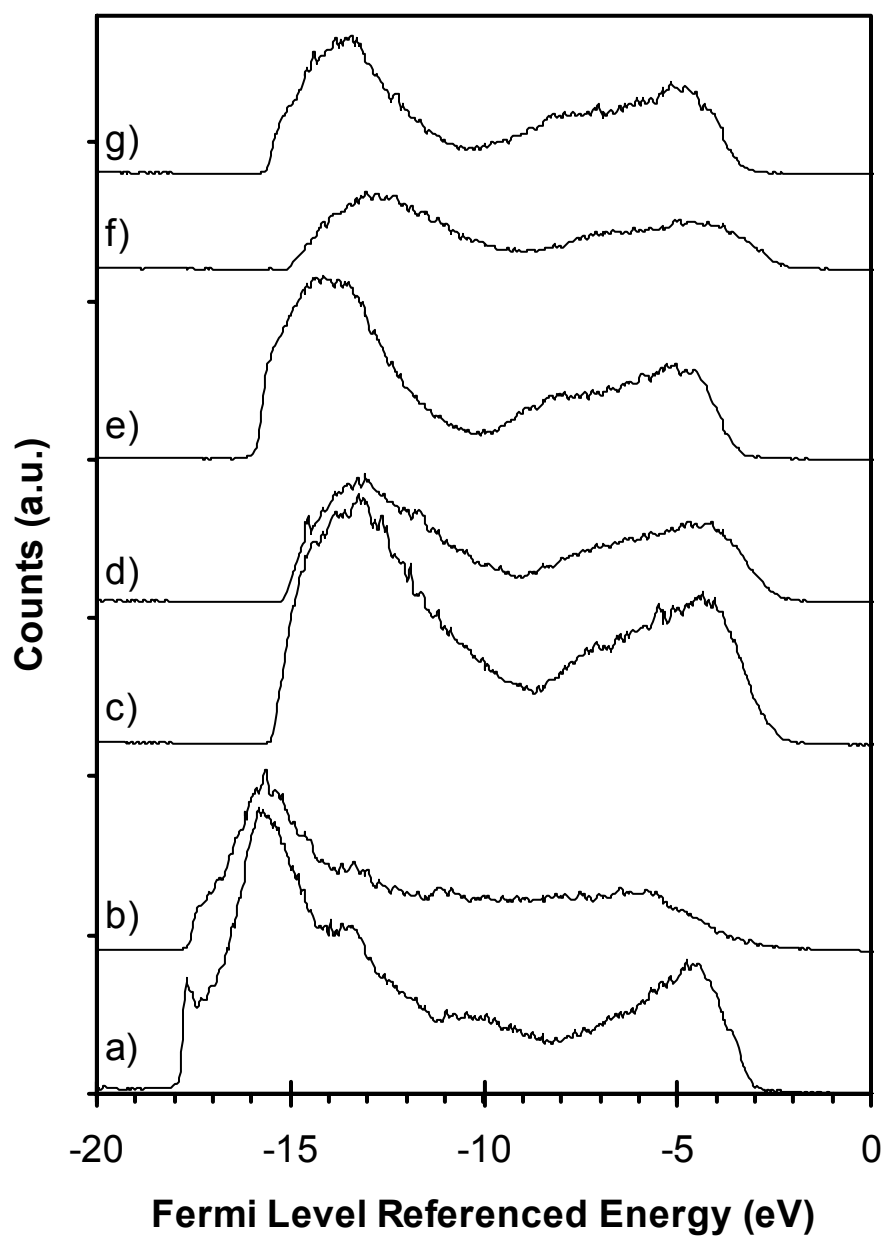


Figure 5.1 UPS spectra of: a) CVC clean n-GaN, b) 4 Å Hf, c) 4 Å Hf and O₂ plasma, d) 8 Å Hf, O₂ plasma and 650°C anneal, e) 12 Å Hf and O₂ plasma, f) 650°C anneal.

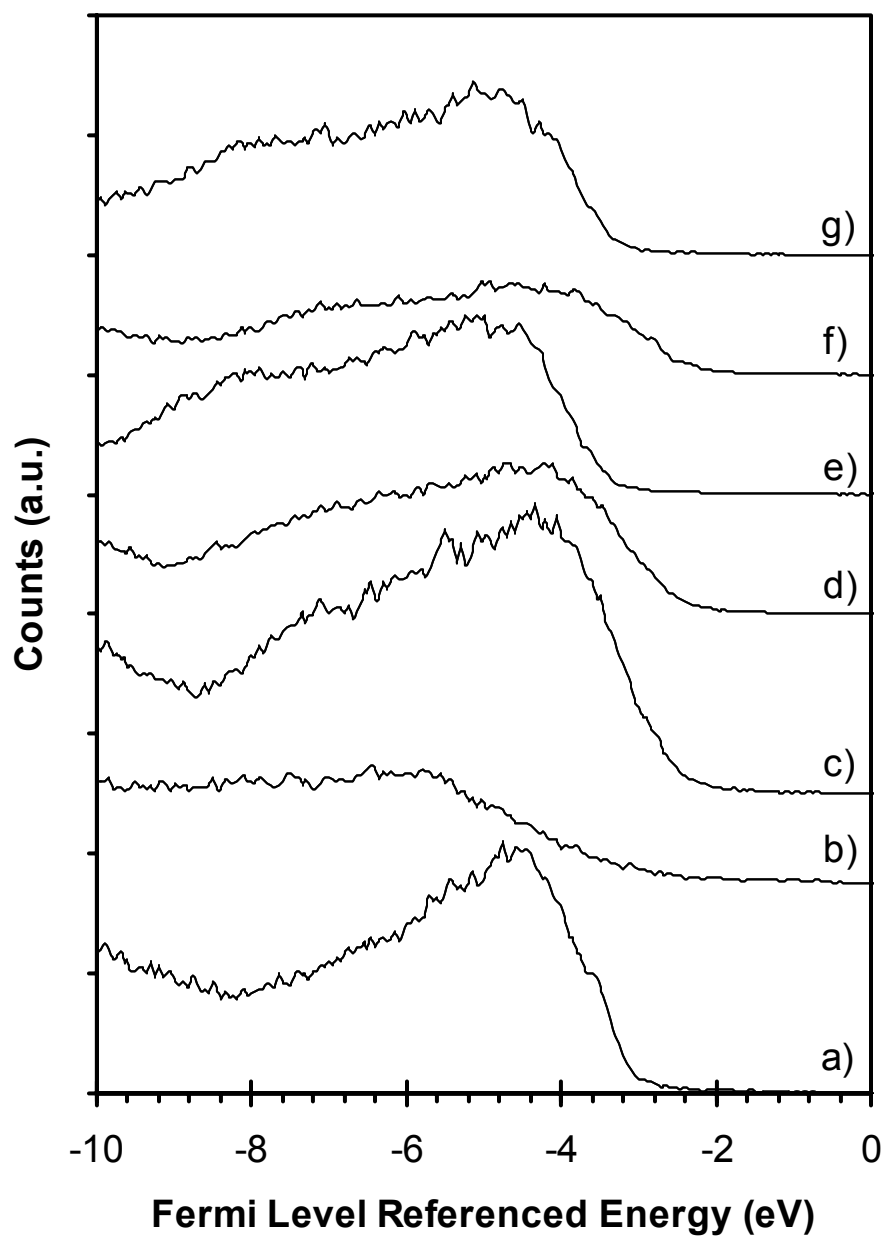


Figure 5.2 UPS spectra of the valence band maximum of: a) CVC clean n-GaN, b) 4Å Hf, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma and 650°C anneal, e) 12Å Hf and O₂ plasma, f) 650°C anneal.

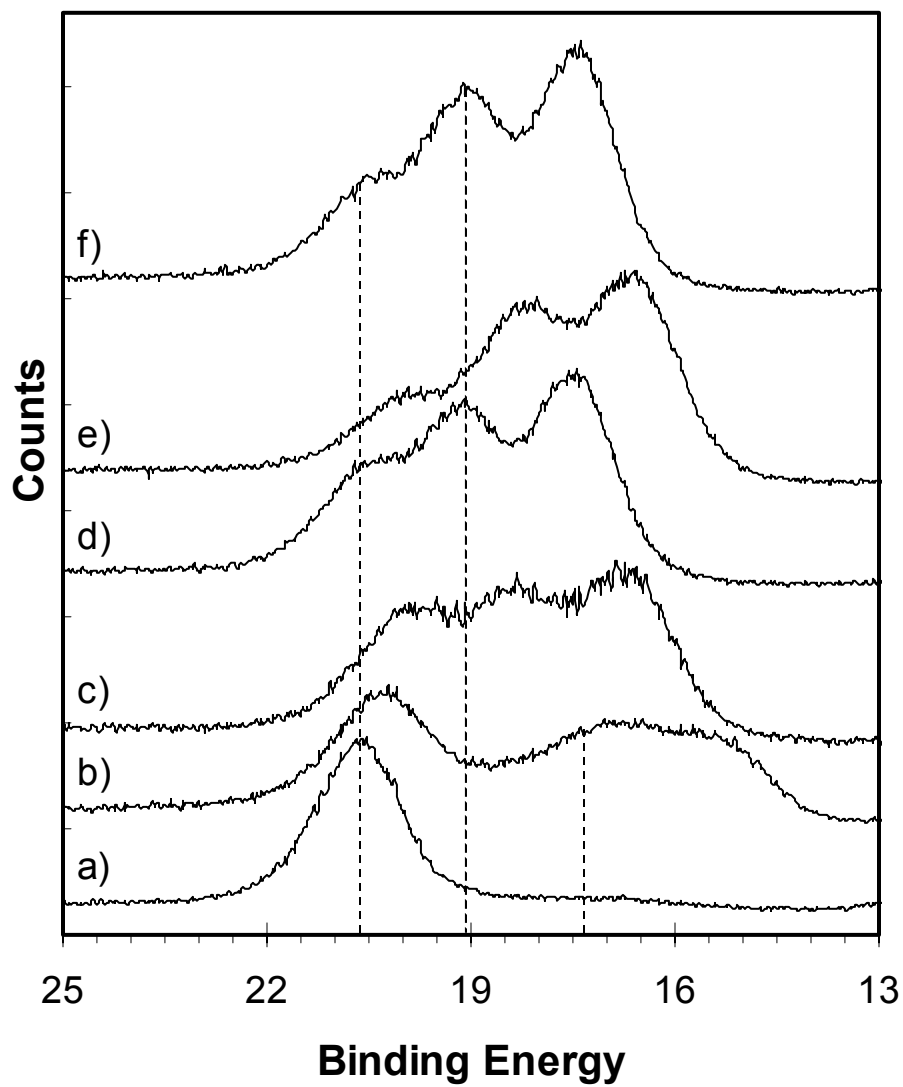


Figure 5.3 Gallium 3d and hafnium 4f XPS spectra for: a) CVC Clean n-GaN, b) 4Å Hf deposition, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma, and 650°C anneal, e) 12Å Hf and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

