

THERMALLY STABLE OHMIC AND SCHOTTKY CONTACTS TO GaN

By

LARS FREDRIK VOSS

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2008

© 2008 Lars Fredrik Voss

To my grandparents.

ACKNOWLEDGMENTS

First and foremost I would like to thank my advisor Prof. Stephen J. Pearton for his guidance and for all of the support and opportunities he provided. I would also like to thank my other supervisory committee members, Fan Ren, Cammy Abernathy, David Norton, and Rajiv Singh, for their help and their time.

Thanks go to Dr. Patrick M. Lenahan for providing me with my first experience working in the semiconductor field while I was an undergraduate at Penn State as well as all of his advice and encouragement.

I thank the members of the Pearton, Ren, and Abernathy research groups with whom I have had the opportunity to work, including Luc Stafford, Kelly Ip, Jon Wright, Wantae Lim, Hungta Wang, Sam Kang, Travis Anderson, Soohwan Jang, Brent Gila, Jerry Thaler, Jennifer Hite, Mark Hlad and many, many more. I would also like to thank Ivan Kravchenko for his support in the UF Nanofabrication Facility.

Thanks also go to all the people at Sandia National Laboratories who gave me the opportunity to work there and with them for two enjoyable summers. I want to say thank you to my mentors, Randy J. Shul, Albert G. Baca, and Jeff E. Stevens, my managers, Charles Sullivan and Dale Hetherington, as well as all of the people I had the pleasure to work with while at Sandia including Carlos Sanchez, David Torres, Melissa Cavaliere, Karen Cross, Mark Overberg, Michael Cich, and many others.

Thanks also go to all of my family and friends as well.

TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS	4
LIST OF TABLES	7
LIST OF FIGURES	8
ABSTRACT	11
CHAPTER	
1 INTRODUCTION	13
2 BACKGROUND	18
2.1 Gallium Nitride Properties	18
2.1.1 Fundamental Properties	18
2.1.2 Electronic Properties	19
2.1.3 Crystal Structure	19
2.2 Properties of the Contact Materials to be Studied	19
2.2.1 Borides	19
2.2.2 Nitrides	20
2.2.3 Iridium	20
2.3 Electrical Contacts	21
2.3.1 Ohmic Contacts	22
2.3.1.1 Ohmic contacts to p-GaN	23
2.3.1.1 Ohmic contacts to n-GaN	24
2.3.2 Schottky Contacts	25
2.4 Experiments	27
2.5 Characterization Techniques	29
2.5.1 Current-Voltage	29
2.5.2 Capacitance-Voltage	30
2.5.3 X-ray Photoelectron Spectroscopy	31
2.5.4 Auger Electron Spectroscopy	31
3 THERMALLY STABLE OHMIC CONTACTS TO p-GaN	46
3.1 Ohmic Contacts	46
3.1.1 Fabrication of Ohmic Contacts	46
3.1.2 Nitride-Based Contacts	47
3.1.2.1 Experiment and discussion	47
3.1.2.2 Summary	50
3.1.3 Tungsten Boride and Chromium Boride-Based Contacts and Long Term Thermal Aging of Borides	50
3.1.3.1 Experiment and discussion	50

3.1.3.2 Summary	52
3.1.4 Contact Resistance for Other Boride-based Contacts	52
3.1.4.1 Titanium boride-based contacts	52
3.1.4.2 Zirconium Boride-based contacts.....	54
3.1.4.3 Gallium Nitride//Tungsten Boride-based contacts	55
3.1.5 Iridium-Based Contacts	57
3.1.5.1 Experiment and discussion.....	57
3.1.5.2 Summary	59
3.2 Conclusions	59
4 OHMIC CONTACTS TO n-GaN.....	89
4.1 Experiment.....	89
4.2 Results and Discussion	90
4.3 Conclusions.....	92
5 BORIDE-BASED SCHOTTKY CONTACTS TO p-GaN.....	103
5.1 Introduction.....	103
5.2 Experimental Details	104
5.3 Results and Discussion	106
5.4 Conclusions.....	110
6 BORIDE AND IR BASED CONTACTS FOR LIGHT EMITTING DIODES	123
6.1 Introduction.....	123
6.2 Experimental.....	124
6.3 Results and Discussion	125
6.4 Conclusions.....	127
7 CONCLUSION.....	132
LIST OF REFERENCES	137
BIOGRAPHICAL SKETCH	144

LIST OF TABLES

<u>Table</u>	<u>page</u>
2-1 Bulk GaN properties	33
2-2 Properties of common semiconductors	34
2-3 Properties of the borides	35
2-4 Properties of the nitrides	36
2-5 Properties of Ir	37
3-1 Concentration of elements detected on the as-received surface (in atom%)	60
3-2 Concentration of elements detected on the as-received surfaces (in atom%).....	61
3-3 Concentration of elements detected on the as-received surfaces (in atom%).....	62
3-4 Summary of specific contact resistances	63
4-1 Percent change in specific contact resistance during thermal aging.....	94
5-1 Comparison of different barrier height calculations	112
6-1 Influence of long-term aging at 200°C and 350°C on the turn-on voltage and reverse current of InGaN/GaN MQW-LEDs.	127

LIST OF FIGURES

<u>Figure</u>	<u>page</u>
1-1 Market forecast for GaN-based devices.....	17
2-1 Intrinsic carrier concentration of GaN, GaAs, and Si.....	38
2-3 Flat band diagram for a p-type Ohmic contact	40
2-4 Flat band diagram for a p-type Schottky contact.....	41
2-5 LED cross section (a) before and (b) after processing.....	42
2-6 Linear transmission line pattern.....	43
2-7 Resistance vs. pad spacing plot.....	44
2-8 Schottky contact schematic.....	45
3-1 Specific contact resistance and sheet resistance under the contact of Ni/Au/ X/ Ti/Au contacts as a function of anneal temperature.	64
3-3 Scanning electron microscopy images of Ni/Au/TaN/Ti/Au contacts (a) as deposited (b) annealed at 600 °C (c) annealed at 700°C and aged at 200 °C until the contacts became non-Ohmic and (d) annealed at 1000 °C.....	66
3-6 Specific contact resistance versus measurement temperature.	69
3-7 Specific contact resistance and sheet resistance under the contact as a function of long term thermal aging at 350°C.	70
3-8 Depth profiles of W ₂ B-based contacts (a) as deposited (b) annealed at 600 °C (c) annealed at 700 °C and aged at 350°C and (d) annealed at 1000 °C.....	71
3-9 Specific contact resistivity of Ni/Au/TiB ₂ /Ti/Au Ohmic contacts and p-GaN sheet resistance under the contact as a function of annealing temperature.....	72
3-10 Secondary electron images of Ni/Au/TiB ₂ /Ti/Au contact pads on p-GaN as-deposited (top) or after annealing at either 800(center) or 900°C (bottom).	73
3-11 Surface scans of Ni/Au/TiB ₂ /Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature. The as-deposited sample is at top, that annealed at 800°C at center and that at 900°C at bottom	74
3-12 Depth profiles of Ni/Au/TiB ₂ /Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature. The as-deposited sample is at top, that annealed at 800 pC at center, and that at 900 oC at bottom.	75

3-13	Specific contact resistance of Ni/Au/ZrB ₂ /Ti/Au and ZrB ₂ /Ti/Au Ohmic contacts and p-GaN sheet resistance under the contact as a function of annealing temperature.....	76
3-14	Surface scans and depth profiles of Ni/Au/TiB ₂ /Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature.	77
3-15	Scanning electron microscopy images of Ni/Au/TiB ₂ /Ti/Au contact pads on p-GaN as-deposited (top) or after annealing at either 750 (center) or 800°C (bottom).....	78
3-16	Surface scans and depth profiles of ZrB ₂ /Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature.	79
3-17	Elemental maps obtained from scanning AES of ZrB ₂ /Ti/Au Ohmic contacts pads on p-GaN.....	80
3-18	Specific contact resistivity of W ₂ B/Ti/Au Ohmic contacts and measured p-GaN sheet resistance under the contact as a function of annealing temperature.....	81
3-19	AES surface scans of W ₂ B/Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature.	82
3-20	Depth profiles of W ₂ B/Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature.	83
3-21	Current-voltage curves for Ni/Au/Ir/Au contacts.	84
3-22	Current-voltage curves for Ni/Ir/Au contacts	85
3-23	Depth profiles for Ni/Au/Ir/Au contacts (a) annealed at 300 °C (b) annealed at 500 °C and (c) annealed at 700 °C.	86
3-24	Depth profiles for Ni/Ir/Au contacts (a) annealed at 300 °C (b) annealed at 500 °C and (c) annealed at 700 °C.	87
3-25	Scanning electron microscopy images of Ni/Au/Ir/Au contacts.....	88
4-1	Specific contact resistance as a function of anneal temperature.....	95
4-2	Scanning electron microscopy images of annealed contacts	96
4-3	Depth profiles of Ti/Al/TaN/Ti/Au contacts (a) as deposited (b) annealed at 600°C. (c) annealed at 800°C and (d) annealed at 800°C and aged at 350°C.	97
4-4	Depth profiles of Ti/Al/TiN/Ti/Au contacts (a) as deposited (b) annealed at 600°C. (c) annealed at 800°C and (d) annealed at 800°C and aged at 350°C.	98
4-5	Depth profiles of Ti/Al/ZrN/Ti/Au contacts (a) as deposited (b) annealed at 600°C. (c) annealed at 800°C and (d) annealed at 800°C and aged at 350°C.	99

4-7	Specific contact resistance as a function of anneal time.....	101
4-8	Specific contact resistance as a function of long term thermal aging.....	102
5-1	XPS spectra without (top) and with (bottom) a boride overlayer. The left-hand spectrum in the top figure corresponds to the Ga 3d core level whereas the right-hand panel presents the spectrum of the valence band region.....	113
5-3	Forward current-voltage characteristic of W ₂ B-based (top) and W ₂ B ₅ -based (bottom) Schottky diodes as a function of annealing.....	115
5-4	Influence of the annealing temperature on the characteristic energy related to the tunneling probability. Dashed and dotted lines correspond to the values of E_0 for $N_A \sim 10^{19}$ and $5 \times 10^{19} \text{ cm}^{-3}$ respectively.	116
5-5	Influence of the annealing temperature on the apparent Schottky barrier height derived from IV measurements.....	117
5-6	Dependence of the apparent Schottky barrier height on the parameter ξ defined as the difference between the valence band maximum and the position of the Fermi level. Low and high	118
5-7	As-measured and after oxide correction dependence of C^{-2} versus V of Au/Pt/W ₂ B/p-GaN Schottky diodes. The measurement frequency was set to 1 kHz.	119
5-8	Reverse current-voltage characteristic of W ₂ B-based Schottky diodes as a function of measurement temperature.	120
5-9	Influence of the annealing temperature on the breakdown voltage.	121
5-10	Depth profiles of W ₂ B/Pt/Au contacts and W ₂ B ₅ /Pt/Au rectifying contacts (a,b) before and (c,d) after annealing at 600°C.	122
6-1	Optical micrograph of an as-fabricated MQW-LED. The p-contact at the center of the diode is 80 μm in diameter.....	128
6-2	I - V characteristics of MQW-LEDs with Ni/Au, Ni/Au/TiB ₂ /Ti/Au, and Ni/Au/Ir/Au p-Ohmic contacts. The inset shows emission spectra from as-fabricated LEDs at various injection currents.....	129
6-3	Influence of long-term aging at 250°C and 350°C on the I - V characteristics of LEDs with (a) Ni/Au, (b) Ni/Au/TiB ₂ /Ti/Au, and (c) Ni/Au/Ir/Au p-Ohmic contacts.....	130
6-4	Image of aged LEDs with (a) Ni/Au and (b) Ni/Au/TiB ₂ /Ti/Au p-Ohmic contacts. In (a), the picture was taken for a forward bias of 10 V ($I = 80 \mu\text{A}$), while the forward voltage in (b) was 4.5 V ($I = 300 \mu\text{A}$).	131

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

THERMALLY STABLE OHMIC AND SCHOTTKY CONTACTS TO GaN

By

Lars Fredrik Voss

May 2008

Chair: Stephen J. Pearton

Major: Materials Science and Engineering

This dissertation is focused on the development of Ohmic and Schottky contacts to both n- and p-type Gallium Nitride for use in microelectronic and optical devices. The goal is to develop low resistance contacts with greater thermal budgets and superior thermal aging characteristics to those commonly in use today as well as to understand the mechanisms by which these contacts may fail. In addition, p-type Ohmic contacts have been used to fabricate light emitting diodes (LEDs) which display far superior aging properties than those made with conventional Ni/Au contacts.

Ohmic contacts to p-GaN were fabricated using a variety of refractory materials. The materials examined were of three basic types: boride, nitride, and the refractory metal Ir. The boride family includes W_2B , W_2B_5 , CrB_2 , ZrB_2 , and TiB_2 . The nitrides examined were TaN, TiN, and ZrN. Contacts based on these materials were fabricated using either a GaN//Ni/Au/X/Ti/Au, GaN//X/Ti/Au, or GaN//Ni/X/Au scheme, where X is the refractory material. Contact resistances as low as $\sim 1 \times 10^{-4} \Omega/\text{cm}^2$ were consistently achieved after annealing at temperatures from 500-1000°C for 60 s in N_2 using these materials for p-GaN with a carrier concentration of $\sim 1 \times 10^{17} \text{ cm}^{-3}$. In addition, high temperature thermal aging was

performed on selected schemes as well as on devices in order to attempt to estimate long term performance.

Next, nitride-based Ohmic contacts to n-GaN are examined. The nitride was used to replace the conventional Pt, Ni, or Mo diffusion barrier in Ti/Al based contacts, for a contact scheme of GaN//Ti/Al/X/Ti/Au. These contacts achieve a similar specific contact resistance of $\sim 1 \times 10^{-4} \Omega/\text{cm}^2$ for samples with a carrier concentration of $1 \times 10^{17} \text{ cm}^{-3}$ as that achieved with a Ti/Au/Pt/Au contact. The contacts are also examined as a function of aging and are found to display less intermixing of layers than those fabricated with a Ni diffusion barrier.

Schottky contacts to p-GaN were also fabricated using the family of boride based materials with the scheme GaN//X/Pt/Au. These were found to exhibit tunneling transport through the metal-semiconductor junction and barrier heights of $>3.5 \text{ eV}$ were determined from the fit of the current-voltage (IV) curves. X-ray Photoelectron Spectroscopy was used to determine a true barrier height for these borides on p-GaN of 2.7 eV , close to that expected from the Schottky-Mott model. Capacitance-voltage (CV) measurements confirm the IV barrier height, but reveal a thin interfacial layer likely arising from oxidation or defects at the surface.

CHAPTER 1 INTRODUCTION

Semiconductor technology and its rapid improvements in device speed, yield, and density have enabled much of the technology and advancements the world has experienced over the past half century. Beginning with the first transistor developed in 1947 at AT&T Bell Labs and then in 1957 with the first integrated circuit by Jack Kilby, the pace of improvement in semiconductors and integrated circuitry is unmatched by any other technological development in human history, and few have been more influential. Today, what once seemed ridiculously optimistic is possible and billions of transistors are present in a single integrated circuit [1]. Silicon based technology has come to dominate an overwhelming share of the semiconductor market, and for good reason. The main advantage of Si-based technology is the overwhelming knowledge base that exists as well as the fact that it possesses a wide range of acceptable properties. It possesses a higher melting point than Ge, from which the first devices were made, as well as a stable oxide which displays low leakage current. Further, nearly all of its properties fall into the acceptable range necessary for use in nearly all applications, including a reasonable band gap, carrier mobility, and breakdown field.