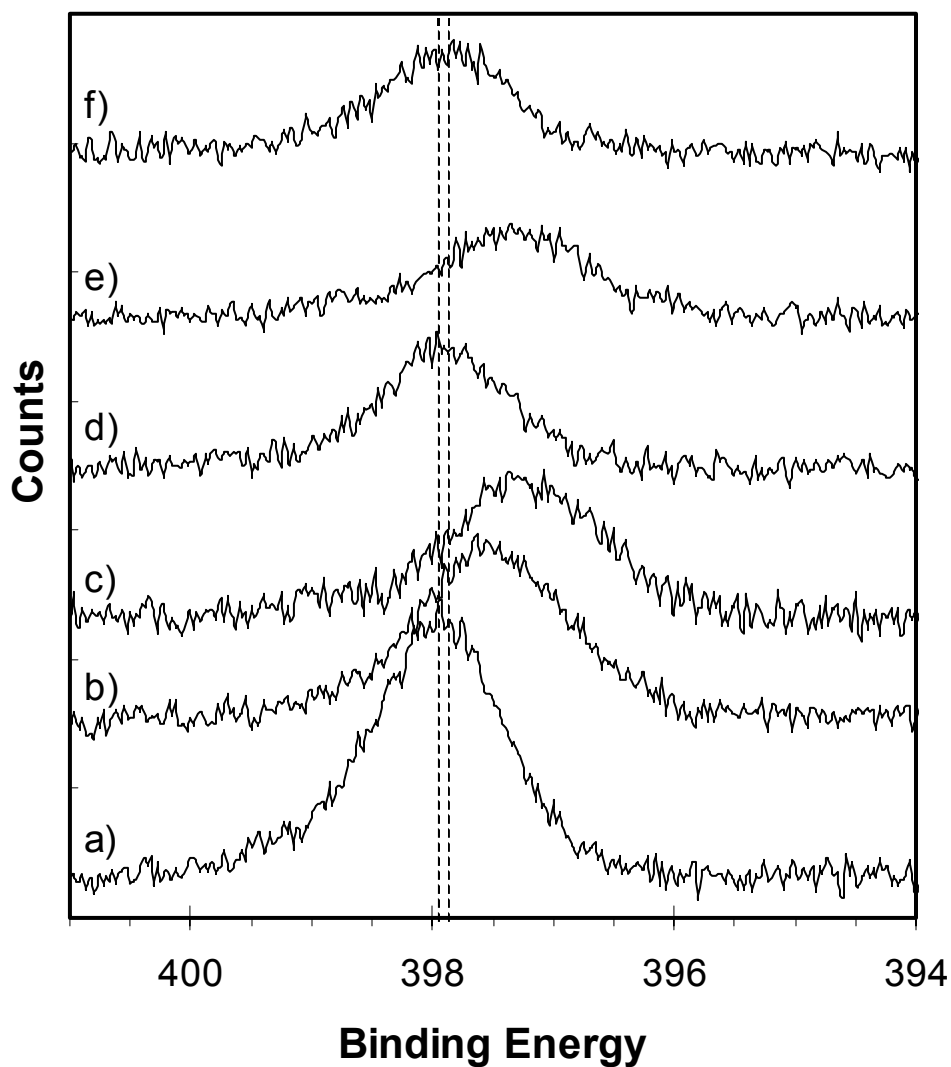


Figure 5.4 Nitrogen 1s XPS spectra for: a) CVC Clean n-GaN, b) 4Å Hf deposition, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma, and 650°C anneal, e) 12Å Hf and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

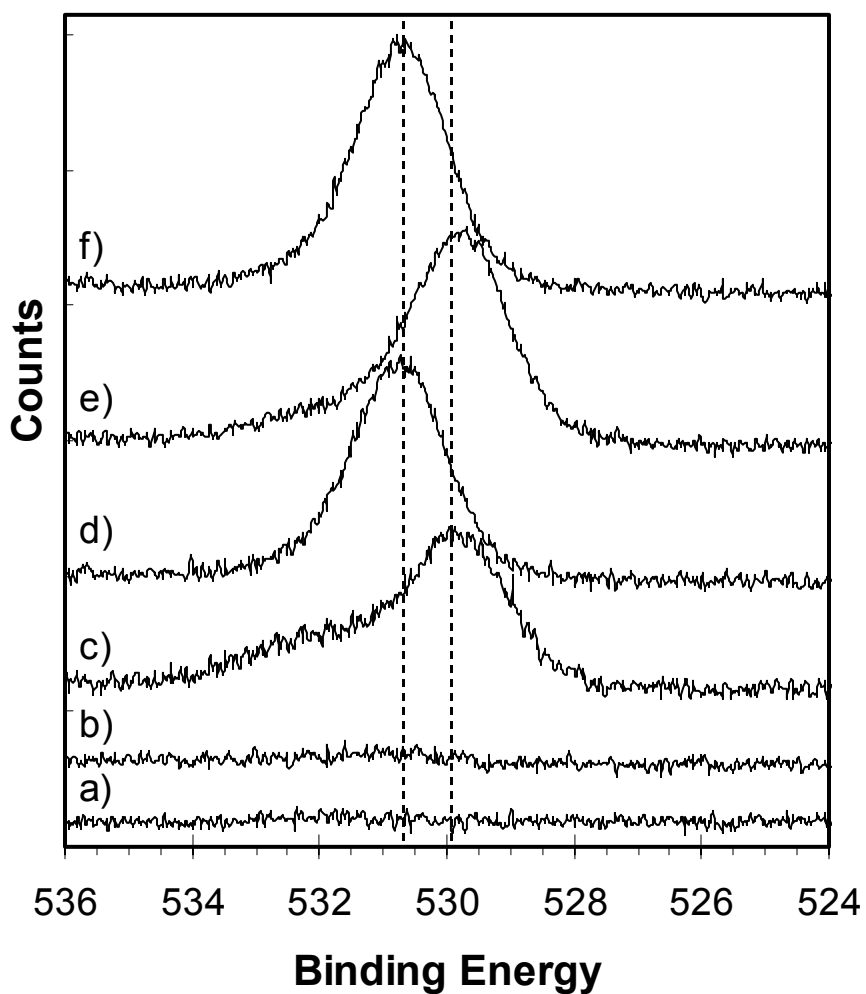


Figure 5.5 Oxygen 1s XPS spectra for: a) CVC Clean n-GaN, b) 4Å Hf deposition, c) 4Å Hf and O₂ plasma, d) 8Å Hf, O₂ plasma, and 650°C anneal, e) 12Å Hf and O₂ plasma, h) 650°C final anneal. The peak positions of the initial surface, as well as the final surface are indicated with dashed lines.

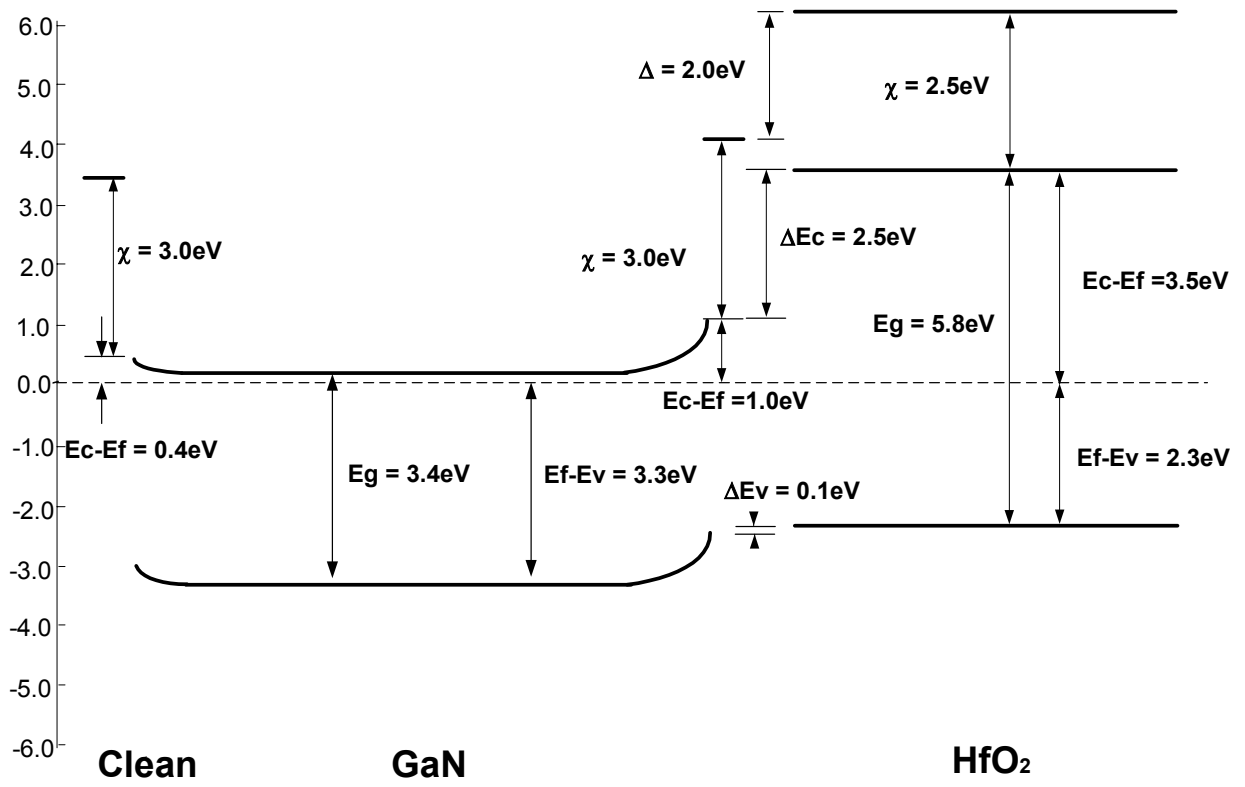


Figure 5.6 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and HfO₂ before annealing. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented.

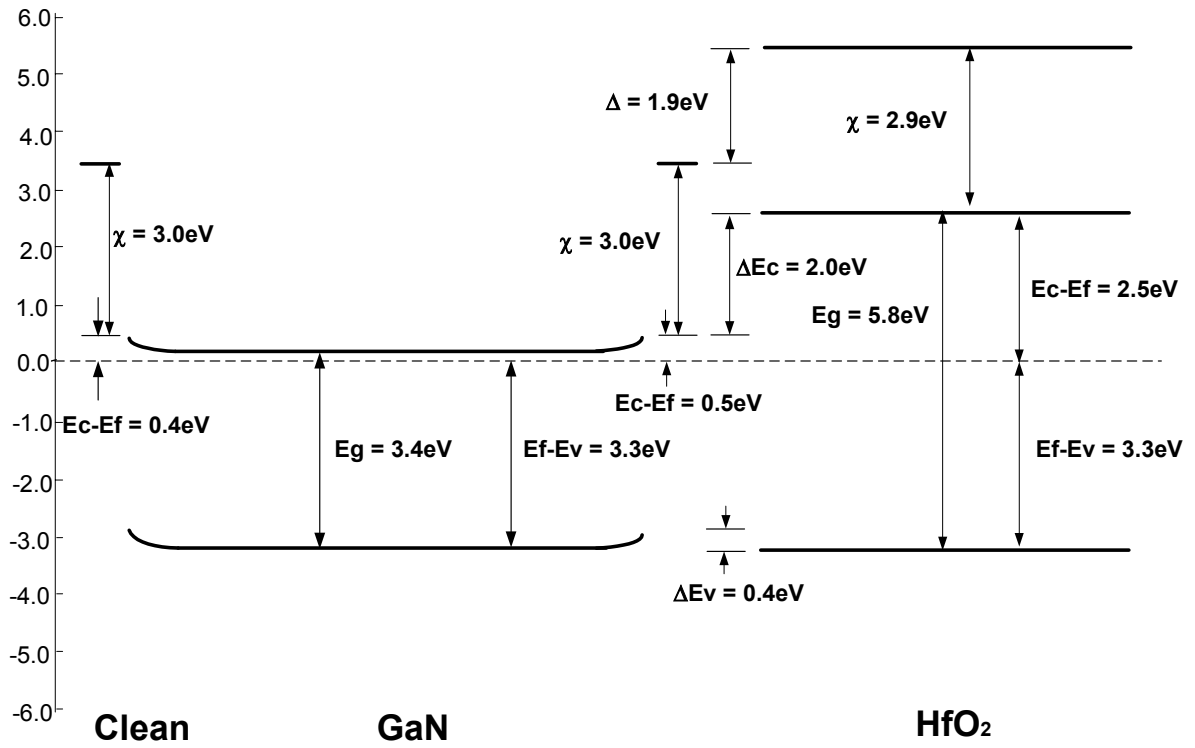


Figure 5.7 Deduced bands for the clean n-type GaN surface (left) and the interface between n-type GaN and HfO₂ after annealing at 650 °C. The valence band offset, ΔE_v , conduction band offset, ΔE_c , band bending, and interface dipole, Δ , are represented.

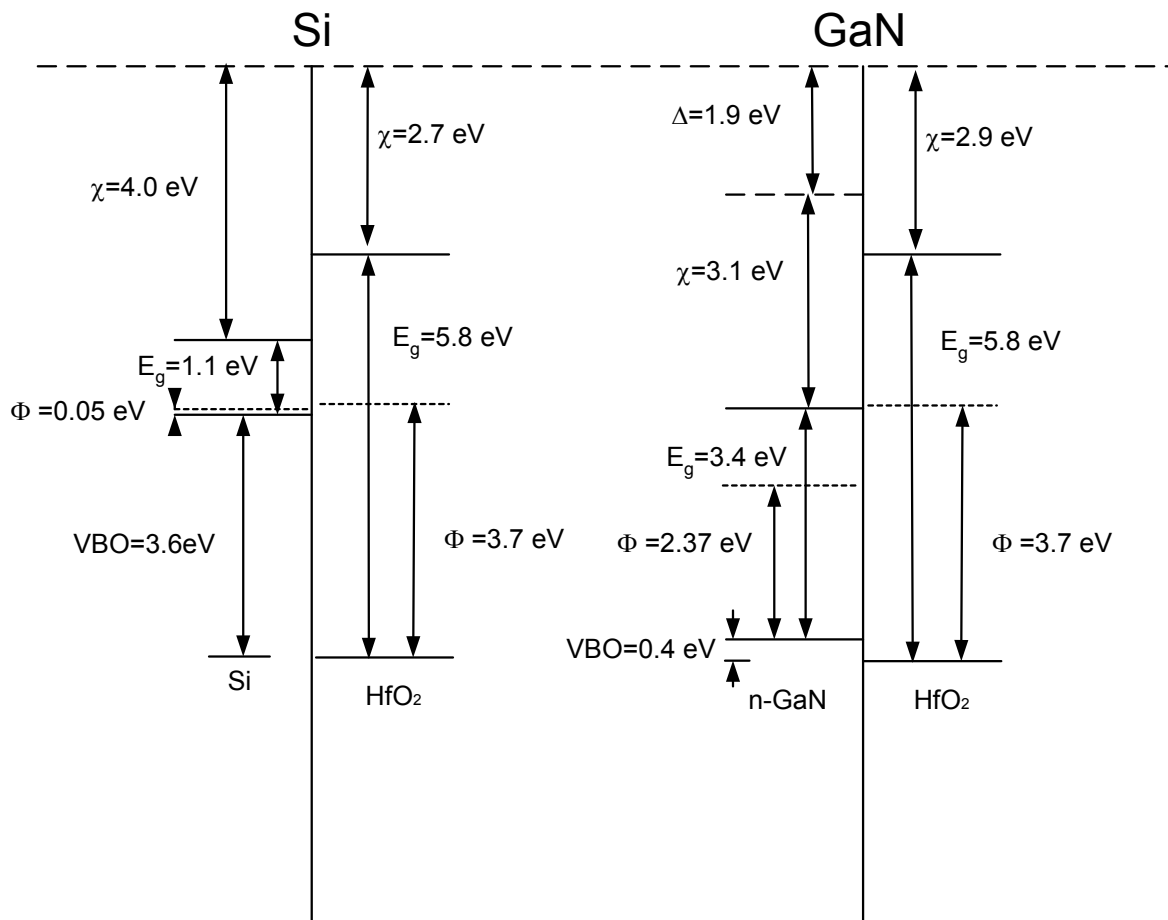


Figure 5.8 Band alignment of Si/HfO₂ and GaN/HfO₂ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the HfO₂ surface, which is common in all three interfaces. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap. The VBO are determined from the measurements.

6. Electrical Characterization of SiO₂ and Si₃N₄ on GaN

6. Electrical Characterization of SiO₂ and Si₃N₄ on GaN

6.1 Introduction

Gallium nitride is viewed as an excellent candidate for the fabrication of high-power and high-frequency transistors operating at elevated temperatures, due to its wide bandgap, high electron saturation velocity, high critical breakdown field, and the potential for lattice-matched heterojunctions with other group III-nitride materials. During the past decade, rapid progress toward the development of GaN-based transistors has been a major area of research.¹⁻³ The power-handling capabilities of these devices are limited by excessive electric fields in the GaN and substantial leakage current through the gate. Using an insulating layer under the gate electrode increases the barrier to current flow, therefore reducing the gate leakage current.

Current flow and breakdown mechanisms in dielectrics are not clearly understood to date, mainly due to the complexity of the phenomena involved, which are associated with charge accumulation, oxide defects, film thickness, and interfacial properties. Understanding the mechanisms leading to defect generation and breakdown of metal-oxide-semiconductor (MOS) devices has been the subject of numerous publications over the past 30 years.⁴⁻⁷ A low-temperature deposition process, as well as low trap densities are required for use as a gate material in III-V MISFET devices.

Electrical measurements in the literature for the GaN/SiO₂ interface show interface state densities of $1-2 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$, suggesting the promise of GaN-dielectric device structures.⁸⁻¹⁰ Unfortunately, the electric field breakdown measurements for this structure are not well defined. Arulkumaran *et al*⁸ found breakdown fields of 2.5 MV/cm

for SiO₂ deposited on GaN. While this is the only reported value, to my knowledge, of the GaN/SiO₂ interface, literature values of 10-12 MV/cm have been established for the breakdown of SiO₂ on Si.¹¹⁻¹⁴ For the GaN/Si₃N₄ interface, Chang *et al*¹⁵ report an interface state density of 5x10¹⁰ eV⁻¹ cm⁻², with a breakdown field of 11.6 MV/cm.

Integrity of the dielectric is determined by I-V measurement of the MIS device with increasing voltage steps until breakdown occurs. This measurement is frequently referred to as “time-zero breakdown” or “intrinsic hard breakdown.”¹⁶ The statistical method for examining oxide integrity is based on the observation that breakdown usually occurs in a small area of the device. If the device contains a multitude of weak spots, the first breakdown occurs at the spot with the lowest dielectric strength. The electric field that results in breakdown of a given dielectric can be calculated using the relation:

$$E_{\max} = \frac{V_{\text{dielectric}}}{d_{\text{dielectric}}} \quad (6.1)$$

with $V_{\text{dielectric}}$ and $d_{\text{dielectric}}$ defined as the voltage of breakdown and thickness of the dielectric, respectively.