For certain areas of application, however, Si is unacceptable. For applications requiring higher speed electronics, GaAs dominates the market. This is due to a much higher electron mobility, greater than 6 times that of Si. In addition, Si is also inappropriate for optoelectronic applications due to its indirect band gap. GaAs-based devices are also useful in this area. However, for high power, high temperature electronics as well as emission of wavelengths in the blue to ultra-violet range, GaAs's properties are insufficient. It is therefore necessary to develop fabrication techniques for alternatives to Si and GaAs [2,3]. For these applications GaN is the material of choice. Its wide, direct band gap of 3.4 eV allows for emission in the UV range,

while the use of InGaN and AlGaN allow for tunable emission over the range 1.92 to 6.2 eV. [4-37]

Development of GaN-based electronics has been necessitated due to the limitations of SiC, another semiconductor used for high power and high temperature electronics. SiC MOSFETs are limited by primarily thermal oxides, as the gate contact degrades and becomes leaky at higher operating temperatures. In addition, the electron mobility is low, only $\sim 400 \text{ cm}^2/\text{V-s}$, resulting in low power-added efficiencies of less than 30% for operation between 1 and 5 GHz. Because of its nature, GaN is a superior choice due to its wider bandgap as well as greater chemical stability, leading to improved performance at higher operating temperatures.

GaN based electronics are already in production, most notably high electron mobility transistors (HEMTs). Other devices of interest include heterojunction bipolar transistors (HBTs) and metal oxide field effect transistors (MOSFETs). In order to fully realize the potential of GaN-based electronics, improvements in their processing must be achieved in addition to the significant improvements in material quality that are necessary. This includes improvements in high temperature processing and operation, one area of which is the development of both Ohmic and Schottky contacts which are able to withstand high temperatures without degradation of device characteristics or contact structure [4]. This becomes especially important as the quality of the materials improves and failure is due to the contacts.

While electronic applications for GaN are important, optoelectronic applications are currently dominant. As Figure 1-1 indicates, most of the current and projected market are for optical applications. The first bright blue LED using GaN to be put into production was demonstrated by Shuji Nakamura in 1993 at Nichia Corporation. Since that time, a great deal of progress has been made in the attempt to realize the full potential of GaN for light emitting

applications. The promise of solid state lighting is one that grows more important with each passing year, as the world's insatiable hunger for energy grows while reserves of conventional fossil fuels struggle to keep up. Because production cannot indefinitely keep up with demand, focus should and is on increasing the efficiency of consumption. Nearly 10% of world energy consumption is used for lighting. Most of this is currently done with extremely inefficient incandescent bulbs. While compact fluorescent lighting has grown more popular and offers a substantial improvement in energy efficiency, it cannot compete with that possible with the wide spread use of LEDs. Further, CFBs present a hazard due to the non-trivial amount of mercury present in each bulb. Because of this, any large scale use of the bulbs must go hand in hand with proper disposal of them in order to prevent contamination of the environment. Solid state lighting does not present this problem.

While many challenges still exist to realizing commercially viable solid state lighting sources, including significant improvement in the efficiency of the green emitting alloys as well as possible improvements in the phosphors used to emit the yellow and white light desired, it is still important to develop improved contact structures in order to allow for longer life times and operation in environments with higher temperatures. For p-type GaN especially, existing contact schemes could be improved to offer more stable performance. Failure of GaN-based devices due to contact failure should be minimized or eliminated.

The goal of this work is to develop improved contact schemes for both electronic and optoelectronic applications that will offer acceptable specific contact resistances and barrier heights which will be stable over a wide range of processing temperatures as well as during long term high temperature aging. Chapter 2 deals with the basic properties of GaN as well as an overview of the processing and characterization techniques that were utilized during this work.

The rest of this dissertation is devoted to the experiments and analysis. First, Ohmic contacts to p-GaN using a variety of high temperature materials are discussed. The next section deals with Ohmic contacts to n-GaN. A section on Schottky contacts to p-GaN follows. The final chapter discusses the use of the Ohmic contacts to p-GaN in light emitting diodes.

MARKET FORECAST FOR GAN-BASED

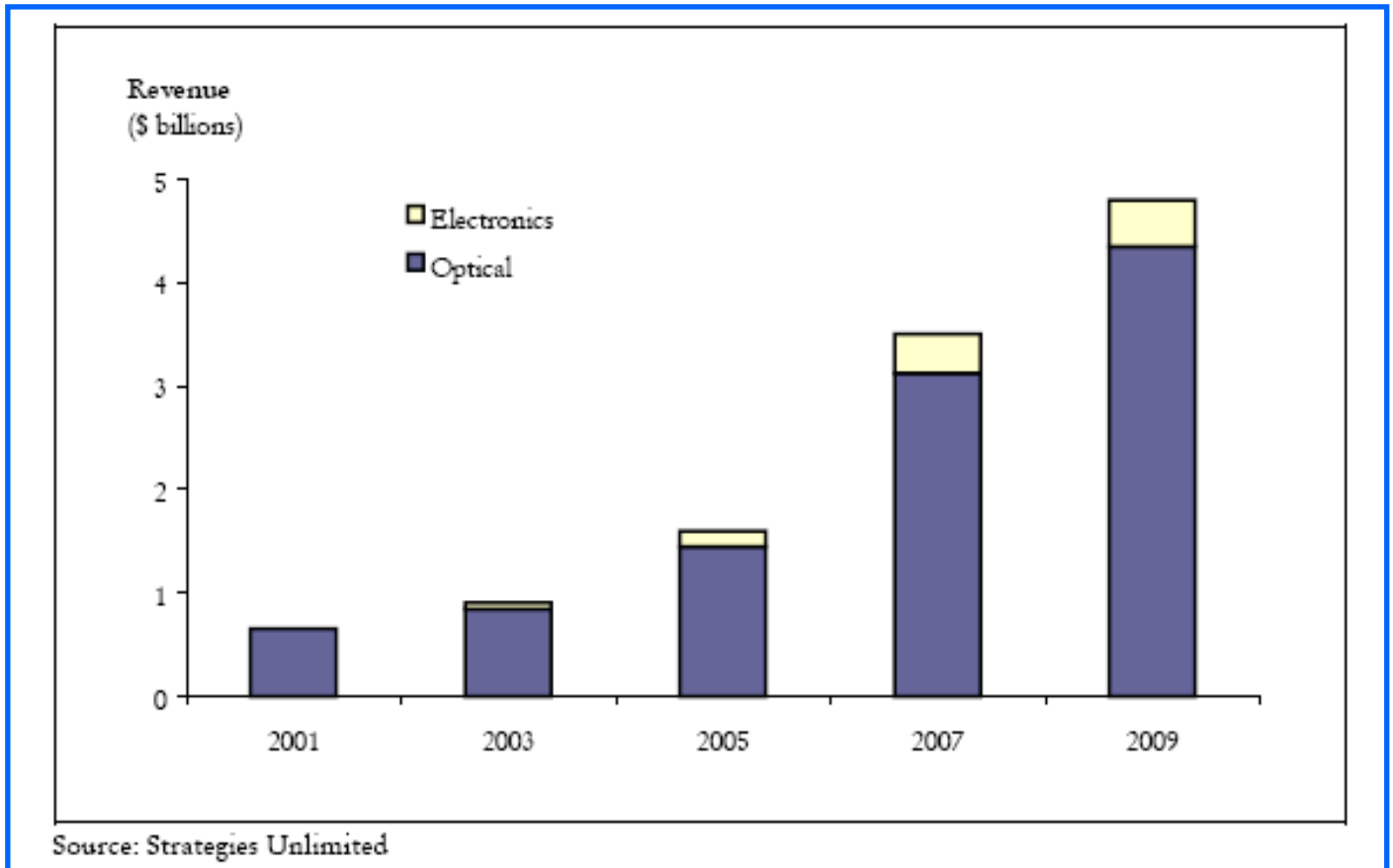


Figure 1-1 Market forecast for GaN-based devices

CHAPTER 2 BACKGROUND

2.1 Gallium Nitride Properties

2.1.1 Fundamental Properties

The materials properties of GaN make it desirable for a variety of applications. For optical electronics, GaN holds great promise. Because it is a direct band gap semiconductor, it is an efficient light emitter. GaN fills the need for a blue and ultraviolet wavelength emitter that is left by other materials due to its band gap of 3.475 eV. Its exciton binding energy is 28 meV. This is not as high as another blue emitters, ZnO, but GaN technology is more developed. The first GaN LED was introduced in 1993; however, further development of the GaN system is necessary for better LEDs and LDs.

In addition to optical applications, GaN is robust and therefore a candidate for high temperature and high power applications, with potentially superior electronic properties when compared with SiC [38]. The reason for this is due to the relatively wide band gap when compared to Si and GaAs. Figure 2-1 displays the intrinsic carrier concentration as a function of temperature of GaN, Si, and GaAs. Because of the wide band gap, the intrinsic carrier concentration is much lower; 10^{15} cm^{-3} is reached at 300°C for Si, 500°C for GaAs, and at 1000°C for GaN. Because of this, GaN can be operated at much higher temperatures before device performance degrades and breaks down.

Table 2-1 contains some basic physical properties of GaN [39,40]. A key problem in device operation is the presence of the lattice mismatch of GaN with the commonly used sapphire (13%) and SiC (3%) substrates, which results in a large number of lattice defects which hinder electrical conduction.

2.1.2 Electronic Properties

The properties GaN possesses are advantageous for a variety of reasons. They, as well as those of other common semiconductors, are displayed in Table 2-2 [40,41,42]. It has a high breakdown field, greater than 50 times that of Si or GaAs, which allows for its use in high power electronic applications. The high electron mobility for its 2D electron gas and saturation velocity allows its use in high speed electronics. In addition, heterostructures such as AlGaIn/GaN allow for the manufacture of interesting and high speed devices such as HEMTs. Recent work suggests that the 1.5 W/cm may be a lower limit for the thermal conductivity of GaN. GaN also shows excellent resistance to irradiation.

2.1.3 Crystal Structure

The thermodynamically stable phase of GaN is the hexagonal wurtzite structure, referred to as the α -phase. In addition, a metastable β -phase with a zinc blende structure exists. These two phases only differ in the stacking sequence of Ga and N; their coexistence in epitaxial layers is possible due to stacking faults [43]. The lattice parameters are $a = 3.189 \text{ \AA}$ and $c = 5.185 \text{ \AA}$. The wurtzite structure of Ga-face and N-face GaN is shown in Figure 2-2.

2.2 Properties of the Contact Materials to be Studied

2.2.1 Borides

The family of borides to be studied includes the refractory compounds W_2B , W_2B_5 , CrB_2 , TiB_2 , and ZrB_2 . Previous work has shown the promise of using refractory materials such as W as contacts to p-GaN. These borides also possess many of the requisite characteristics for use as electrical contacts for semiconductor devices. Table 2-3 summarizes known properties of the borides to be studied. Each of the borides possesses a high melting temperature, good thermal and electrical conductivities, high work functions, and large heats of formation. Each of these properties is important when considering a material for use in electrical contacts. The high

melting temperature is necessary in order to ensure that the material is able to withstand the elevated annealing temperatures which are generally necessary for Ohmic contact formation. A high melting temperature is an indication of material stability as well. A large electrical conductivity is necessary so as to achieve a low resistance within the contact itself as well as to avoid too much self heating, which can lead to inconsistent performance and diffusion between contact layers during operation. A large thermal conductivity is necessary for this reason as well. For a p-type material, a large work function is desirable in order to achieve the proper band bending for thermionic carrier transport or at least to minimize the barrier for tunneling transport. Finally, a large heat of formation is desirable in order to minimize reactions at the semiconductor-contact interface during operation. These materials have previously been examined for use in contacts to n-GaN and have displayed good characteristics as a diffusion barrier in a Ti/Al-based contact compared to more conventional metals such as Pt or Ni.

2.2.2 Nitrides

The second class of materials to be studied is the nitrides. The materials chosen were TaN, TiN, and ZrN. Table 2-4 summarizes the properties of these nitrides. They possess many of the same characteristics as the borides and are therefore also worthwhile to study. These include a high melting temperature, good thermal and electrical conductivities, a work function, and large heats of formation. These nitrides have been studied for use in thin film resistors, wear-resistant coatings on tools, thermal printer heads, gate electrodes, and diffusion barriers in Cu interconnection, which suggest their suitability as diffusion barriers for GaN-based electronics. They will be examined in this case for Ohmic contacts to both n- and p-type GaN.

2.2.3 Iridium

The final material to be studied for use in contacts to p-GaN will be Iridium. Properties of Ir are summarized in Table 2-5. Note that Ir has the required high melting temperature, large

work function, and reasonable thermal and electrical conductivities. Ir has previously been studied for use as a contact to p-GaN. Here, it will be examined for use in Ni-based contacts to p-GaN as an intermediate layer. It has already been demonstrated that Ir acts a superior diffusion barrier in Ti/Al-based contacts to n-GaN compared to Ni.

2.3 Electrical Contacts

High quality electrical contacts to semiconductors are critical for the manufacture of all types of devices. While the requirements for specific devices and applications may differ, it is always necessary to connect these devices to the outside world. Generally, a contact that displays the lowest specific contact resistance with minimal drift during extended operation is the most desirable, although for certain applications other properties may be more critical. For instance, in light emitting devices it is often desirable to have either transparent contacts or contacts with high reflectivities in the range of emission wavelengths in order to maximize light output. For high temperature applications it is critical that contacts are stable during operation at high temperature; thus materials which display little intermixing and minimal reactions are necessary in addition to the requirement of good electrical and thermal conductivities.

Electrical contacts to semiconductors are generally understood as the junction between the semiconductor and a metal or other contact material, as well as any layers of metal or other material above this. The electrical properties of the contact are controlled by the materials at the junction and it is often necessary to anneal the contacts at elevated temperatures in order to achieve the required properties through elimination of defects, removal of compensators such as Hydrogen, or formation of low resistance intermetallic phases. In addition, the layers above the junction itself can also influence the performance of the contact. It may be necessary to use an overlayer such as Au in order to promote current spreading so that the conduction is spread evenly over the area of the contact as well as to prevent oxidation of the contact at room

temperature. Other materials may be used as diffusion barriers in order to minimize intermixing between various contact layers which may lead to the formation of undesirable secondary phases, segregation of layers when it is desirable that they be intermixed, or even to prevent out-diffusion of the semiconductor to the surface of the contact. Two types of contacts exist, and it is important to understand what materials properties may be important in order to fabricate each.

2.3.1 Ohmic Contacts

Ohmic contacts are those which obey Ohm's Law:

$$V = IR \quad (2.1)$$

Note that this is a linear relationship and thus current is allowed to flow into and out of the semiconductor without distortion of the signal. In general, the most critical component of an Ohmic contact is a low specific contact resistance. This will minimize the power consumption of the contact, which will also serve to minimize the internal heating of the contact and thus allow for prolonged operation with predictable performance. An ideal Ohmic contact would have no noticeable effect on device performance, as it would consume none of the power in the system nor would it cause any rise in temperature during operation.

In theory, fabrication of Ohmic contacts should be straightforward. For semiconductors with moderate doping, the dominant mechanism of current flow is generally thermionic emission, which is governed by Equation 2-2:

$$\rho_c = \frac{k}{qA^{**}T} \exp\left(\frac{q\phi_b}{kT}\right) \quad (2.2)$$

where k is Boltzmann's constant, q the electronic charge, A^{**} is the Richardson's constant, T the temperature, and ϕ_b the barrier height. In this model, electrons are excited over a barrier. It is clear, then, that the barrier height should be small in order to produce a low contact resistance.

For p-type conduction, a metal with a work function larger than that of the semiconductor should

be sufficient. The desired flat band diagram for this situation is shown in Figure 2-3 [40]. It is clear from this diagram that holes may pass easily between the metal and the contact at the junction.

However, for some semiconductors it can be difficult to find materials systems that produce an Ohmic contact through thermionic emission, especially for p-type semiconductors. A wide band gap and large electron affinity, such as with GaN, effectively limits the choices to materials which have a very high work function. A second approach for formation of Ohmic contacts to semiconductors utilizes another form of carrier transport: tunneling. This type of transport is characterized by the carriers tunneling through the potential barrier at the semiconductor-contact junction. Equation 2-3 describes the specific contact resistance for this type of transport:

$$\rho_c = \exp\left(\frac{2\sqrt{\epsilon_s m^*} \phi_b}{\hbar \sqrt{N_D}}\right) \quad (2.3)$$

The relevant terms to consider in this equation are the barrier height and the doping density, N_D or N_A for p-type semiconductors. It is obvious that in order to achieve a low contact resistance the barrier height must be minimized and the doping density must be maximized. Barrier height is determined by material choice. Doping density can be determined during growth of the material, with ion implantation, or use of contacts which can increase doping through interactions with the semiconductor.

2.3.1.1 Ohmic contacts to p-GaN

High quality, low resistance Ohmic contacts to p-GaN are difficult to achieve. This is due to several factors: the relative dearth of appropriate metal systems due to the large work function of GaN, low hole densities due to the difficulty in achieving a high doping concentration during growth, the presence of compensating hydrogen interstitials, and the presence of compensating

nitrogen vacancies. Despite this, several materials systems have been found to produce Ohmic behavior. These are generally based on a high work function metal such as Ni, Pd, or Pt with an overlayer of Au and have been found to achieve specific contact resistances in the range of $1 \times 10^{-4} \Omega\text{-cm}^2$ for hole concentrations of $\sim 10^{17} \text{ cm}^{-3}$ [44-48]. Ni/Au contacts are the most common. The Ni serves to remove hydrogen from the near surface region of the p-GaN at elevated annealing temperatures, as the Ni hydride is thermodynamically favorable. In addition, at these elevated temperatures Au begins to diffuse in towards the GaN and it has been found that the Au can form intermediate phases with the Ga in the form of AuGa and AuGa₂ [49]. This can serve to further increase the near surface doping through the formation of Ga vacancies in the GaN which act as acceptors. However, at these anneal temperatures of $> 500^\circ\text{C}$, the Au and Ni may completely exchange places at the GaN surface [44]. This leads to a severe roughening of the contact surface and degraded performance and limits the temperature at which anneals may take place as well as the lifetime of the contacts when operated at high temperature or, equivalently, high powers. Because one of the most attractive features of GaN is its ability to operate reliably under these conditions, it is important to find a contact system that will perform better.

2.3.1.1 Ohmic contacts to n-GaN

Ohmic contacts to n-GaN are more studied, better understood, and easier to achieve compared to those to p-GaN. The most common materials system used is GaN//Ti/Al/X/Au, where X is a material chosen to act as a diffusion barrier to separate the Al and Au. This is necessary, as Al and Au will react to form AlAu₄ [50]. This phase is viscous at low temperatures and lateral flow can create problems, especially as the gate/source separation becomes small. Because of this, there is great interest in the use of high temperature metals. The Ti is present at the junction in order to form TiN through reaction with the GaN, which creates nitrogen

vacancies and thus increases the donor density. The Au overlayer is present in order to prevent oxidation as well as to promote current spreading in the contact.

2.3.2 Schottky Contacts

The other type of electrical contact required for electronic devices are known as Schottky contacts or diodes. Schottky contacts allow little or no current to flow through them until a critical voltage is reached, above which large amounts of current flow. This is called the forward biased region. In the reverse bias region, voltage is applied in the opposite direction and no current flows initially. However, if the voltage is pushed high enough then breakdown occurs, a huge amount of current flows through the contact and the contact is generally destroyed.

Ideal Schottky contacts are formed in the absence of any surface states. When a metal and semiconductor are brought together, the Fermi levels must line up. In order for this to occur, a charge exchange occurs between the two materials. When this occurs, a space charge or depletion region is formed and a barrier to current flow is created. For p-type semiconductors, the flat band diagram is shown in Figure 2-4.

The barrier height, ϕ_{bp} , for a p-type semiconductor is given by the equation

$$q\phi_{bp} = E_g - q(\phi_m - \chi) \quad (2.4)$$

where E_g is the band gap, ϕ_m is the metal work function, and χ is the electron affinity of the semiconductor. Invariably, however, surface states are present. This makes the prediction of barrier height using the equation above inaccurate. In order to determine barrier height in this case, it is necessary to fabricate a specimen to test.

The predominant carrier in Schottky contacts is the majority carrier unlike a pn junction diode. Two mechanisms for current flow exist: thermionic emission (TE) and thermionic field emission (TFE) or tunneling. While some authors have reported values for barrier heights on p-

GaN using the TE model, most of the work has demonstrated that TFE is the dominant transport mechanism. Reported barrier heights on p-GaN range from ~0.5 to 2.9 eV even for the same metallization scheme because the mechanism of current flow is not definitively established [51-65].

In the case of TE, electrons or holes are excited over the potential barrier and the forward current is given by the following expression:

$$J_F = A^* T^2 \exp\left(-\frac{e\phi_B}{k_B T}\right) \exp\left(\frac{eV}{nk_B T}\right) \quad (2.5)$$

where $A^*=103.8 \text{ Acm}^{-2}\text{K}^{-2}$ is the effective Richardson's constant for p-GaN, T is the absolute temperature, e is the electronic charge, ϕ_B is the SBH, k_B is the Boltzmann's constant, and V is the applied voltage.

In the case of TFE, quantum tunneling of charge carriers through the barrier occurs and the forward current can be described by

$$J_F = J_0 \exp\left(\frac{qV}{E_0}\right) \quad (2.6)$$

where the saturation current density J_0 is given by

$$J_0 = \frac{A^* T \left[\pi E_{00} q (\phi_B - V - \xi) \right]^{0.5}}{k_B \cosh(E_{00}/k_B T)} \exp\left(-\frac{q\xi}{k_B T} - \frac{q(\phi_B - \xi)}{k_B T}\right) \quad (2.7)$$

In Eq. (2.7), $\xi=(E_F-E_V)/q$ is the difference between the valence band maximum and the position of the Fermi level and $E_0 = E_{00} \coth(E_{00}/k_B T)$ is the characteristic energy related to the tunneling probability.

2.4 Experiments

The goal of this work is to find suitable contact systems for use at high temperatures on n- and p-GaN. Towards this end, the previously discussed materials will be investigated in order to determine which of them allow good quality Ohmic and Schottky contacts. In addition, a study will be made of devices which use p-GaN, mainly LEDs. The contacts will be aged at high temperatures and compared with more conventional schemes. A variety of techniques will be used to characterize the contacts and devices in order to determine their performance and to better understand what is happening.

The main experiments that will be done are the processing of the Ohmic and Schottky contacts for electrical characterization. The following schemes will be produced and analyzed:

1. GaN//Ni/Au/X/Ti/Au for p-type Ohmic contacts, where X indicates the refractory material to be examined
2. GaN//X/Ti/Au for p-type Ohmic contacts
3. GaN//Ni/Ir/Au for p-type Ohmic contacts
4. GaN//Ti/Au/X/Ti/Au for n-type Ohmic contacts
5. GaN//X/Pt/Au for p-type Schottky contacts

In case (1), the Ni/Au should act as an Ohmic contact while the boride layer provides a diffusion barrier to prevent breakdown of the metallization at elevated temperatures. The Ti layer is present in order to promote adhesion of the Au to the rest of the contact. The Au overlayer is to prevent oxidation and act as a current spreading layer. In case (2), it is hoped that at least some of the borides may provide an Ohmic contact on p-GaN. Case (3) may provide some insight into the importance of Au at the GaN surface for these types of contacts. Case (4) is based on standard Ohmic contacts to n-GaN, with a nitride used as the diffusion barrier. Case

(5) will be used to fabricate Schottky contacts, as the Pt should not be as reactive as Ti should it reaches the GaN surface and is therefore used as the adhesion layer.

Samples will be prepared on p-GaN and n-GaN wafers grown in an MOCVD reactor. P-GaN will be 3 μm thick Mg-doped and grown on c-plane Al_2O_3 . Hole concentration after activation obtained from Hall measurements is $\sim 1 \times 10^{17} \text{ cm}^{-3}$. The same doping will be used for both Ohmic and Schottky contacts. This is because it is extremely difficult to obtain a higher doping level for use in Ohmic contacts. At lower doping concentrations, it is not possible to obtain an Ohmic contact for use in Schottky contacts. For Ohmic contacts to n-GaN, epilayers 3 μm thick Si-doped and grown on c-plane Al_2O_3 with an electron concentration of $\sim 1 \times 10^{17} \text{ cm}^{-3}$ will be used.

In order to fabricate the samples, photolithography will be performed using a Karl Suss MJB3 aligner using positive photoresists. Samples for Ohmic contacts will then be etched in a Unaxis ICP tool in order to isolate devices and prevent current spreading. Prior to patterning for the metal layers, p-GaN samples will be dipped in a 1M KOH solution for one minute in order to remove surface oxide. Following patterning, surface treatments may be necessary to improve performance. A 30 s RIE O_2 plasma exposure to remove carbon followed by a 10% HCl dip for one to ten minutes immediately prior to insertion into the deposition chamber will be employed to ensure a clean surface. Initial Ni/Au layers for contacts to p-GaN will be deposited using an e-beam evaporator in order to minimize surface damage. For deposition of all other layers, a Kurt Lesker sputterer will be employed. This is necessary, as the refractory materials cannot be evaporated. In addition, it is necessary to deposit all overlayers in the sputterer in order to minimize oxidation. Following lift off of the metal layers, rapid thermal annealing will be

performed at a range of temperatures from 300-1000°C in order to determine how the properties of the contacts are affected at a variety of annealing temperatures.

Following the development of these contacts, devices will be fabricated. While p-GaN is unsuitable for use in HEMTs due to its low hole mobility, it is necessary for use in LEDs, LDs, and HBTs. LEDs will be fabricated on wafers with the structure shown in Figure 2-5. These will be compared to devices using more traditional metal schemes such as Ni/Au. They will then be thermally aged in order to determine the performance relative to Ni/Au when maintained at an elevated temperature.

2.5 Characterization Techniques

A variety of techniques will be utilized in order to determine device characteristics as well as to observe the physical and chemical structure of the contacts. The techniques to be employed are

1. Current-voltage measurements
2. Capacitance-voltage measurements
3. X-ray Photoelectron Spectroscopy
4. Auger Electron Spectroscopy
5. Scanning Electron Microscopy

2.5.1 Current-Voltage

Current-voltage (IV) measurements will be performed using an Agilent 4156 Semiconductor Parameter Analyzer. Two probe measurements will be performed when possible. However, if problems which make it impossible to extract contact resistance arise due to high sheet resistance and the resistance of the probes, a four probe measurement technique will be employed. Using this method, current will be injected with two outer probes while the voltage drop is measured between two inner probes. This allows for measurement of only the voltage

drop between pads. IV measurements will be the main technique employed to determine the suitability of both Ohmic and Schottky contacts. The IV curves allow for the extraction of contact resistance for the former and barrier height and reverse breakdown voltage for the latter. IV measurements can be performed using either a circular or linear transmission line method. The CTLM is useful for materials which are difficult to etch and therefore may demonstrate problems with current spreading. In this study, linear TLM patterns will be used, as shown in Figure 2-6. Data from these curves allow for the creation of a plot such as that shown in Figure 2-7. Characterization of the pads is then performed using the relation

$$R_T = 2R_C + R_s \left(\frac{L}{W} \right)$$

$$\rho_c = \left(\frac{R_C^2 W^2}{R_s} \right) \quad (2.8a,b)$$

Figure 2-8 shows a schematic for Schottky contacts. Schottky pads are formed using an inner Schottky contact with an outer Ohmic contact.

2.5.2 Capacitance-Voltage

Capacitance-voltage (CV) measurements will be employed on Schottky contacts in order to further confirm results of IV measurements as well as to provide a deeper understanding of the barrier. If an interstitial layer exists between the contact and the p-GaN, utilizing a CV measurement can reveal this. This is a distinct possibility that could arise either from an interstitial oxide layer forming or from defects at the surface possibly caused by sputtering damage. Measurements were performed using an Agilent 4284A precision LCR meter in the parallel mode. The modulation frequency was set to 1 kHz. Barrier height is determined using

$$\phi_B = V_{int} + E_A + (k_B T / q) \ln g \quad (2.9)$$

where V_{int} is the extrapolated intercept voltage of the reverse bias in the $1/C^2$ versus V plot, $E_A \approx 0.12$ eV is the activation energy of Mg dopants in p-GaN, and $g=2$ is the degeneracy factor for acceptors. Note that in our case, the series resistance (~ 2 k Ω) and the junction conductance ($\sim 10^{-8}$ - 10^{-9}) were low enough so that the measured capacitance corresponds to the proper junction capacitance.

2.5.3 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) measurements will be further used to confirm the barrier height of Schottky contacts. XPS functions by bombarding a specimen with soft x-ray radiation to examine core energy levels. When an x-ray collides with an atom, an electron is ejected from its shell. The electron is then collected and its energy measured. Each element has a characteristic binding energy for its core electrons, and thus each element has a characteristic spectrum. Comparison of the spectrums of a bare specimen, such as GaN, and a specimen with a thin film coating, such as GaN//W₂B, can yield the barrier height of the surface. The barrier height can be determined from the binding energy of the Ga 3d core level E_B and the energy difference between that core level and the valence band maximum E_{VC} according to

$$\phi_B = E_B - E_{VC} \quad (63,64) \quad (2.10)$$

2.5.4 Auger Electron Spectroscopy

Auger Electron Spectroscopy (AES) will be used to determine the elemental composition versus depth of the contacts. This will allow for an understanding of how diffusion plays a role in the behavior of the contacts. AES functions by bombarding the surface of a specimen with a

beam of focused electrons. These electrons penetrate into the sample and collide with the atoms of the specimen. A core shell electron is then ejected, creating a vacancy. Following this, an electron from an outer shell relaxes and fills this lower energy state, releasing energy. This excess energy then results in the ejection of an electron from an outer shell. This Auger electron possesses an energy characteristic of the element from which it is ejected, allowing for the composition of the specimen to be determined. Using an ion gun in combination with the electron beam allows for information about the composition versus depth to be collected.