During heterojunction formation, a redistribution of charge occurs at the interface and a resulting electric field is generated. This electric field sweeps out any charge carriers that exist in the transition region, creating a depletion region, W . This assumption of carrier depletion within W and neutrality outside W is known as the depletion approximation.¹⁷ The depletion region must be considered when measuring the electric field breakdown of a GaN-dielectric heterostructure. The depletion width that exists in GaN during heterojunction formation can be expressed by the relation:

$$W = \sqrt{\frac{2V_s \epsilon_s}{eN_d}} \quad (6.2)$$

with V_s representing the measured band bending at the interface, ϵ_s as the permittivity of the GaN, e as the charge of an electron, and N_d as the number of ionized donors in the GaN.

The statistics of oxide breakdown are usually described by extreme value distributions.⁶ The assumptions underlying the use of extreme value distribution functions are (1) a breakdown may take place at any spot out of a large number of spots, (2) the spot with the lowest dielectric strength gives rise to the breakdown event, (3) the probability of breakdown at a given spot is independent of the occurrence of breakdown at other spots. In this study, I-V measurements of dielectric films will be examined with failure analysis statistics.

6.2 Experimental Procedure

The GaN films used in this study were grown via metallorganic chemical vapor deposition (MOCVD) on 50 mm diameter on-axis Si-face, 6H SiC (0001) substrates with a conducting AlN (0001) buffer layer. The thickness of the GaN epilayer and the AlN buffer were 1.1 μ m and 0.1 μ m, respectively. Silicon was used as the n-dopant, and magnesium was used as the p-dopant. Ionized donor concentrations (N_d-N_a) of 1×10^{17} cm⁻³ and 2×10^{18} cm⁻³ were measured for the n-type and p-type samples using capacitance-voltage measurements with a mercury probe.

The samples were cleaned through an ammonia exposure at an elevated temperature, details of which can be found in the literature.¹⁸ To limit the oxidation of the clean GaN surface, a 4 Å Si layer was deposited after cleaning. For SiO₂ formation, SiO₂ was deposited by remote plasma enhanced chemical vapor deposition (RPECVD) at

300°C. The operating parameters were 20 W with flow rates of 10, 10, and 50 sccms of 1% SiH₄:He, O₂, and He, respectively. A deposition rate was established using a combination of varying thickness and ellipsometry measurements. SiO₂ films of 200 Å were prepared with a deposition rate of ~2.5 Å.

The Si₃N₄ was formed in an electron cyclotron resonance (ECR) plasma system. Nitrogen was introduced into the chamber by a needle valve until a pressure of 7.5x10⁻⁴ Torr was reached. The silicon layer was nitrided by the plasma for 30 seconds, with power and temperature settings of 300 W and 300 °C, respectively. A second 4 Å Si deposition followed, with a sequential nitridation. This process was performed a total of 5 times, with the total thickness of Si₃N₄ being ~40 Å.

After dielectric formation, *ex situ* processing and characterization was performed. Photolithography was used to fabricate contacts on the dielectric surface. Contacts were formed on the 2000 Å aluminum layer using JSR 10-CP photoresist. The metal exposed between the contacts was subsequently removed via etching with HCl and Aqua Regia acid to form an array of 6.0x10⁻⁴ cm² rectangular contacts on the surface of the dielectric. A 2000 Å tungsten layer was deposited on the backside of the SiC substrate for heating served as the ohmic contact.

Electrical characterization of the capacitors involved both current-voltage (I-V) and capacitance-voltage (C-V) measurements. The I-V measurements were conducted using a Keithley 236 source measure unit. The unit could apply voltages in the range of 0 to 110 V and measure currents in the range 1 pA to 100 mA. A voltage on the contact was applied, and the resulting current measured. This voltage was increased by 0.5 V until intrinsic hard breakdown was reached for the device. Intrinsic hard breakdown is

defined as the voltage at which the dielectric fails and the current exceeds the limit of the measurement device.

The C-V measurements were performed using a Hewlet-Packard LCR meter. The LCR can measure capacitances in the range of 0.001 fF to 9.9999 μ F. Interfaces were characterized with C-V measurements only to obtain dielectric thickness. All electrical measurements were controlled using a computer with custom software that collected and output the data in an ASCII format.

6.3 Results and Discussion

MIS structures formed for electrical characterization are schematically represented in Figure 6.1. XPS measurements reveal flat bands for the n-type GaN/SiO₂ interface, with downward band bending of 2.2 and 1.8 eV for the p-type GaN/SiO₂ and Si₃N₄ interfaces, respectively. Figure 6.2 represents the electrical measurements conducted for each interface. In each case, the electric field is dropped over the dielectric, as well as partially over the GaN. This requires the depletion width to be considered when calculating electric field breakdown measurements.

A typical I-V curve for SiO₂ on n-type GaN is shown in Figure 6.3. Positive and negatively biased Al contacts exhibited symmetric behavior. Leakage currents of 1.2×10^{-8} A exist for a 5 V bias, which is similar to reported values for RPECVD grown SiO₂ films on GaN.^{8,19}

There is minimal band bending as the device is biased, as the Fermi level is ~ 0.1 eV below the conduction band. Figure 6.4 shows intrinsic hard breakdown of the SiO₂ dielectric under applied positive bias to the Al contact. Defect related breakdown begins

to occur around 10 V, with leakage current of 1×10^{-8} A. The leakage current does not rise above 5×10^{-7} A before intrinsic hard breakdown occurred at 22 V. , The electric field breakdown can be calculated using Eq. 6.1, with a value of 11 MV/cm obtained for the SiO₂ film. A statistical analysis of the n-GaN/SiO₂ breakdown measurements is presented in Figure 6.5. While the range of dielectric breakdown is from 13 to 25 V, a majority of the breakdown occurs around 22 V. This suggests the oxide integrity is similar to SiO₂ on Si. The somewhat broad range of breakdown voltages could be a result of a number of contact issues regarding uniformity and defects.

The intrinsic hard break down of negatively biased p-GaN/SiO₂ capacitor and subsequent statistical analysis are represented in Figures 6.6 and 6.7, respectively. Initially, the MIS structure was tested as shown in Figure 6.2b, with a positive bias on the GaN. In this case, breakdown of the device could not be achieved within the 110 V limits of our equipment. Depletion width calculations show the field is dropped over the entire GaN film, as well as the dielectric. The terminals were reversed, and breakdown was achieved. Defect related breakdown begins to occur ~10 V, with leakage in the 10^{-7} A range. The leakage current increased to $\sim 1 \times 10^{-5}$ A range before intrinsic hard breakdown occurred at 28 V. The depletion region for the unbiased p-type GaN as the SiO₂ was deposited was calculated to be 72 Å. Thirty-one contacts were measured for the p-GaN/SiO₂ capacitors, with ~80 % breaking down in the 24-27 V range, giving rise to a breakdown field of ~9.5 to 10 MV/cm. These values, as well as the small range of breakdown, suggest the oxide film quality is similar to published reports for SiO₂ films.¹¹⁻

A typical I-V plot and statistical analysis of the intrinsic hard breakdown of the p-type GaN/Si₃N₄ interface is shown in Figure 6.8 and 6.9, respectively. The depletion region width is calculated to be 125 and 66 Å for the unbiased n-type and p-type GaN/Si₃N₄ interfaces, respectively. A positive bias on the Al top contact resulted in minimal leakage until the maximum current of 0.1 A was reached ~50 V. This was repeatable for the same contact, suggesting field was dropped over the GaN as well as the dielectric without breakdown. When a negative bias was applied to the contact, substantial leakage current was measured until intrinsic hard breakdown was achieved. The breakdown voltage consistently occurred at ~40V. Eq. 6.1 gives a value of ~25 MV/cm for the electric field that would cause this breakdown.

6.4 Conclusions and Future Work

Electrical characterization was performed on GaN/SiO₂ and GaN/Si₃N₄ interfaces, with intrinsic hard breakdown information obtained. Electric fields of 9.5-11 MV/cm were found to breakdown the oxide films. Statistical analysis of the intrinsic hard breakdown showed high quality oxide films grown on p-type GaN surfaces. Negatively and positively biased n- and p-type GaN structures, respectively, result in the electric field drop over the entire nitride film, without the occurrence of breakdown.

While this investigation provides some information about the GaN-dielectric interfaces, a more thorough, systematic experiment should be conducted. Electrical measurements should be conducted over the dielectric only, with contacts fabricated on the dielectric and on the surface of the GaN. Measurements in this fashion would remove the W/SiC, SiC/AlGaN, and AlGaN/GaN interfaces from the calculations. Additionally,

C-V measurements would provide interface state densities. Electrical characterization should confirm observations found in photoemission studies of GaN-dielectric interfaces.

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FIGURE CAPTIONS

Figure 6.1 Schematic representation of the equilibrium state for the following measured interfaces: a) n-GaN/SiO₂, b) p-GaN/SiO₂, c) p-GaN/Si₃N₄.

Figure 6.2 Schematic representation of the electrically biased interfaces: a) n-GaN/SiO₂, b) p-GaN/SiO₂, c) p-GaN/Si₃N₄.

Figure 6.3 I-V curve for typical n-type GaN/SiO₂ measurement. The GaN is grown on SiC substrates, with a conducting AlGaN buffer layer. The doping levels of the GaN and AlGaN are 1×10^{17} and 1×10^{18} ($N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.

Figure 6.4 I-V curve showing intrinsic hard breakdown for typical n-type GaN/SiO₂ measurement. The GaN is grown on SiC substrates, with a conducting AlGaN buffer layer. The doping levels of the GaN and AlGaN are 1×10^{17} and 1×10^{18} ($N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.

Figure 6.5 Statistical analysis of the voltage at which intrinsic hard breakdown occurs in SiO₂ deposited on n-type GaN. The oxide thickness was 80 Å. Fifty-two 6×10^{-4} cm² contacts were measured, with the voltage varied from 0-110 V in 0.5 V increments.