Table 2-1: Bulk GaN properties

Property	Value
Lattice parameters at 300 K (nm)	$a_0 = 0.3189$ nm $c_0 = 0.5185$ nm
Density ($\text{g}\cdot\text{cm}^{-3}$)	6.095 $\text{g}\cdot\text{cm}^{-3}$
Stable phase at 300K	Wurtzite
Melting point ($^{\circ}\text{C}$)	2500
Thermal conductivity ($\text{W}/\text{cm}\cdot\text{K}$)	1.3, 2.2 +/- 0.2 for thick, free-standing GaN
Linear thermal expansion coefficient	Along $a_0 = 5.59 \times 10^{-6}$ K^{-1} Along $c_0 = 7.75 \times 10^{-6}$ K^{-1}
Static dielectric constant	8.9
Refractive index	2.67 at 3.38 eV
Energy bandgap (eV)	Direct, 3.45
Exciton binding energy (meV)	26
Electron effective mass	0.20
Hole effective mass	0.59

Table 2-2: Properties of common semiconductors

	Si	GaAs	GaN	AlN	6H-SiC
Bandgap (eV) @300°C	1.1 indirect	1.4 direct	3.4 direct	6.2 direct	2.9 indirect
Electron mobility (cm ² /V-s), RT	1400	8500	1000 (bulk) 2000 (2DEG)	135	600
Hole mobility (cm ² /V-s), RT	600	400	30	14	40
Saturation velocity (cm/s), 10 ⁷	1	2	2.5	1.4	2
Breakdown field (V/cm) x 10 ⁶	0.3	0.4	>5		4
Thermal conductivity (W/cm)	1.5	0.5	1.5	2	5
Melting temperature (K)	1690	1510	>1700	3000	>2100

Table 2-3: Properties of the borides

Properties	TiB ₂	ZrB ₂	W ₂ B	W ₂ B ₅	CrB ₂
Melting Point (°C)	2980 ~3225	3040 ~3200	~2670	~2385	2200
Structure	Hexagonal	Hexagonal	-	Hexagonal	Hexagonal
Thermal expansion coefficients x 10 ⁶ (/deg)	4/6	5.9	-	-	10.5
Phonon component of heat conduction (wt/m-deg)	20.6	18.9	-	-	10.4
Elastic modulus E x 10 ⁻⁶ (kg/cm ²)	5.6	4.3	-	-	2.5
Characteristic Temperature (K)	1100	765	-	-	726
Density of electronic state g x 10 ⁻²¹ (eV ⁻¹ cm ⁻¹)	4.5	4.76	-	-	54.6
Work function (eV)	4.19(?)	3.94(?)	-	-	3.18(?)
Heat of Formation (kcal/mol)	71.4	76	-	-	31
Lattice constant (Å)	3.028	3.169	-	2.982	2.969
Thermal conductivity (W/m-K)	26	80	-	Unknown	32
Electrical resistivity (uOhm-cm)	28	4.6	-	19	21

Table 2-4: Properties of the nitrides

Properties	TaN	TiN	ZrN
Melting point (K)	3633	3203	3253
Structure	FCC	FCC	FCC
Thermal expansion coefficients x 10 ⁶ (/deg)	3.6	9.4	8.7
Work function (eV)	4.7	3.74	4.6
Lattice constant (Å)	4.3	4.32	4.574
Thermal conductivity (W m ⁻¹ K ⁻¹)	57.5	19.2	20
Electrical resistivity (μΩ-cm)	15.52	25	13.6

Table 2-5: Properties of Ir

Properties	Ir
Melting point (K)	2719
Structure	FCC
Thermal expansion coefficients x 10 ⁶ (/deg)	6.4
Work function (eV)	5.27
Lattice constant (Å)	3.8
Thermal conductivity (W m ⁻¹ K ⁻¹)	147
Electrical resistivity (μΩ-cm)	4.71

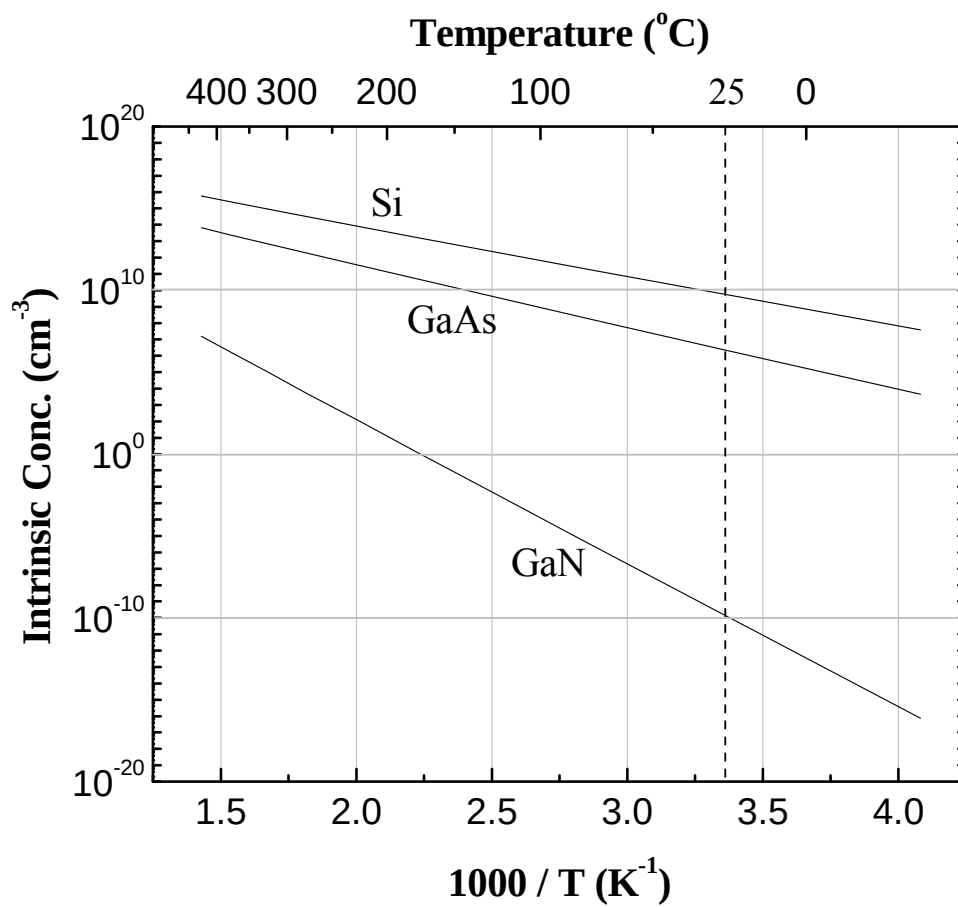


Figure 2-1 Intrinsic carrier concentration of GaN, GaAs, and Si

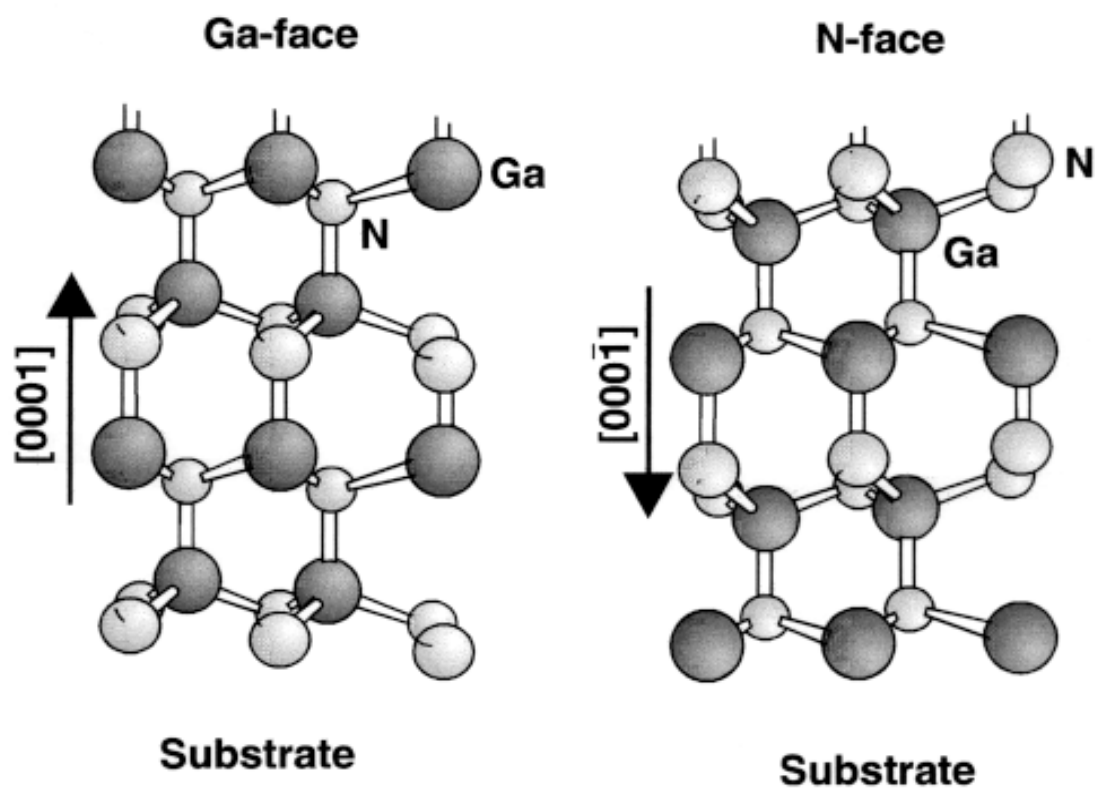


Figure 2-2: Stable wurtzite GaN crystal

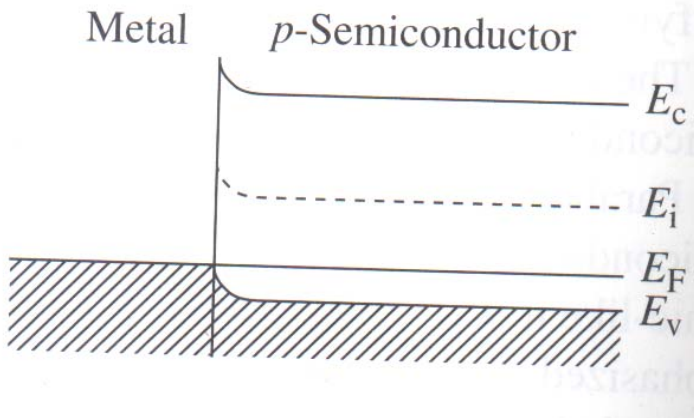


Figure 2-3: Flat band diagram for a p-type Ohmic contact

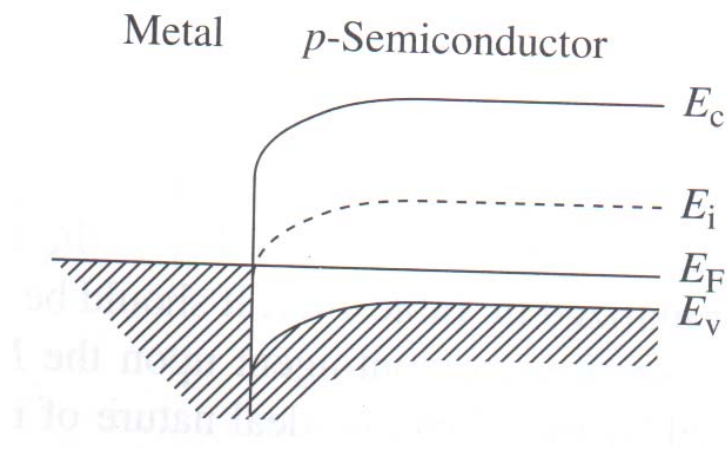
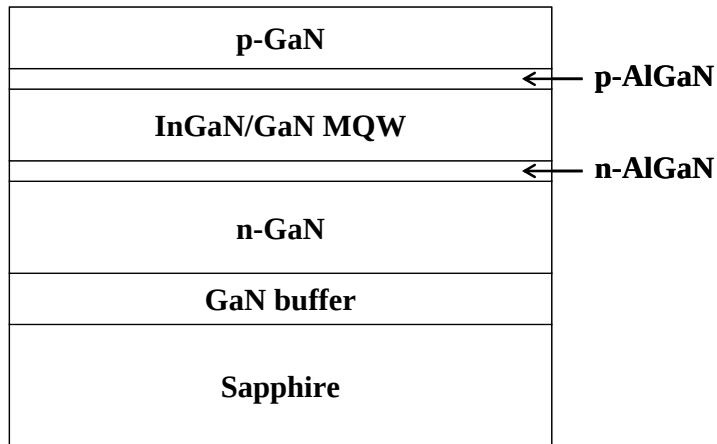


Figure 2-4: Flat band diagram for a p-type Schottky contact

(a)



(b)

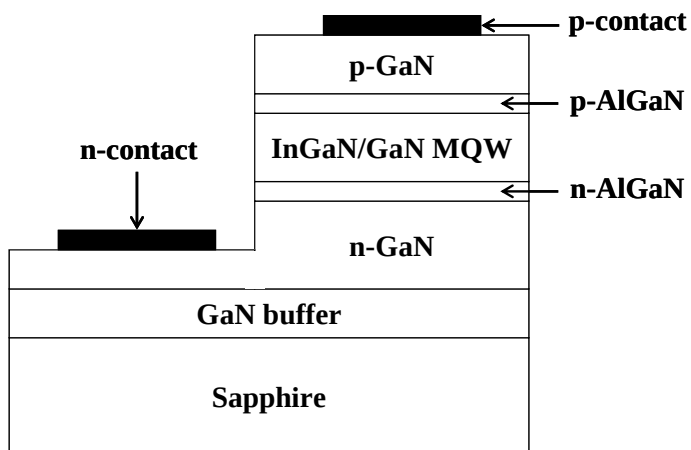


Figure 2-5: LED cross section (a) before and (b) after processing

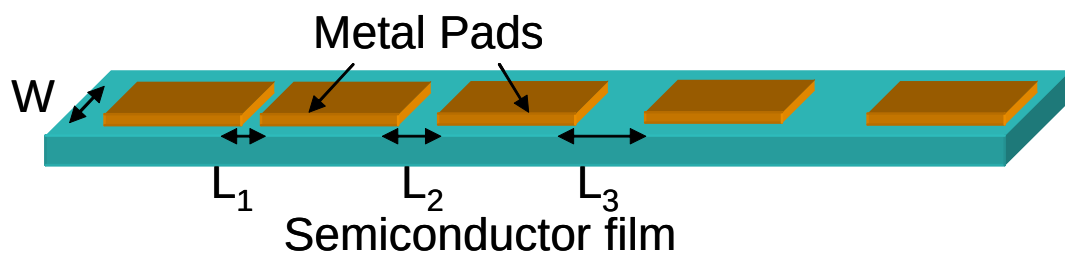


Figure 2-6: Linear transmission line pattern

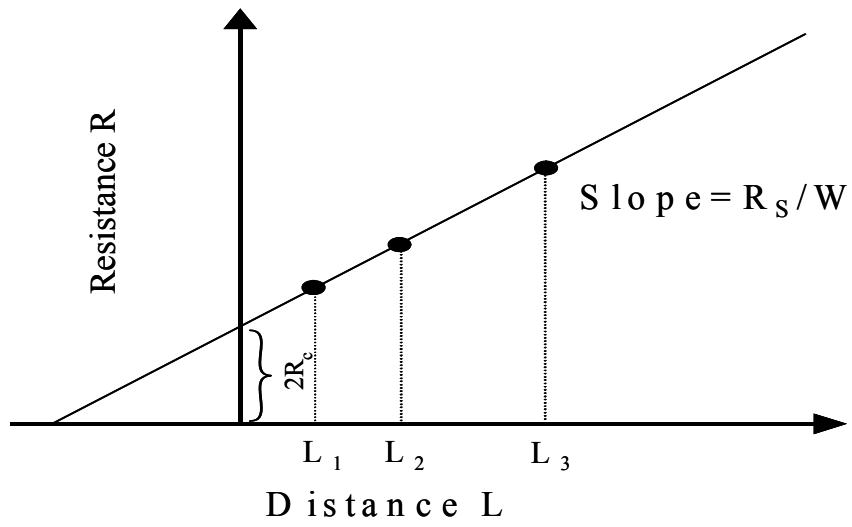


Figure 2-7: Resistance vs. pad spacing plot

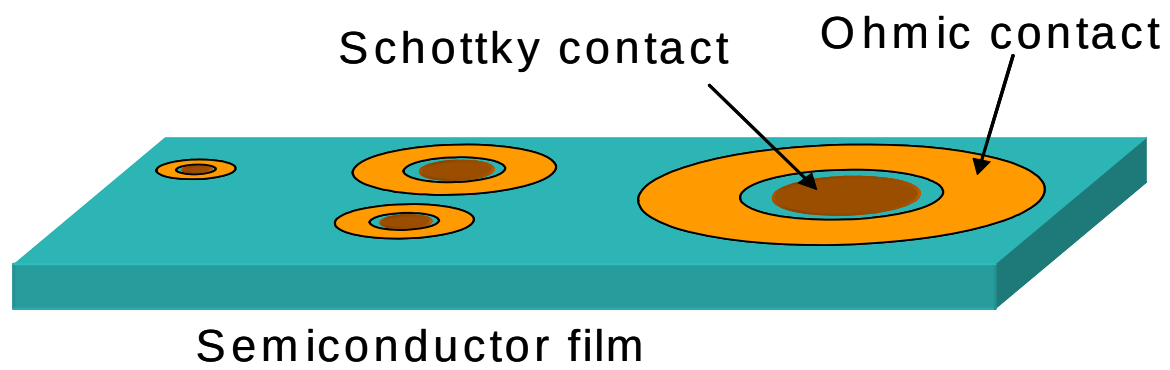


Figure 2-8: Schottky contact schematic

CHAPTER 3 THERMALLY STABLE OHMIC CONTACTS TO P-GAN

3.1 Ohmic Contacts

In this section, two approaches to fabricating Ohmic contacts using the boride family of materials will be discussed. The first is as an overlayer on conventional Ni/Au contacts and the second as the actual contact material. Because these borides have a large work function, it is expected that both approaches will be successful in yielding Ohmic behavior, provided that sputter damage and oxygen incorporation into the borides during deposition does not compromise the contacts, especially the latter.