Figure 6.6 I-V curve showing intrinsic hard breakdown for typical p-type GaN/SiO₂ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 2×10^{18} and 1×10^{18} ($N_a - N_d$, $N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å

Figure 6.7 Statistical analysis of the voltage at which intrinsic hard breakdown occurs in SiO₂ deposited on p-type GaN. The oxide thickness was 80 Å. Forty-one 6×10^{-4} cm² contacts were measured, with the voltage varied from 0-110 V in 0.5 V increments

Figure 6.8 I-V curve for typical p-type GaN/Si₃N₄ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 2×10^{18} and 1×10^{18} ($N_a - N_d$, $N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å

Figure 6.9 Statistical analysis of the voltage at which intrinsic hard breakdown occurs in Si₃N₄ deposited on p-type GaN. The nitride thickness was 40 Å. Thirty-five 6×10^{-4} cm² contacts were measured, with the voltage varied from 0-110 V in 0.5 V increments

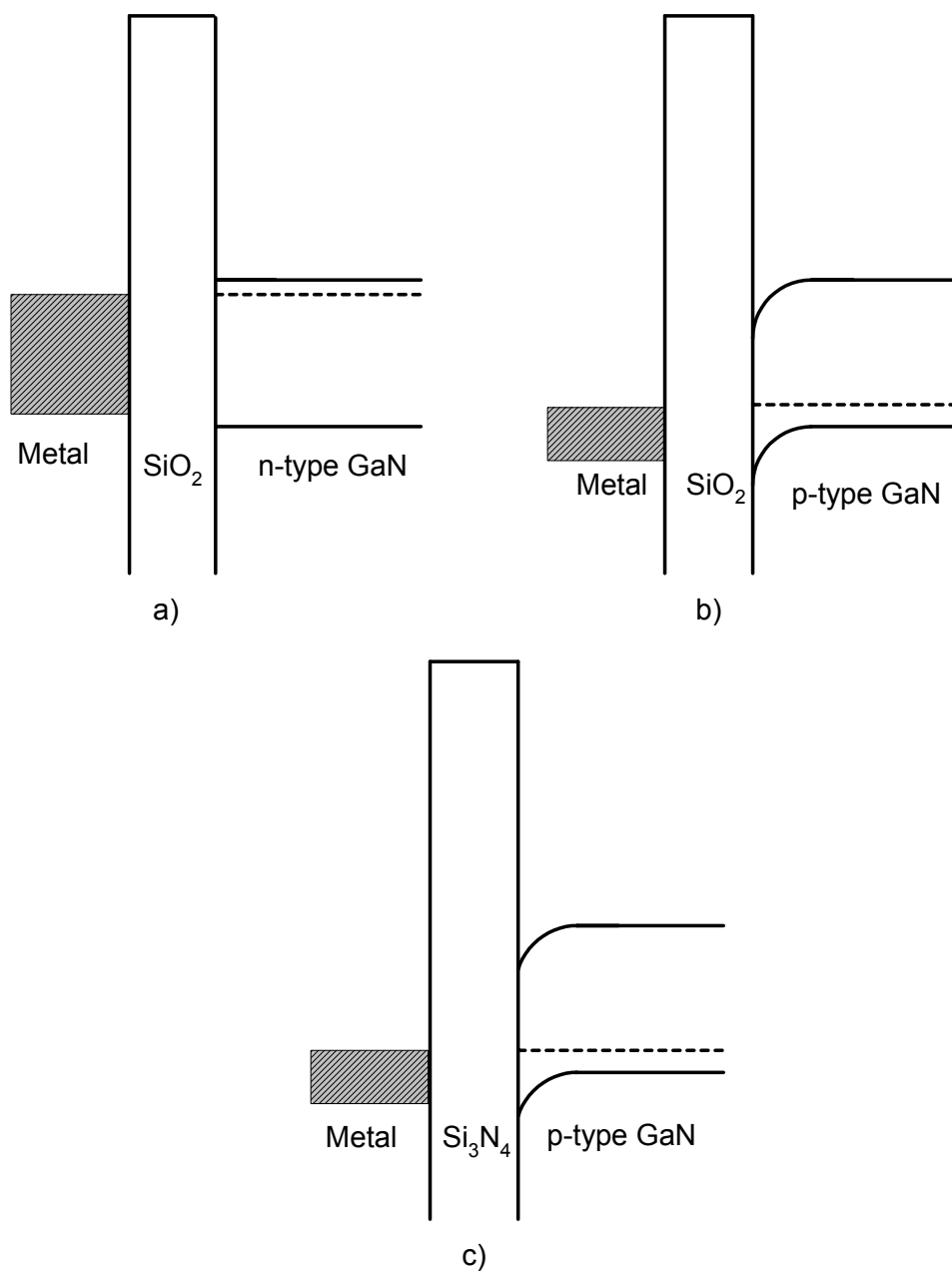


Figure 6.1 Schematic representation of the equilibrium state for the following measured interfaces: a) n-GaN/SiO₂, b) p-GaN/SiO₂, c) p-GaN/Si₃N₄.

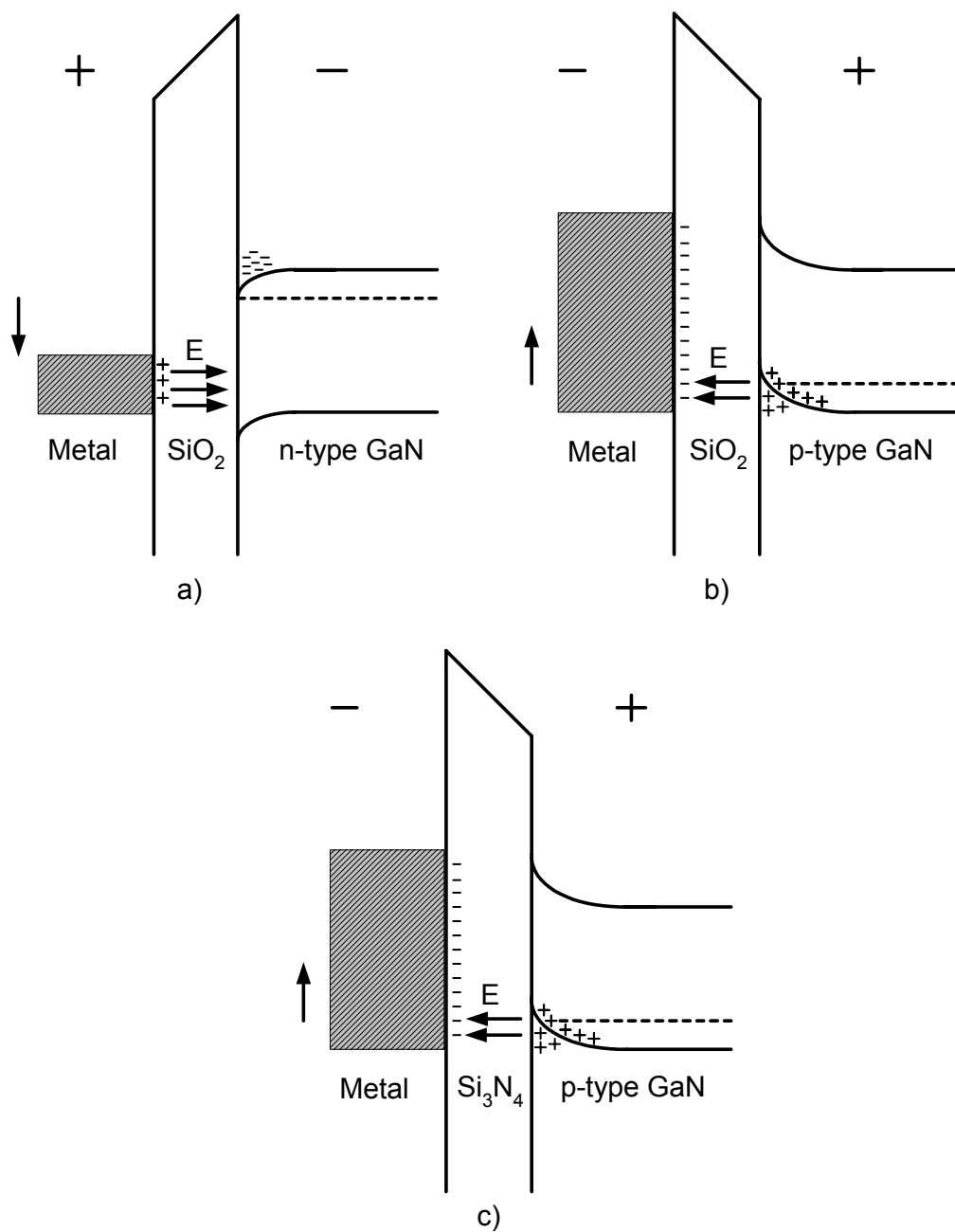


Figure 6.2 Schematic representation of the electrically biased interfaces: a) n-GaN/SiO₂, b) p-GaN/SiO₂, c) p-GaN/Si₃N₄.