3.1.1 Fabrication of Ohmic Contacts

The samples used were light-emitting diode wafers with a 0.1 μm Mg-doped p-GaN layer on top of a 0.1 μm p-AlGaN layer followed by a 0.3 μm InGaN/GaN superlattice on top of a n-type GaN layer grown on 2 μm -thick undoped buffers on c-plane Al_2O_3 substrates. Hole concentrations in the p-GaN layer were 10^{17} cm^{-3} obtained from Hall measurements. Mesas for the linear transmission line method (LTLM) method were etched using a Cl_2/Ar inductively coupled plasma for pad isolation and to minimize current spreading. Samples were dipped in 1 M KOH for 1 minute and then rinsed in acetone and ethanol prior to photolithography. Prior to insertion into the evaporation chamber, the samples were exposed to a 30 s O_2 RIE plasma in order to remove any residual carbon and then dipped in 10:1 $\text{H}_2\text{O}:\text{HCl}$ for 5 minutes, which serves to remove any native oxide. A Ni/Au contact of 500 $\text{\AA}$ /800 $\text{\AA}$ was deposited using an e-beam evaporator in order to minimize surface damage. After unloading, the samples were put into a sputtering system for deposition of the X/Ti/Au layer of thickness 500 $\text{\AA}$ /200 $\text{\AA}$ /800 $\text{\AA}$, where X is the refractory metal used. Au is necessary to decrease the sheet resistance while the Ti is necessary to prevent peeling of the Au from the surface due to the large lattice mismatch.

In the case of Ir, this Ti layer is unnecessary. Contacts were also fabricated of the form Ni/Ir/Au, in order to confirm the importance of the Au near the GaN surface, and of the form X/Ti/Au to investigate the use of the refractory materials without the increased doping present due to the Ni/Au layer. Sputtering was performed using an Ar plasma-assisted rf sputter at 5 mTorr and rf (13.56 MHz) power of 150 W. The sputter rates were 5 Å/s for Au, 0.5 Å/s for Ti, and were 0.8-2 Å/s for the refractory materials. Following lift-off, the contacts were annealed in a flowing N₂ ambient for 60 s in a rapid thermal annealing furnace at temperatures up to 1000 °C.

3.1.2 Nitride-Based Contacts

3.1.2.1 Experiment and discussion

Ohmic contacts based on Ni/Au but with a nitride overlayer were fabricated in order to improve the temperature stability. Figure 3-1 shows the specific contact resistivity of the nitride-based contacts as a function of annealing temperature, as well as the sheet resistance of the p-GaN under the contacts. At annealing temperatures of less than 500 °C, contacts were rectifying. The contacts transition to Ohmic behavior at higher temperatures. The specific contact resistance was not a function of temperature in the range 25-175°C, indicating that tunneling is the dominant transport mechanism. The specific contact resistance is fairly stable on annealing up to 1000 °C, with a minimum of $\sim 2 \times 10^{-4} \Omega\text{-cm}^2$ at 600°C for the Ni/ Au/ ZrN/ Ti / Au contacts. This indicates that there is minimal change in the doping of the near surface region of the GaN at these elevated anneal temperatures. The formation of AuGa and AuGa₂ occurs at 600°C at the interface [49]. A sharp maximum in the sheet resistance is observed at 800 °C, with a drop at higher temperatures. This is likely due to increased in-diffusion of metal to the GaN without complete alloying, resulting in interstitial atom incorporation into the lattice. The drop in sheet resistance at higher temperatures is an indication that these interstitials are increasingly incorporated into the GaN. The magnitude of the increase in sheet resistance is related to the

size of the metallic atom in the nitride, with the largest increase seen with the smallest atom Ti and vice versa for Ta, suggesting the atoms causing the spike are from the nitride. The reason the smaller atoms cause a more pronounced increase is the greater ease of diffusion into the GaN as well as a likely higher solid solubility.

Figure 3-2 shows the AES depth profiles for the TaN-based contacts under a variety of conditions. Upon annealing at intermediate temperatures, most of the Ti has migrated to the surface and oxidized while Ni and Au are both present at the GaN interface. In addition, the nitride layer is present at the GaN surface, suggesting that the increase in sheet resistance is due to incorporation of the metallic atoms from the nitride into the GaN. After annealing at 700 °C and aging at 200 °C or annealing at 1000 °C, there is a large amount of intermixing between the metals and the GaN. Note that upon annealing at 600°C the Ta and N peaks are still correlated, indicating that TaN has not reacted a great deal with the GaN yet. However, in the profile of the thermally aged contact there is no longer a correlation between the peaks of the Ta and N. This is an indication that the nitride is breaking down during the thermal aging. In fact, the profile of the aged contacts bears a much stronger resemblance to that of those annealed at much higher temperatures. SEM micrographs are shown in Figure 3-3 for the TaN-based contacts. The contacts show a smooth morphology upon deposition, with an increasingly rough surface as anneal temperature increases due to the increased intermixing of the contacts as well as oxidation of the surface. TiN and ZrN contacts display the same type of profile structure upon annealing and after thermal aging.

As mentioned previously, the Ni/Au/GaN structure is preferred due to the greater difference in electronegativities between Au and Ga than between Ni and Ga. By incorporating a layer on top of the Au, the dynamics of this relationship may change. The electro-negativities of

Ta, Ti, and Zr are 1.5, 1.5, and 1.33, respectively. The values for Au, Ni, and Ga are 2.4, 1.8, and 1.6, respectively. From this, it is apparent that the differences between Au and either Ti, Ta, Zr, or Ga are roughly the same, indicating no preferred bonding to any of them. Various equilibrium phases exist for Au-Ti, Au-Zr, and Au-Ta, but none for Au-N, supporting the conjecture that Au is bonded to the metal. Thus, neither configuration is strongly preferred. From the Au-Ni phase diagram, a miscibility gap exists with a maximum of 810.3 °C at around 70 at% Au. At higher and lower Au concentrations, the temperature above which Au and Ni intermix freely is lower; for example, at 10 at% Au, it is below 500 °C and at 30 at% Au below 700 °C. Since there is no driving force in terms of greater bond strength to cause Au and Ni to switch places when using these diffusion barriers, the Ni and Au should each be present at the surface of the GaN. It is expected that the Ni and Au would separate with slow enough cooling but the layered structure of pure Ni/Au contacts may not form. The AES depth profiles confirm this, displaying significant intermixing at the GaN interface. We also see that the boundary between the GaN and the Ni-Au is not well-defined. This is consistent with the formation of the Au-Ga phases. From the Au-Ga phase diagram, these phases have melting points of 461.3 °C and 491.3 °C, respectively. These are lower than the temperatures required to obtain Ohmic behavior, suggesting it is beneficial to have some Ni present at the GaN interface in order to maintain contact integrity. [67]

Figure 3-4 shows specific contact resistance and sheet resistance under the contacts as a function of thermal aging at 200 °C. This simulates long term operation of these contacts in devices. These contacts display poor stability upon aging at this temperature, lasting for nearly 10 days before the I-V characteristics are no longer completely linear. From the AES depth profiles of the contacts that failed, there was significant in-diffusion of metals into the GaN. The

temperature during aging is not sufficient for the formation of the Au-Ga phases and as a result the metal in-diffused to the GaN is in the form of interstitials, which hinder electrical conduction. In addition to this, the presence of the nitride on the surface of the GaN will lead to a breakdown the near surface GaN layer. Failure is attributed to the fact that the nitrides will intermix with the GaN. Since no change in chemical composition is expected to take place, only for Ga to exchange places with a metal such as Ti, there is no contribution to a change in the Gibb's free energy from formation or decomposition of compounds. In fact, it is expected that the intermixing may be favorable, as it will serve to increase the entropy of the system. From the equation $\Delta G = \Delta H - T\Delta S$ it is apparent that an increase in entropy leads to a lower free energy, and is therefore favorable. This leads to decomposition of the GaN. This is in agreement with the sheet resistance under the contacts increasing in the failed contacts. It is also consistent with the finding in the AES profiles that the aged contacts display a breakdown in the nitride barrier layer.

3.1.2.2 Summary

In conclusion, nitride-based contacts display low specific contact resistance and are stable upon anneals up to 1000 °C, with reasonable stability upon aging at elevated temperatures. Due to the nature of the contacts, they display extremely poor stability during aging and are therefore unsuitable for long term device operation.

3.1.3 Tungsten Boride and Chromium Boride-Based Contacts and Long Term Thermal Aging of Borides

3.1.3.1 Experiment and discussion

Figure 3-5 displays the specific contact resistance of the contacts as a function of anneal temperature as well as the sheet resistance under the contact. The contacts transition to Ohmic behavior at annealing temperatures of $> 600^{\circ}\text{C}$. This likely corresponds to the creation of Ga

vacancies due to the formation of AuGa and AuGa₂ at the GaN surface and thus a localized increase in the hole concentration. This implies that the current transport mechanism is tunneling. Figure 3-6 supports this conclusion, as the contact resistance is not dependent on measurement temperature in the measured range 25-140 °C. The sheet resistance is also relatively stable as a function of annealing temperature, suggesting that there is little intermixing between the boride and the GaN, even during elevated anneal temperatures.

Figure 3-7 displays the specific contact resistance of the W₂B and CrB₂ contacts as a function of long term thermal aging at 350°C. Both W₂B and CrB₂ display excellent stability for the duration of the aging, 23 days. While the nitrides provided good stability over the same range of anneal temperatures, the contacts failed after approximately 9 days at a lower temperature. This is attributed to the fact that the nitrides will intermix with the GaN. In the case of the borides, however, changes in the compounds must occur for significant intermixing to take place. This could take several forms, including the reactions $XB + GaN \Rightarrow XN + GaB$ or $XB + GaN \Rightarrow XGa + BN$. GaB phases are not present in phase diagrams [51]. Full thermodynamic evaluation of these is not possible, as most of the values for the Gibb's free energy are not available. However, it would be expected that these reactions could only proceed at very elevated temperatures, as the compounds involved are each very stable while any Ga-metal phases have relatively low melting temperatures and thus can be assumed to be less stable [51]. For example, the maximum melting temperatures of selected Ga-metal phases are 1670°C for GaTi, 1863°C for GaCr, and 1855°C for GaZr. These are much lower than the melting temperatures of either GaN or the borides or nitrides. Thus, while a reaction of this nature may proceed during very high temperature anneals, during the thermal aging it will only proceed very slowly, if at all.

Figure 3-8 displays the AES depth profiles for the W_2B -based contacts as deposited, annealed at 600 °C, annealed at 700 °C and aged at 350 °C, and annealed at 1000 °C. Upon annealing at 600 °C, the Ni and Au show strong mixing at the GaN interface. However, the boride barrier prevents most intermixing between the Ni/Au and the Ti/Au overlayer. The boride has minimal reaction with the GaN surface and the surface had excellent morphology at 600°C. Note that the boride peak remains strongly correlated, indicating the W and B atoms remain together. This is the case even at 1000°C anneals and after long term thermal aging at 350 °C, indicating that the boride is not chemically active in these contacts. At higher temperatures, the AES profiles were not entirely reliable due to non-uniformity depending on where the profile was taken. However, the IV characteristics were still Ohmic and the surface still had reasonable morphology. At temperatures of 1000°C and higher, the contact layers became totally intermixed, although the peaks of W and B still correspond to one another. Similar results were obtained with CrB_2 -based contacts.

3.1.3.2 Summary

These boride-based contacts display excellent thermal stability both upon high temperature anneals and during long term thermal aging at very high temperature. This is due to the fact that there is little intermixing between the boride and the GaN itself, due to the large change in Gibbs Free Energy that would be necessary for any chemical reaction to occur. This is supported by the depth profiles obtained from AES, which show that the boride has not broken down during experiments.

3.1.4 Contact Resistance for Other Boride-based Contacts

3.1.4.1 Titanium boride-based contacts

Contacts with a TiB_2 diffusion barrier for enhancing the thermal stability of Ni/Au Ohmic contacts on p-GaN were fabricated. Figure 3-9 shows the specific contact resistivity of the

Ni/Au/TiB₂/Ti/Au/p-GaN structure as a function of annealing temperature, along with the sheet resistance of the p-GaN under the contacts, extracted from the TLM measurements. The contacts are rectifying below an anneal temperature of 500°C but transition to Ohmic behavior for higher temperatures. The specific contact resistivity improves steadily with temperature above 700°C and reaches a minimum of $\sim 2 \times 10^{-4} \Omega \cdot \text{cm}^{-2}$ after annealing at 800 °C for 60 secs. Note that the contact resistance stays at a similar value even for temperatures up to 950°C, even though the higher annealing temperatures produced increases in the sheet resistance of the GaN and less reproducible contact properties due to roughening of the contact morphology. The mechanism for the increase in sheet resistance may include loss of N (producing nitrogen vacancy-related donors) or a reduction in the soluble Mg concentration. This specific contact resistance is comparable to that achieved on the same samples with Ni/Au metallization annealed at 500°C. The incorporation of the TiB₂ diffusion barrier clearly provides a much wider range of thermal stability compared to the standard Ni/Au contacts.

Figure 3-10 shows SEM pictures of the TLM contact pads as a function of annealing temperature. After 800°C annealing the morphology is degraded, but is still much smoother than conventional Ni/Au contacts under these conditions. The darker appearance of the contacts after high temperature anneals is mainly a result of the outdiffusion of Ti, which rapidly oxidizes.

Figure 3-11 shows the AES surface scans from the as-deposited sample (top) and those annealed at 800°C (center) and 900°C (bottom). Ti is evident on the surface after annealing at 800°C and the concentration increases with annealing temperature. The increased oxygen concentration evident from the summary of the data in Table 3-1 most likely comes from oxidation of this out-diffused Ti. The carbon signal in all cases comes from adventitious carbon on the surface.