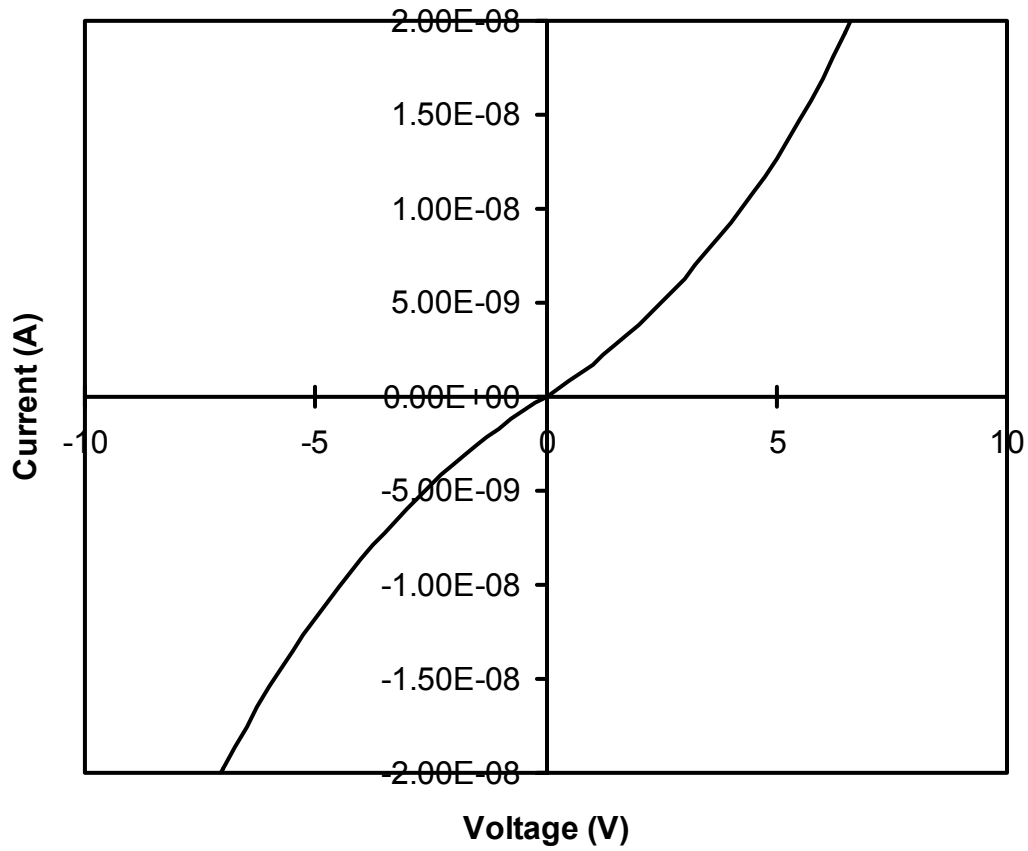


Figure 6.3 I-V curve for typical n-type GaN/SiO₂ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 1×10^{17} and 1×10^{18} ($N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.

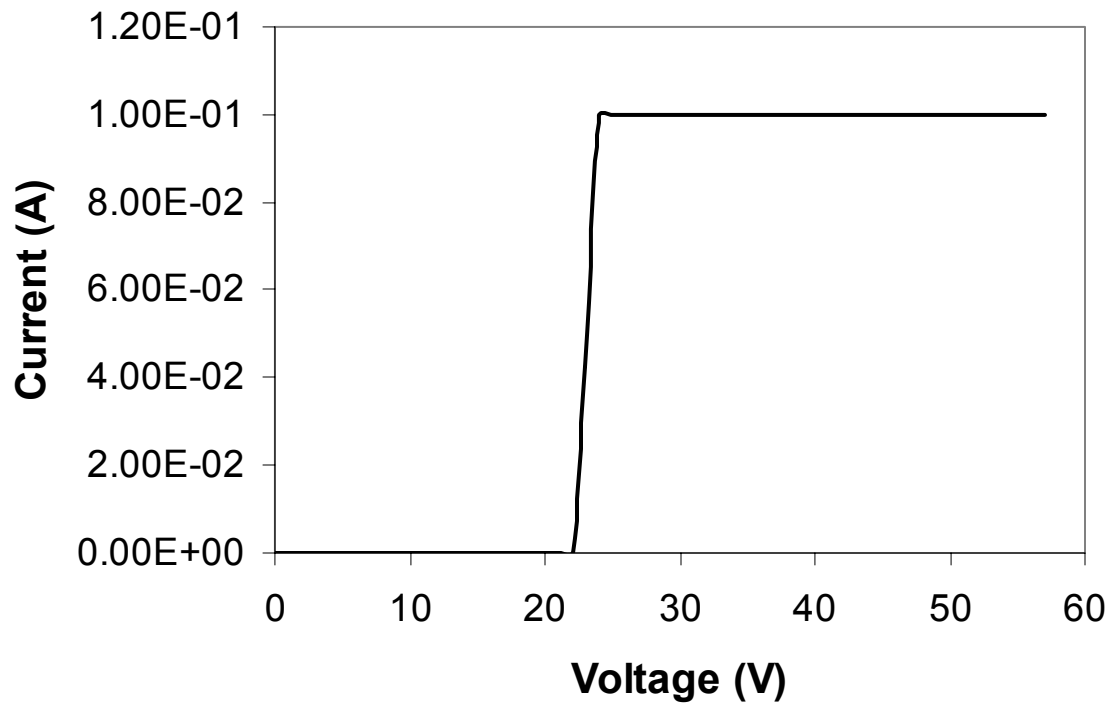


Figure 6.4 I-V curve showing intrinsic hard breakdown for typical n-type GaN/SiO₂ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 1×10^{17} and 1×10^{18} ($N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.

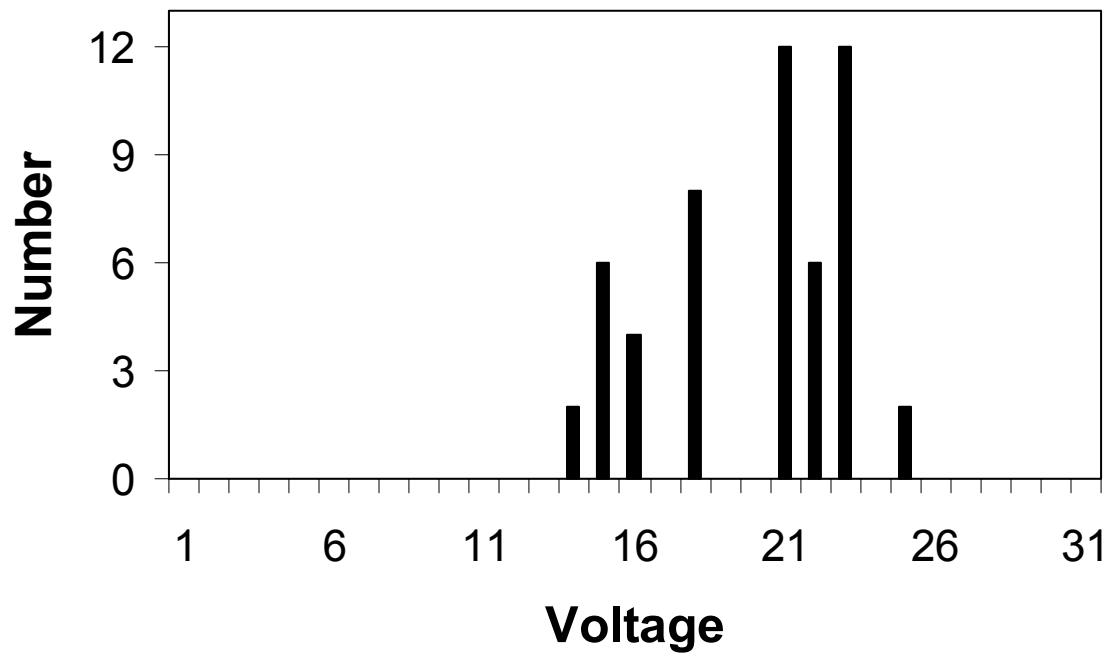


Figure 6.5 Statistical analysis of the voltage at which intrinsic hard breakdown occurs in SiO₂ deposited on n-type GaN. The oxide thickness was 80 Å. Fifty-two 6x10⁻⁴ cm² contacts were measured, with the voltage varied from 0-110 V in 0.5 V increments.

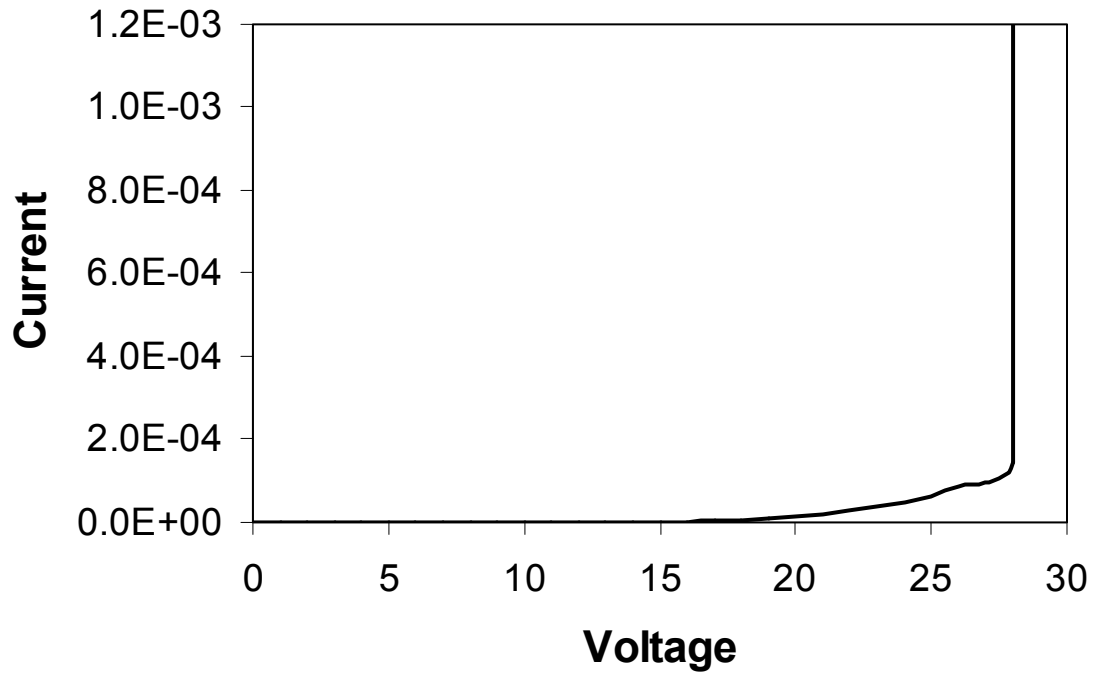


Figure 6.6 I-V curve showing intrinsic hard breakdown for typical p-type GaN/SiO₂ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 2×10^{18} and 1×10^{18} ($N_a - N_d$, $N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.