The AES depth profiles from the as-deposited and 800 and 900°C annealed samples are shown in Figure 3-12. The as-deposited sample shows sharp interfaces between the metals and between the Ni and the GaN. After annealing at 800°C, the Ni shows significant movement through all of the overlying layers and by 950°C, most of the contact metallurgy is intermixed and the Ti is essentially all removed to the surface. There is an accompanying decrease in abruptness of the TiB₂ interfaces with the metals on either side. The TiB₂ appears to be a barrier for Ti diffusion, so this probably excludes formation of TiN phases at the interface of the GaN to account for the improved contact resistance.

3.1.4.2 Zirconium Boride-based contacts

ZrB₂-based contacts were also fabricated. Figure 3-13 shows the specific contact resistance of the ZrB₂/Ti/Au and Ni/Au/ZrB₂/Ti/Au/p-GaN structures as a function of annealing temperature, along with the sheet resistance of the p-GaN under the contacts, extracted from the TLM measurements. The contacts are rectifying below an anneal temperature of 750°C but transition to Ohmic behavior for higher temperatures. The Ni/Au/ZrB₂/Ti/Au contact resistance improves with higher anneal temperature, at the expense of poorer morphology. The ZrB₂/Ti/Au contacts do not show low resistance values until 800°C and the value degrades at higher temperatures. The associated sheet resistance generally decreases with temperature. The specific contact resistance values obtained with both types of ZrB₂-based schemes is comparable to that achieved on the same samples with Ni/Au metallization annealed at 500°C but the former have much higher thermal stability, as expected from the high melting temperature of the ZrB₂.

Figure 3-14 shows the AES surface scans and depth profiles from the as-deposited Ni/Au/ZrB₂/Ti/Au/p-GaN sample (left) and from the sample annealed at 750°C (right). Ti, Ni and Zr are evident on the surface after annealing at 750°C and the concentration increased with annealing temperature. The as-deposited sample shows sharp interfaces between the metals and

between the Ni and the GaN. Table 3-2 summarizes the near-surface composition AES data. The increased oxygen concentration evident from this data most likely comes from oxidation of the out-diffused Ti. The carbon signal in all cases comes from adventitious carbon on the surface. After annealing at 750°C, the Ni shows significant movement through all of the overlying layers and even the Zr diffuses out of the boride later, leaving the boron in its original location. Both Zr and Au diffuse to the interface with GaN. The increased contact intermixing at higher annealing temperatures did roughen the contact morphology as shown in the SEM pictures of the TLM contact pads as a function of annealing temperature in Figure 3-15. After 800°C annealing the morphology is degraded, but is still much smoother than conventional Ni/Au contacts under these conditions. The darker appearance of the contacts after high temperature anneals is mainly a result of the outdiffusion of Ti, which then oxidizes.

The same basic trends were observed with the ZrB₂/Ti/Au structures. Figure 3-16 shows the AES surface scans and surface scans of ZrB₂/Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature. The as-deposited sample shows abrupt interfaces but after annealing at 900°C, the Zr shows a very broad distribution (more so than the B). The contacts after annealing showed the presence of reacted islands, as shown in the elemental maps of Figure 3-17. The islands contain both Au and Ga and show that the GaN epi layer has begun to dissociate at this temperature, at least under the contact metallurgy. Note that the areas with Au and Ga overlap, indicating that they are indeed forming the Au-Ga phases reported in the literature.

3.1.4.3 Gallium Nitride//Tungsten Boride-based contacts

Figure 3-17 shows the specific contact resistivity of the W₂B/Ti/Au/p-GaN structure as a function of annealing temperature, along with the sheet resistance of the p-GaN under the contacts, extracted from the TLM measurements. The contacts are rectifying below an anneal temperature of 500°C but transition to Ohmic behavior at this temperature. The specific contact

resistivity improves steadily with temperature and a minimum of $1.7 \times 10^{-3} \Omega \cdot \text{cm}^{-2}$ was obtained after annealing at 800 °C for 60 secs. Higher annealing temperatures produced sharp increases in the sheet resistance of the GaN and irreproducible contact properties. The mechanism for the increase in sheet resistance may include loss of N (producing nitrogen vacancy-related donors) or a reduction in the soluble Mg concentration. However the contact morphology as determined by SEM was similar over the entire annealing range used here. This specific contact resistance is comparable to that achieved on the same samples with Ni/Au metallization annealed at 500°C.

Figure 3-18 shows the AES surface scans from the as-deposited sample and those annealed at 500, 700 and 800°C. Ti is evident on the surface after annealing at 500°C and the concentration increases with annealing temperature. The increased oxygen concentration evident from the summary of the data in Table 3-3 most likely comes from oxidation of this out-diffused Ti. The carbon signal in all cases comes from adventitious carbon on the surface.

The AES depth profiles from the as-deposited and annealed samples are shown in Figure 3-19. The as-deposited sample shows sharp interfaces between the metals and between the W_2B and the GaN. After annealing at 500°C, the Ti shows significant movement through the Au layer and by 800°C is essentially all removed to the surface. There is an accompanying decrease in abruptness of the W_2B /GaN interface, which suggests the onset of reactions that are responsible for the improved contact resistance. Since the W_2B appears to be a barrier for Ti diffusion, this probably excludes formation of TiN phases. Cole et al.[29] reported the formation of the $\beta\text{-W}_2\text{N}$ and W-N interfacial phases after annealing sputtered W on GaN [68]. The former appeared after anneals at 600°C and the latter after 1000°C. That work demonstrated the importance of these interfacial phases in the resulting contact properties. The specific contact resistance obtained for the W_2B -based contacts is lower than reported previously for pure W on p-GaN [69], likely due

to the lack of these phases and the resulting compensation of holes by nitrogen vacancies. The absence of Ti diffusion through the W_2B also suggests that an optimum metal scheme might involve a thin sandwich of the boride layers around the Ti, with the Au overlayer to reduce the sheet resistance. The reflectivity of pure W is around 60% at 460 nm, while that of Au is around 95% [70], so clearly the thickness of the boride layers should be small relative to the Au thickness. The long-term stability and reliability of the boride-based contacts must still be established on LEDs and laser diodes. In the former case, the reflectance of the multi-layered contacts at the emission wavelength of the LEDs must also be established.

3.1.5 Iridium-Based Contacts

3.1.5.1 Experiment and discussion

Figures 3-21 and 3-22 show the IV plots for both types of contacts at different anneal temperatures and 20 μm spacing. Only the Ni/Au/Ir/Au contacts annealed at 500 °C were found to have Ohmic characteristics. It was observed that these contacts displayed a specific contact resistance of $\sim 2.3 \times 10^{-4} \Omega\text{-cm}^2$, comparable to results previously achieved on similar wafers for other schemes. Table 3-4 shows a summary of previous results achieved using a similar approach with other thermally stable materials as well as the anneal temperatures above which the contacts failed either due to unreasonable morphology or breakdown of Ohmic characteristics. From the IV curves for the Ni/Au/Ir/Au contacts, we see a decrease in the amount of current upon annealing at 300 °C, which likely corresponds to indiffusion into the GaN of Ni but at a temperature too low for the Ni hydride to form and increase the doping. At 500 °C the contacts transition to Ohmic behavior due to increased near surface doping. At higher temperatures the contacts revert to rectifying behavior. For the Ni/Ir/Au contacts, the as deposited display the largest amount of current. At 300 °C the amount of current decreases

again, only to increase at 500 °C due to removal of H by Ni. At 700 °C it begins to decrease again.

Figures 3-23 and 3-24 show the Auger electron spectroscopy (AES) depth profiles for the Ni/Au/Ir/Au and Ni/Ir/Au contacts, respectively, at several different anneal temperatures. At 300°C, the contacts maintain well defined layers, with a distinct lack of intermixing. At this temperature, the contacts do not display Ohmic characteristics because the Ni has not depassivated the H-Mg complexes. At 500 °C, the Ni/Au/Ir/Au contacts display significant interaction between the GaN and the Ni/Au underlayer. This likely corresponds to the formation of the Au-Ga phases, which serve to increase the doping. The Ni/Ir/Au contacts show that the Ni has diffused towards the Au, but the Au has not diffused in towards the GaN. With little or no Au at the surface of the GaN, the hole concentration is not expected to increase as much as with the Ni/Au-based contact. This is the reason why Ohmic behavior is not observed in the Ni/Ir/Au contacts. In addition, we can observe that the Au seems to be essentially insoluble in the Ir at the moderate temperature anneals. At 700 °C, we can see that the layer structure has broken down and the metals are completely intermixed.

Figure 3-25 displays scanning electron microscopy (SEM) images of the Ni/Au/Ir/Au contacts as deposited and annealed at several temperatures. The surface at 500 °C displays good morphology while that of the 700 °C anneal shows signs of the breakdown of the layer structure.

The failure of any contacts to display Ohmic behavior at high anneal temperatures is likely due to the nature of the Ir. Ir is expected to be stable on the GaN surface because it is not expected to form extensive secondary phases with the Ga or the N. While IrN has been recently been observed, it has only been synthesized at very high pressures. For the high temperature anneals, the Ir diffuses into the GaN. However, because no nitride can be formed under these

conditions, the Ir must occupy interstitial sites and cannot be incorporated into the crystal structure of the GaN itself. Because the Ir atoms are very large and are likely sitting in interstitial sites, they can cause significant lattice distortions and it is expected that the crystallinity of the GaN would be significantly decreased. These distortions, as well as the Ir atoms themselves, would act as scattering sites for charge carriers. It is in this manner that the contacts fail when annealed at high temperatures. Thus, even when Au arrives at the surface in the Ni/Ir/Au contacts at 700 °C, the Ir has already caused enough disruption to the GaN that it does not matter.

This same lack of chemical interaction of the Ir on the GaN may allow for improved long term operation of LEDs using the Ni/Au/Ir/Au contacts. Because the Ir is not expected to interact chemically with the GaN, at the lower temperatures which were examined during aging, and which would be present during long term operation, the GaN itself is not expected to decompose over a long period of time.

3.1.5.2 Summary

Ir diffusion barriers for contacts to p-GaN have been fabricated. The importance of Au being in contact with the GaN for the formation of low resistance Ohmic contacts has been confirmed, as the Ni/Ir/Au contacts do not display Ohmic characteristics.

3.2 Conclusions

Ohmic contacts have been fabricated to p-GaN using three classes of materials. It has been determined that boride based contacts are superior to either Ir or nitride based ones due to both their ability to withstand a wide range of annealing temperatures and to withstand long term thermal aging. From these results, it can be noted that it is important to choose materials for contacts which will not display a great deal of either chemical reaction or indiffusion.

Table 3-1: Concentration of elements detected on the as-received surface (in atom%)

Filename	Sample ID	C(1)	O(1)	Ti(1)	Au(3)
	<i>Sensitivity factors</i>	<i>[0.076]</i>	<i>[0.212]</i>	<i>[0.188]</i>	<i>[0.049]</i>
051829101	As deposited	36	1	nd	64
051829201	800°C annealed	38	31	19	12
051829301	900°C anneal	27	33	28	12
051829401	950°C Anneal A	30	26	33	nd
051829401	950°C Anneal B	28	26	35	nd

Table 3-2: Concentration of elements detected on the as-received surfaces (in atom%)

Sample ID	C(1)	O(1)	Ti(1)	Ni(1)	Zr(2)	Au(3)
Sensitivity factors	0.076	0.212	0.188	0.227	0.043	0.049
As deposited	44	4	nd	nd	nd	52
Ni/Au/ZrB ₂ /Ti/Au						
annealed 750C	45	19	2	1	14	19
annealed 800C	42	22	9	1	16	10
As deposited	37	4	nd	nd	nd	59
ZrB ₂ /Ti/Au						
annealed 800C	43	23	nd	nd	12	22
annealed 1000C	48	19	nd	nd	14	19

Table 3-3: Concentration of elements detected on the as-received surfaces (in atom%)

Sample	C(1)	O(1)	Ti(2)	Au(3)
	[0.076]	[0.212]	[0.296]	[0.049]
As deposited	41	nd	nd	59
500°C annealed	43	24	5	28
700°C annealed	44	34	7	15
800°C annealed	38	34	15	13

Table 3-4: Summary of specific contact resistances

Contact Scheme	$\rho_{sc, \text{minium}} (\Omega\text{-cm}^2)$	Anneal temperature ($^{\circ}\text{C}$)	Failure temperature ($^{\circ}\text{C}$)
Ni/Au/W ₂ B/Ti/Au	3.5×10^{-5}	1000	>1000
W ₂ B/Ti/Au	1.69×10^{-3}	800	>900
Ni/Au/CrB ₂ /Ti/Au	7×10^{-5}	1000	>1000
Ni/Au/TiB ₂ /Ti/Au	1.93×10^{-4}	850	>900
Ni/Au/ZrB ₂ /Ti/Au	1×10^{-4}	900	>900
ZrB ₂ /Ti/Au	1.8×10^{-3}	800	>900
Ni/Au/TaN/Ti/Au	2.5×10^{-4}	800	>1000
Ni/Au/TiN/Ti/Au	2.45×10^{-4}	600	>1000
Ni/Au/ZrN/Ti/Au	2×10^{-4}	600	>1000
Ni/Au/Ir/Au	2.3×10^{-4}	500	>500
TaN/Ti/Au	3.7×10^{-4}	800	>1000
ZrN/Ti/Au	3.1×10^{-4}	600	>700

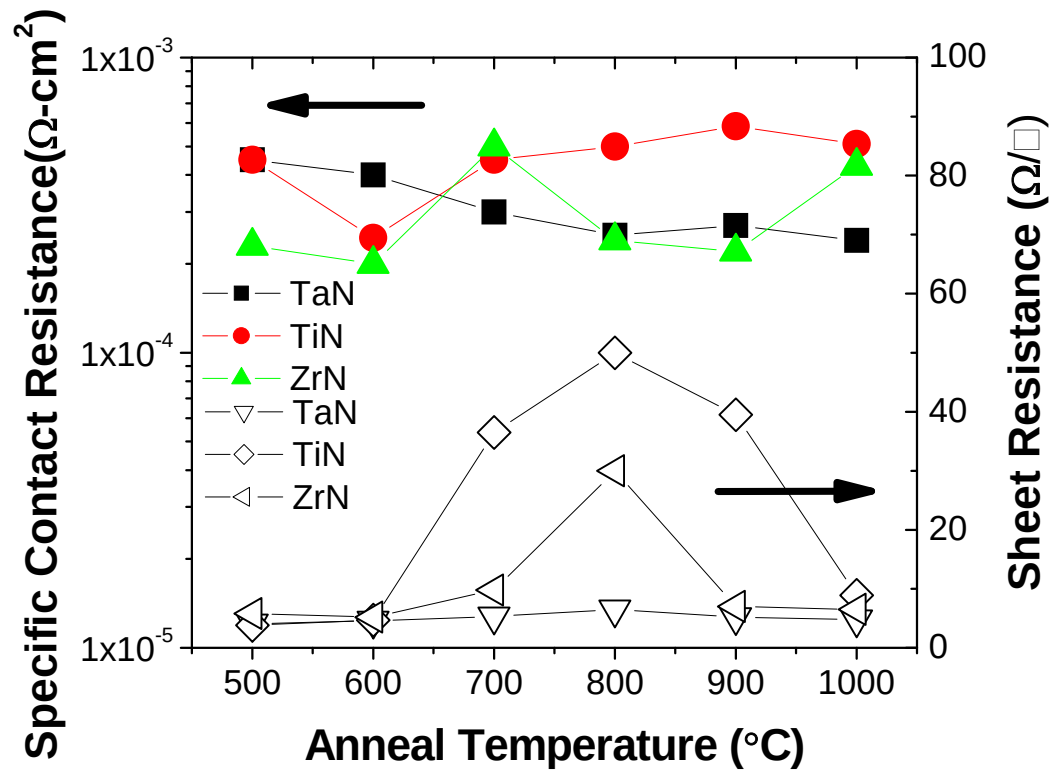


Figure 3-1: Specific contact resistance and sheet resistance under the contact of Ni/Au/ X/ Ti/Au contacts as a function of anneal temperature.