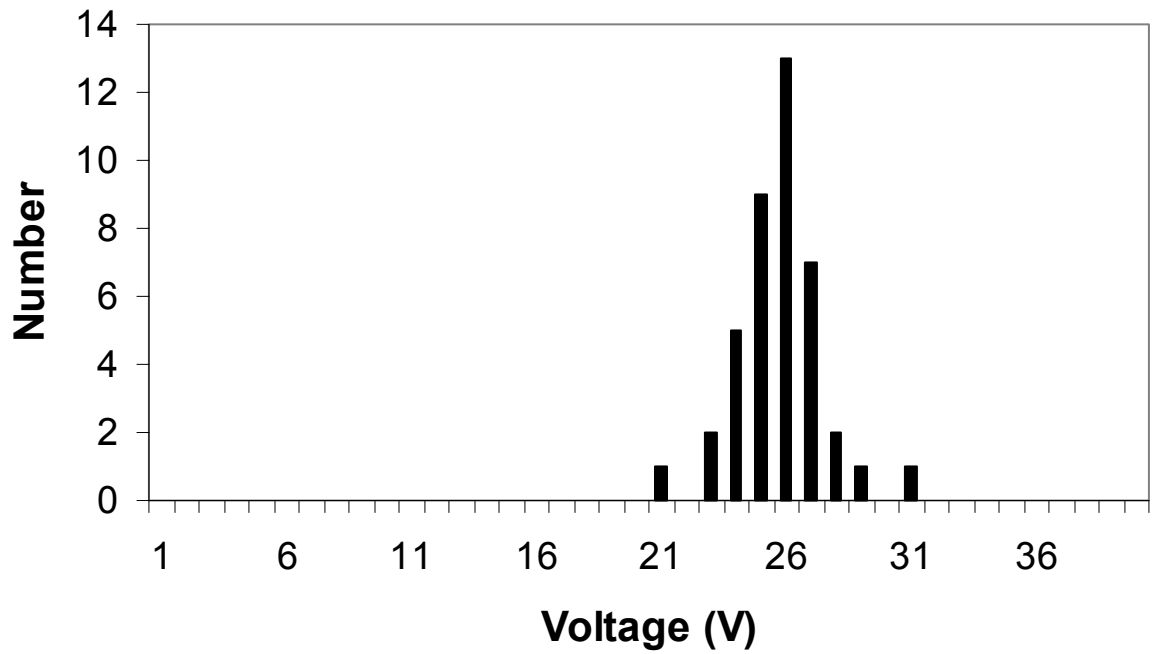


Figure 6.7 Statistical analysis of the voltage at which intrinsic hard breakdown occurs in SiO₂ deposited on p-type GaN. The oxide thickness was 80 Å. Forty-one 6x10⁻⁴ cm² contacts were measured, with the voltage varied from 0-110 V in 0.5 V increments.

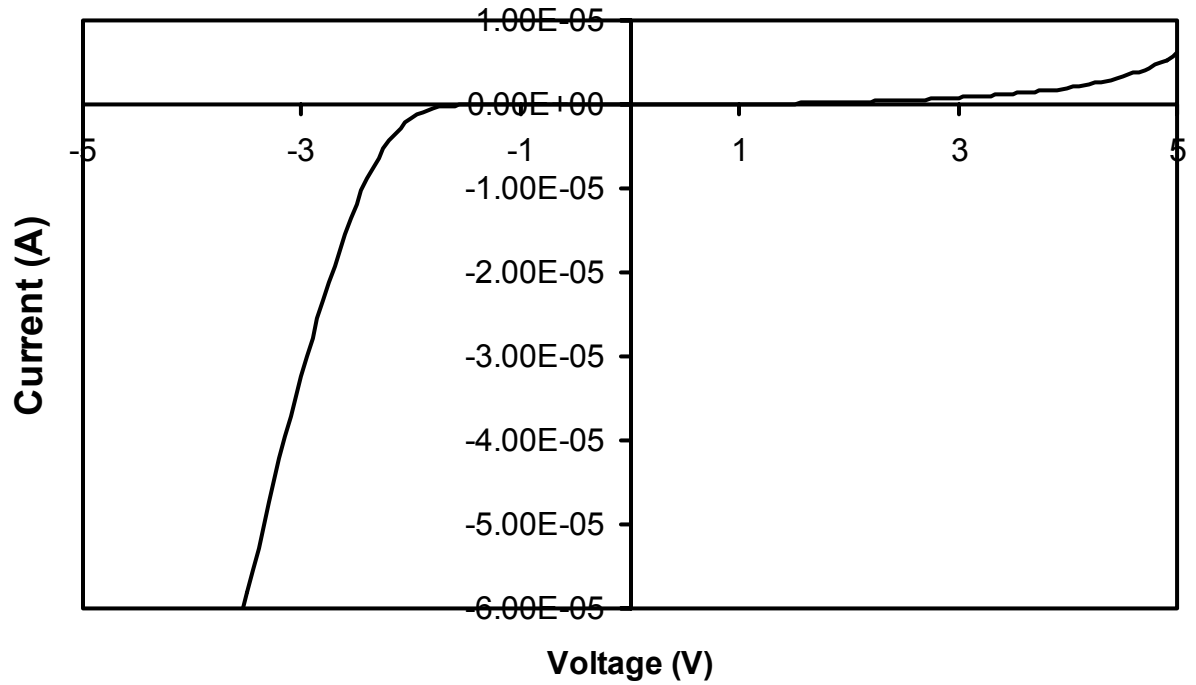


Figure 6.8 I-V curve for typical p-type GaN/Si₃N₄ measurement. The GaN is grown on SiC substrates, with a conducting AlGaIn buffer layer. The doping levels of the GaN and AlGaIn are 2×10^{18} and 1×10^{18} ($N_a - N_d$, $N_d - N_a$), respectively. The backside ohmic contact is 2000 Å tungsten, and the top contact is 2000 Å aluminum. The oxide thickness was 200 Å.

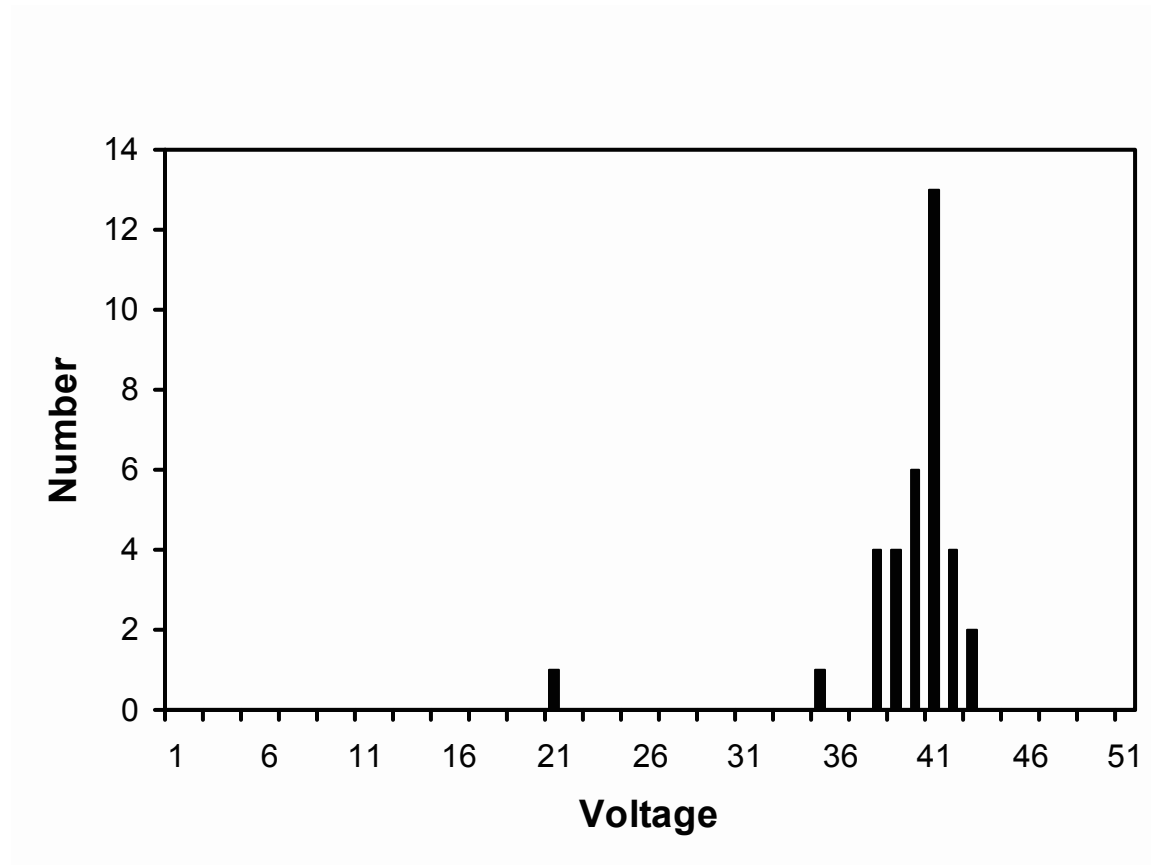


Figure 6.9 Statistical analysis of the voltage at which intrinsic hard breakdown occurs in Si_3N_4 deposited on p-type GaN. The nitride thickness was 40 Å. Thirty-five $6 \times 10^{-4} \text{ cm}^2$ contacts were measured, with the voltage varied from 0-110 V in 0.5 V increments.

7. Summary

The surfaces and heterojunction interfaces of GaN were examined by x-ray and UV photoemission spectroscopy. The substrates used in these experiments were n- and p-type Ga-face GaN grown on 6H-SiC with a AlGaIn buffer layer. GaN surfaces were cleaned with an ammonia atmosphere, and C and O contamination was reduced to the detection limits of XPS ($<1\%$). The SiO_2 , Si_3N_4 , and HfO_2 were prepared using oxidation and nitridation plasma techniques to minimize disruption of the GaN surface.

Table 1 contains a summary of the electronic properties obtained for the GaN/ SiO_2 , GaN/ Si_3N_4 , GaN/ HfO_2 interfaces and respective surfaces. XPS was used to measure band bending as the interface is formed. UPS was used to measure the valence band maximum and the spectral width of the material, which allows the electron affinity to be calculated. A combination of XPS and UPS measurements provides a more complete understanding of the band alignment of the heterostructure.