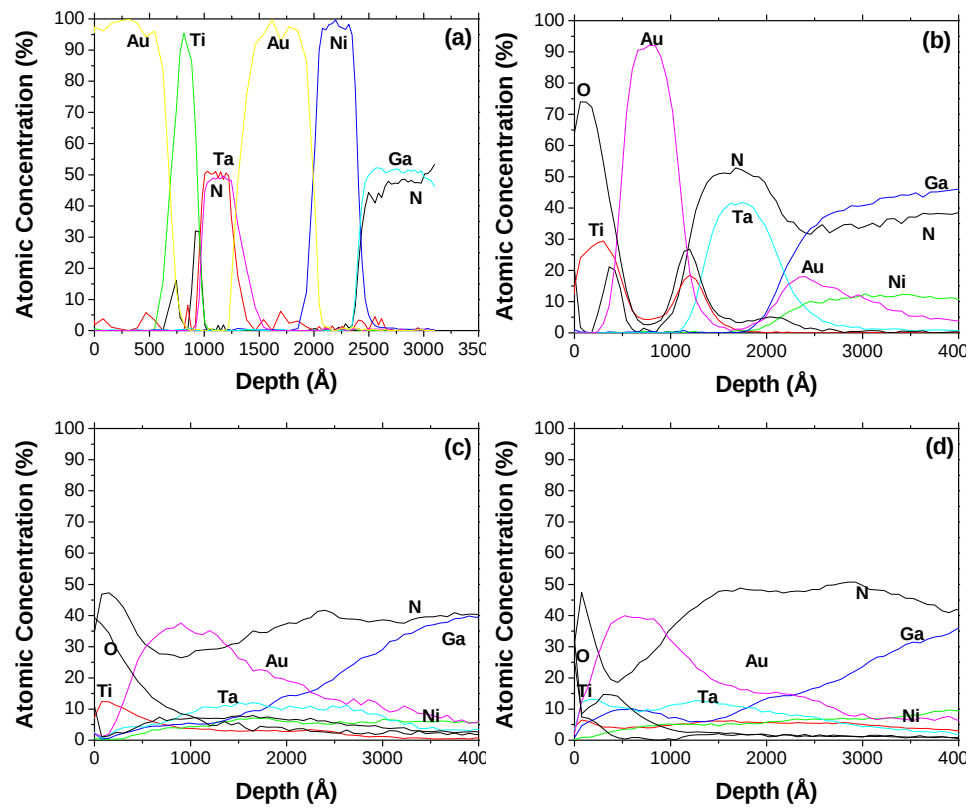


Figure 3-2: Depth profiles of Ni/Au/TaN/Ti/Au contacts (a) as deposited (b) annealed at 600 °C (c) annealed at 700°C and aged at 200 °C until the contacts became non-Ohmic and (d) annealed at 1000 °C.

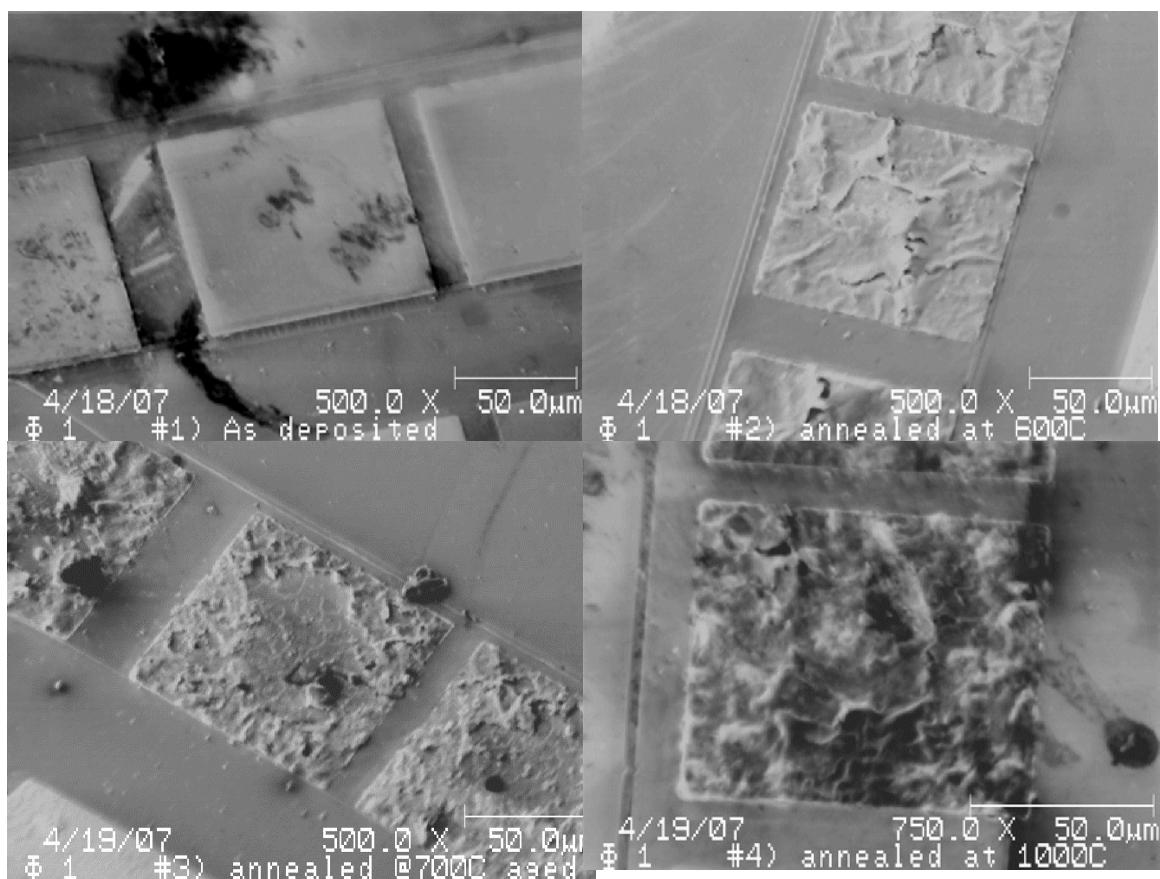


Figure 3-3: Scanning electron microscopy images of Ni/Au/TaN/Ti/Au contacts (a) as deposited (b) annealed at 600 °C (c) annealed at 700°C and aged at 200 °C until the contacts became non-Ohmic and (d) annealed at 1000 °C.

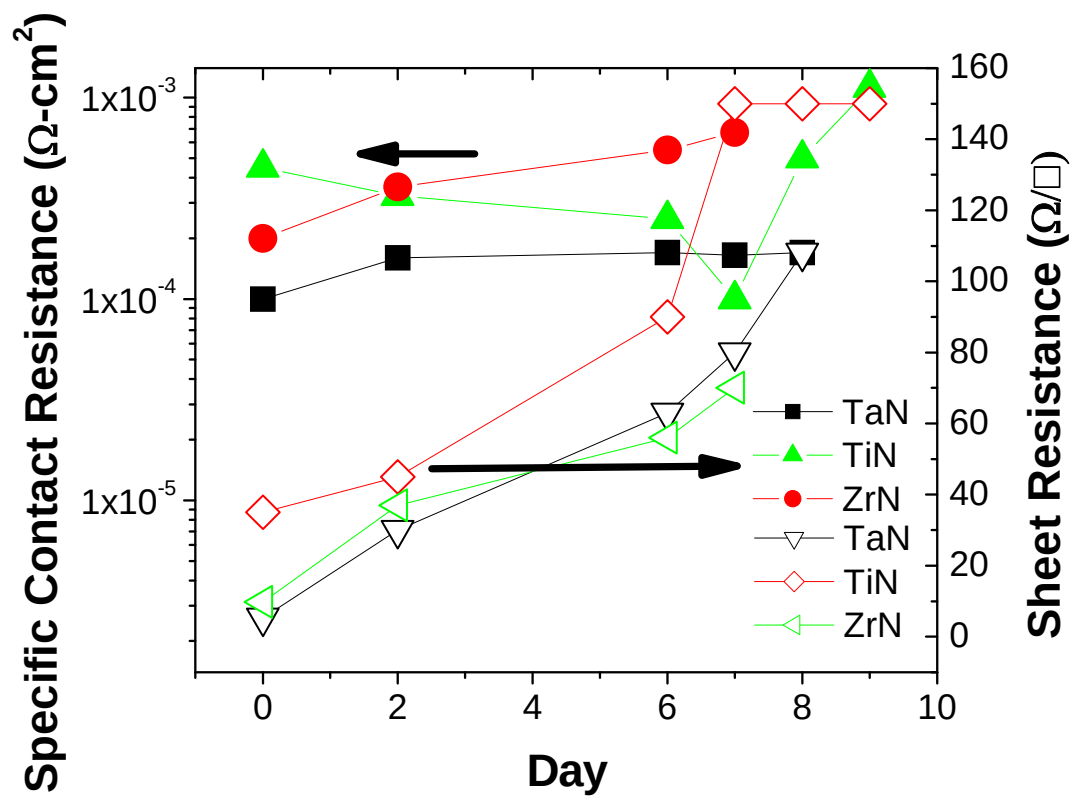


Figure 3-4: Specific contact resistance of Ni/Au/X/Ti/Au contacts as a function of aging at 200 °C.

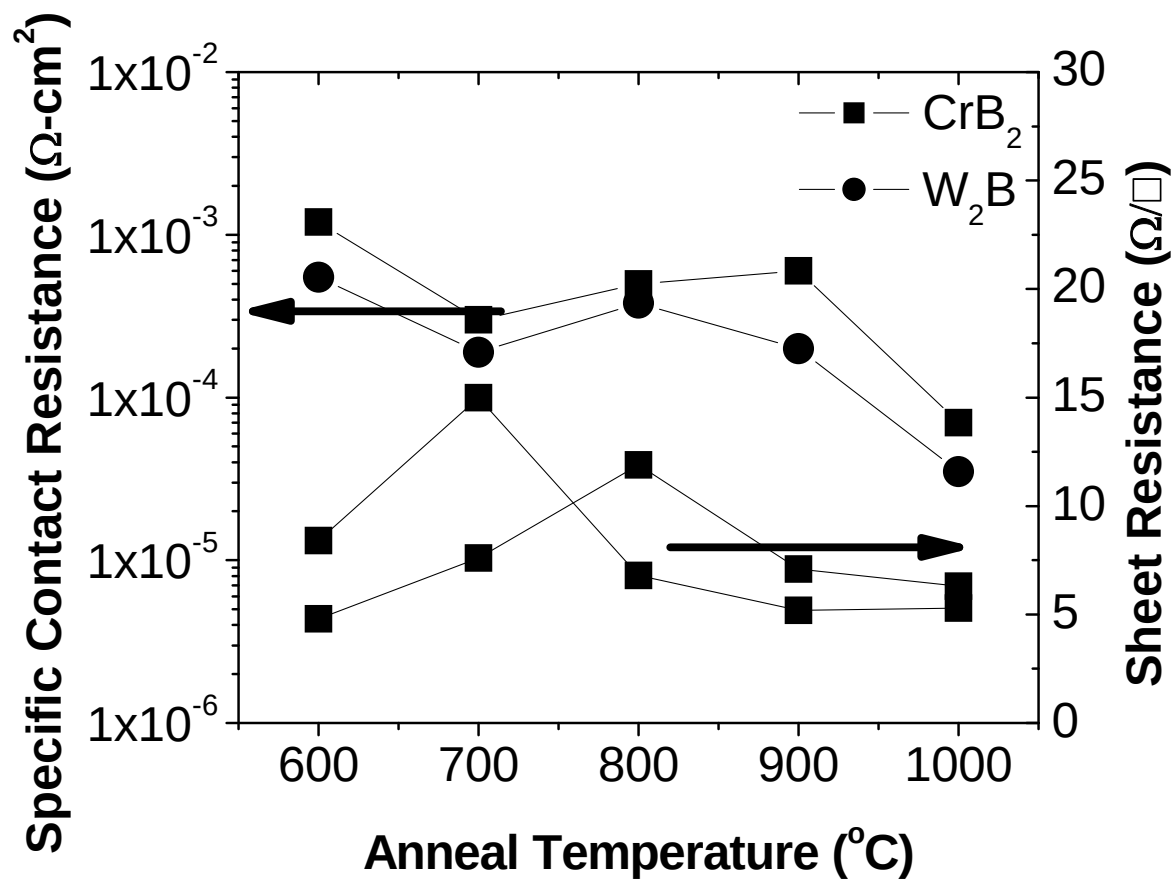


Figure 3-5: Specific contact resistance and sheet resistance under the contact versus anneal temperature.

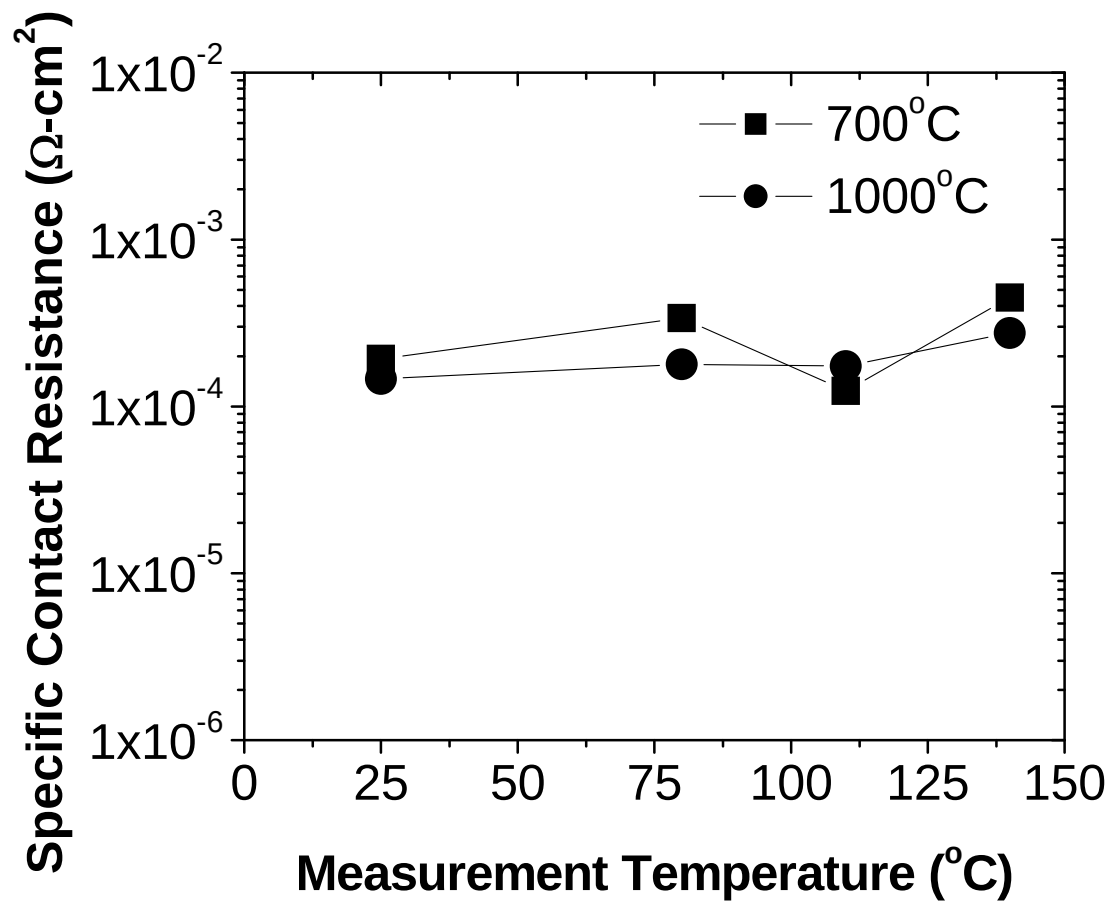


Figure 3-6: Specific contact resistance versus measurement temperature.