The valence and conduction band offsets for the GaN/ SiO_2 interface were 2.0 and 3.6 ± 0.2 eV. The electron affinities of the GaN and SiO_2 surfaces were measured to be 2.9 and 1.1 ± 0.1 eV, respectively. A deviation from the electron affinity model of 1.7 ± 0.2 eV was observed, which was ascribed to a change in the interface dipole. Electrical data suggests the integrity of the oxide is similar to that grown on Si, with breakdown voltages of ~ 11 MV/cm. Band alignment measurements predict SiO_2 should passivate both n- and p-type GaN surfaces, making it an excellent choice for device fabrication.

For the GaN/ Si_3N_4 interface, the valence and conduction band offsets were 0.5 and 2.4 ± 0.2 eV. The interface represents type II band alignment, where the valence

band of the GaN lies below the valence band of the Si_3N_4 . The electron affinities of each material were measured to be 3.1 and 1.8 ± 0.1 eV. An interface dipole of 1.1 ± 0.2 eV was deduced for the GaN/ Si_3N_4 interface. These measurements predict that Si_3N_4 should passivate n-type GaN surfaces, but may not be appropriate for p-type surfaces.

The valence and conduction band offsets for the GaN/ HfO_2 interface were found to be 0.4 and 2.2 ± 0.2 eV. The electron affinities of each material were measured to be 3.0 and 2.7 ± 0.1 eV, respectively. A deviation from the electron affinity model of 1.9 ± 0.2 eV was observed. An instability of the HfO_2 film was demonstrated, as energy levels shifted by ~ 0.5 eV to during an 650 °C anneal. Band alignment measurements suggest HfO_2 should passivate n-type GaN surfaces. The valence band offset of ~ 1.0 eV should passivate p-type GaN surfaces, but the thermal instability should be examined further before device fabrication is brought forth.

In an attempt to understand the relation of the measured band alignments and the different models for heterostructure band alignment, our measured interface alignments for GaN/ SiO_2 , GaN/ Si_3N_4 , and GaN/ HfO_2 are compared in Figure 7.1. In each case the diagrams are aligned to the vacuum level at the dielectric. The bandgap of each material is indicated, as is the VBO. The position of the vacuum level of the clean GaN surface is indicated, and the difference between these values and the surface vacuum level is the deviation from the EAM. This difference represents the change in the interface dipole, and was found to be 1.7, 1.1, and 1.9 ± 0.2 eV for SiO_2 , Si_3N_4 , and HfO_2 on GaN, respectively. It is evident from the figure that the electron affinity model does not adequately describe the GaN-dielectric interface.

Also indicated in Figure 7.1 is the CNL of the materials based on the literature. Though the values for the CNL of SiO_2 and Si_3N_4 have not been reliably determined, a calculated value for the level of Si_3N_4 was obtained. The high value (0.86) for the dielectric screening parameter, S , as well as the large bandgap of SiO_2 does not allow the CNL to be reliably determined. A combination of the charge neutrality level of Si_3N_4 and experimental band alignment information allowed the dielectric screening parameter ($S = 0.26$) to be calculated. This suggests the band alignment and resulting interfacial dipole should be similar to the relative charge neutrality levels, which is the case shown in the Figure 7.1. For the GaN/HfO_2 interface, a value of S does not exist between 0 and 1 that can make the CNL's align. As such, the charge neutrality model does not adequately describe the interface.

A developing trend shown in Figure 7.1 is the interface dipole in relation to the dielectric. Though below the detection limits of XPS, Ga-O bonding undoubtedly exists at the GaN-oxide (SiO_2 and HfO_2) interface. With the Ga atomic layer more positive and the O layer more negative, the resulting interface dipole would be expected to significantly increase the oxide levels with respect to the GaN electronic levels, which is consistent with our observations. The interface dipole for the $\text{GaN}/\text{Si}_3\text{N}_4$ is significantly lower than that of the other two interfaces, as Ga-N-Si bonding may be present at the interface. A study of the source of the dipole would be complicated by the heterovalent nature of the interface. Results from this study indicate the presence of a Ga-O layer may substantially change the band alignment as the heterostructure is formed.

Of the dielectrics characterized for this dissertation, SiO_2 is the dielectric of choice for passivation of n- and p-type GaN. Careful considerations must be made if an

oxide is chosen to passivate GaN devices, as Ga-O bonding will occur at the interface. As compared to oxides, Si_3N_4 shows a significant reduction of the interface dipole. Alternatively, HfO_2 can be used for passivation, but the thermal instability must be carefully considered before device design can be implemented.

Table 7.1 BB and EA are defined as band bending and electron affinity, respectively. The positive or negative sign on the band bending represents upward or downward band bending, respectively. The negative values for the VBO for the GaN/Si₃N₄ interface represents type II band alignment, where the valence band of the GaN lies below the valence band of the Si₃N₄. For the GaN/SiO₂ and GaN/HfO₂ interfaces, type I band alignment is observed.

Material	Initial GaN BB	Interface BB	VBO	CBO	EA (GaN)	EA (dielectric)	Interface Dipole
n-GaN/SiO ₂	0.3	0.0	2.0	3.6	2.9	1.1	1.8
p-GaN/SiO ₂	-1.3	-2.2	2.0	3.6	3.2	1.1	1.5
n-GaN/Si ₃ N ₄	0.2	0.4	-0.6	2.5	3.1	1.8	1.2
p-GaN/Si ₃ N ₄	-1.1	-1.8	-0.4	2.3	3.1	1.8	1.0
n-GaN/HfO ₂	0.3	0.8	0.8	1.8	3.0	2.7	1.8
(as deposited)							
n-GaN/HfO ₂	0.3	0.4	0.4	2.2	3.0	2.7	1.8
(annealed)							

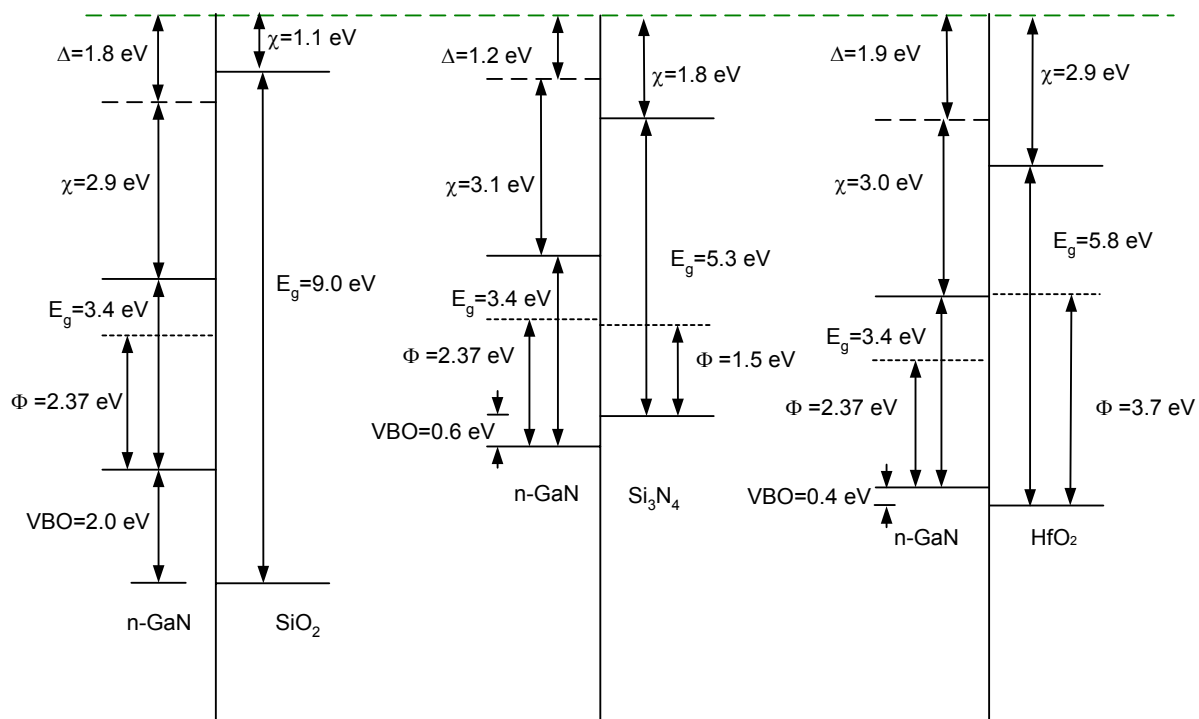


Figure 7.1 Experimental summary of the band alignment of GaN/SiO₂, GaN/Si₃N₄ and GaN/HfO₂ interfaces. The dashed line at the top of the figure corresponds to the electron affinity of the dielectric surfaces, which is common in each interface. The deviation from the electron affinity model is shown as Δ , and the charge neutrality level (CNL) is indicated as a dashed line within the band gap.

8. Recommended Future Research

The work presented in this dissertation is a systematic investigation of GaN-dielectric interfaces. There are substantial issues that are unresolved and some that were not investigated in this study. For high quality MISFET devices to be realized, further investigation must be conducted with the suggestions presented below.

Completion of the electrical characterization of the interfaces presented in this dissertation is a next step. Current-voltage and capacitance-voltage measurements would provide a more complete understanding of the electronic properties of each interface. The density of interface states, flat-band voltage shift, thickness, and leakage currents should be obtained for the GaN-dielectric interfaces. Though the SiC, AlGaN, and GaN were conducting, the breakdown measurements should be carefully conducted to ensure the field drop is only over the dielectric. Additionally, the number of interfaces can be reduced, improving the accuracy of the measurements.

Further investigation of the GaN/HfO₂ interface via photoemission should be conducted to examine the thermodynamic instability of the HfO₂ film. Additionally, ZrO₂ would prove advantageous to examine in parallel with HfO₂, as there are questions regarding its thermodynamic stability on Si. This systematic approach allows examination of various dielectrics, which will prove useful to take advantage of unique electrical properties of each material.

Finally, a continued photoemission study of GaN-dielectric interfaces could verify a trend proposed in this dissertation, namely that the Ga-O bonding at the interface greatly contributes to an interface dipole. After a more complete understanding of this

phenomenon is achieved, devices could be engineered to incorporate an ultra-thin nitride layer to reduce the interfacial dipole created during heterostructure formation. While additional studies must be completed on the GaN-dielectric interfaces, this dissertation provides the groundwork for the future fabrication of MISFET devices.