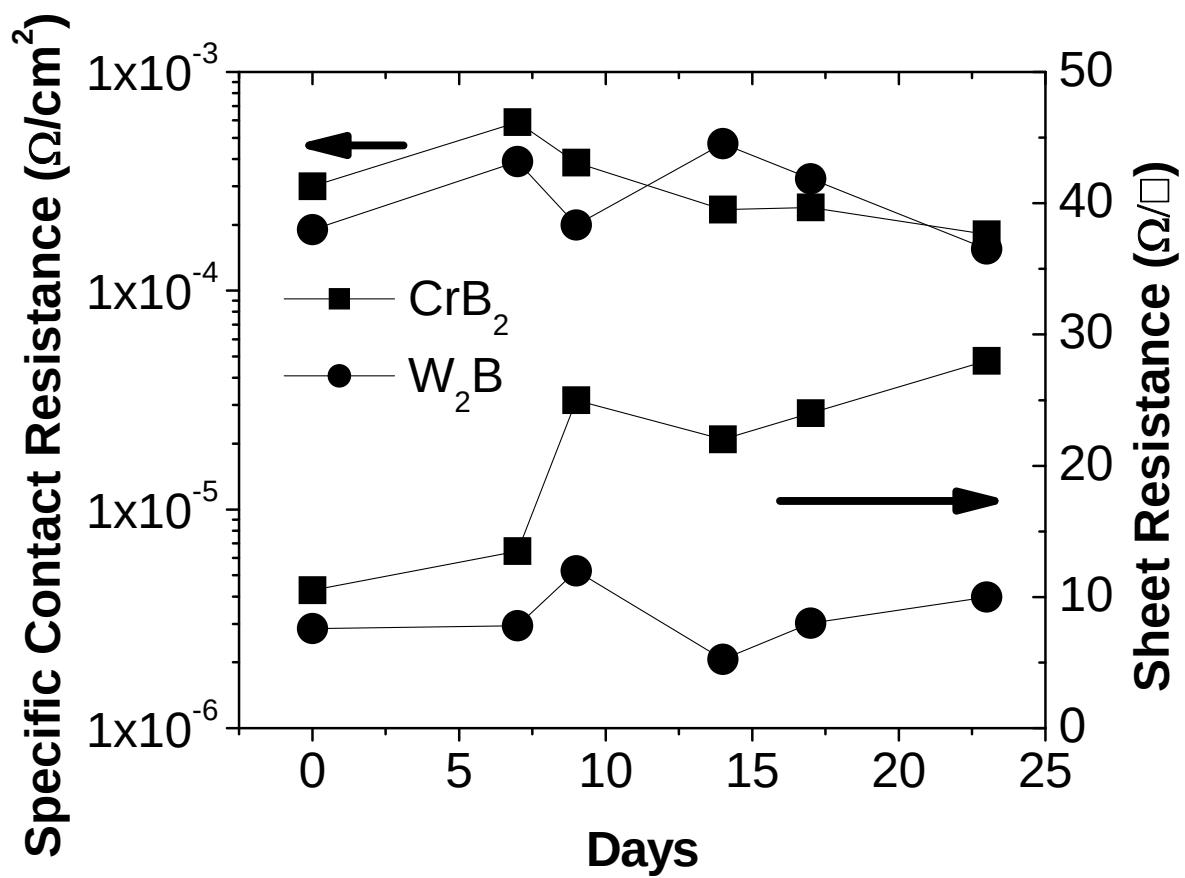


Figure 3-7: Specific contact resistance and sheet resistance under the contact as a function of long term thermal aging at 350°C.

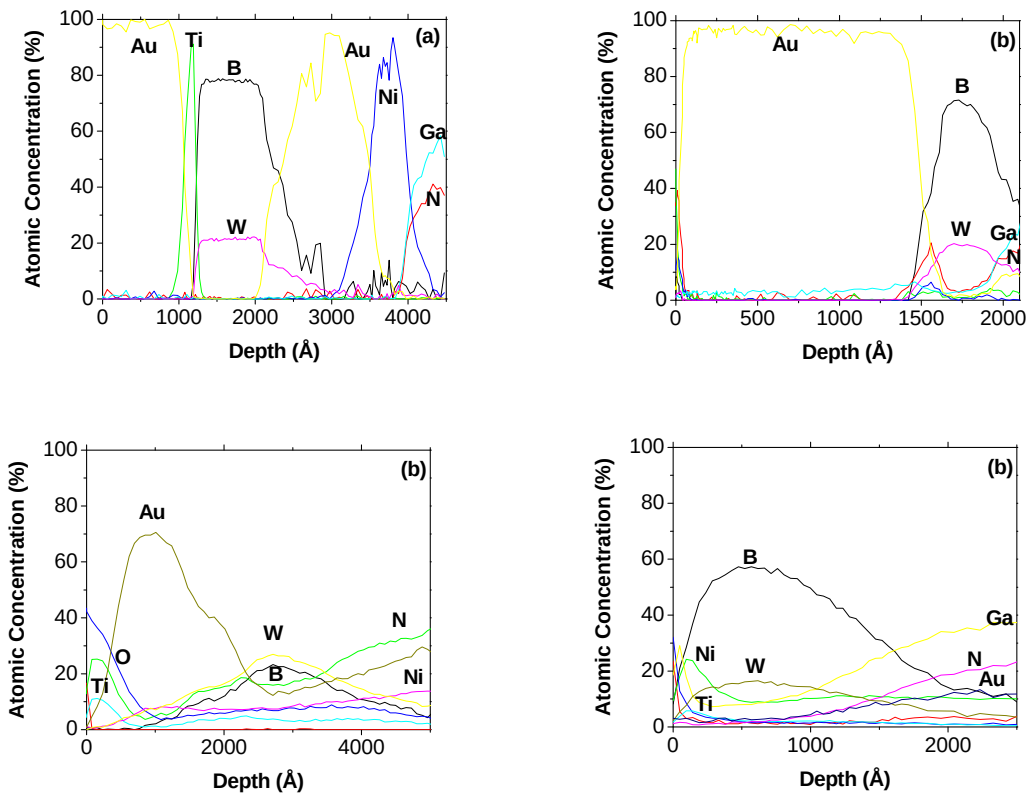


Figure 3-8: Depth profiles of W_2B -based contacts (a) as deposited (b) annealed at 600 °C (c) annealed at 700 °C and aged at 350°C and (d) annealed at 1000 °C

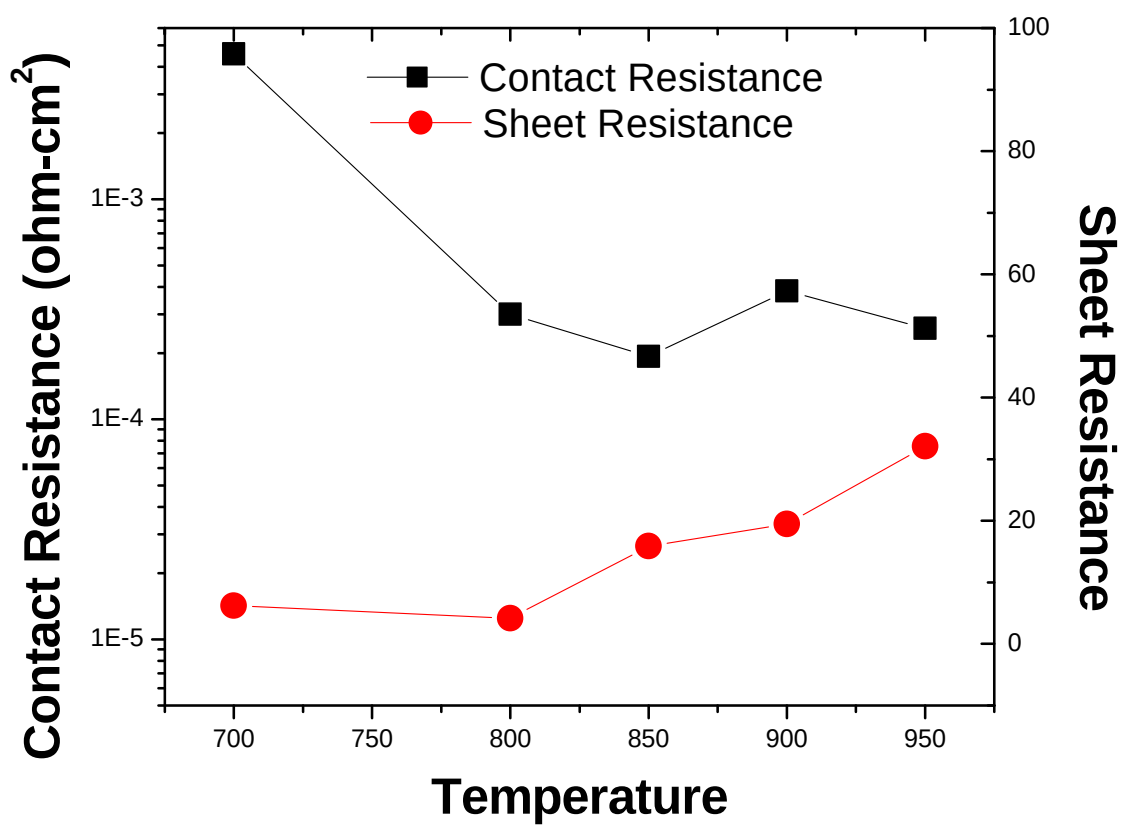


Figure 3-9: Specific contact resistivity of Ni/Au/TiB₂/Ti/Au Ohmic contacts and p-GaN sheet resistance under the contact as a function of annealing temperature.

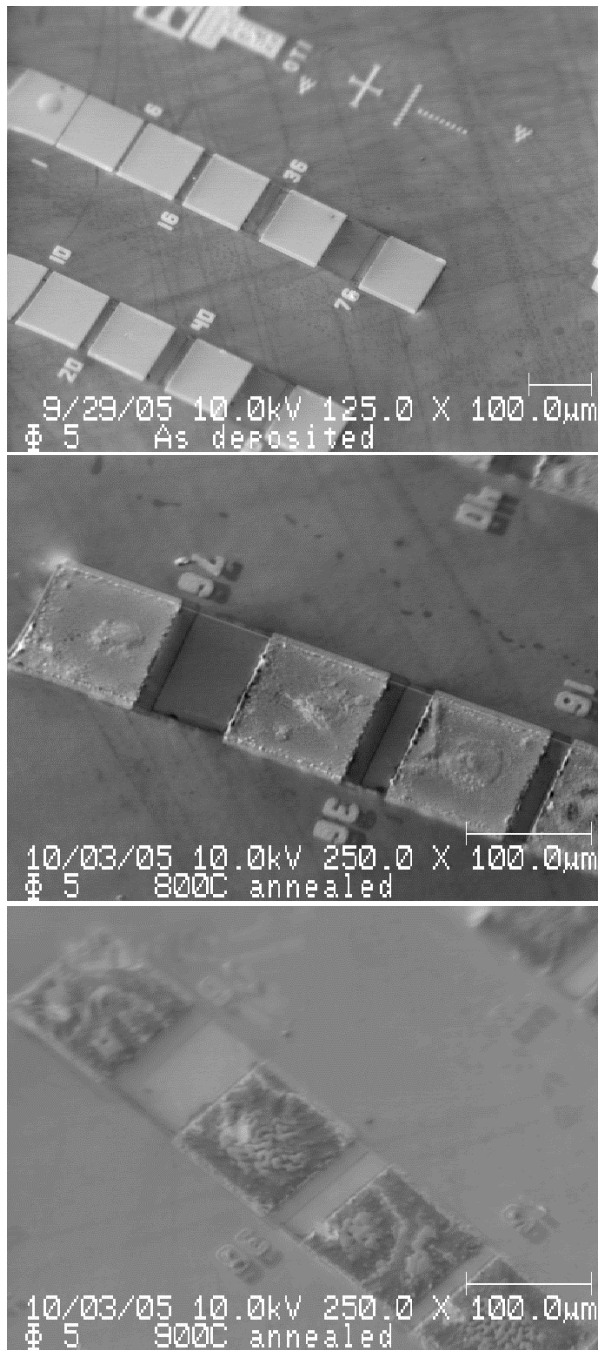


Figure 3-10: Secondary electron images of Ni/Au/TiB₂/Ti/Au contact pads on p-GaN as-deposited (top) or after annealing at either 800(center) or 900°C (bottom).

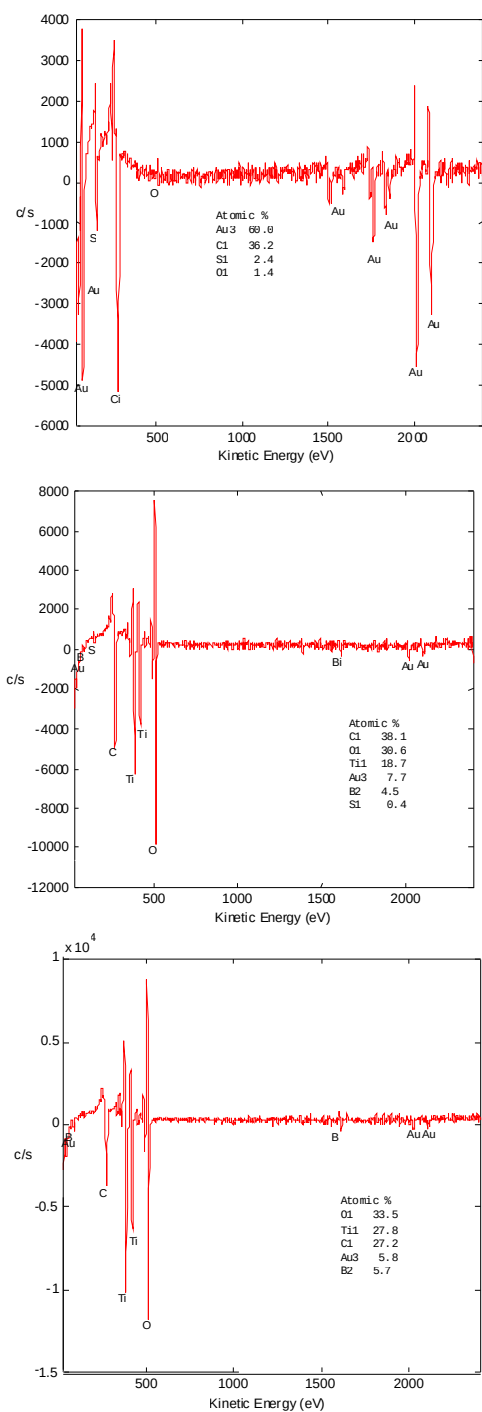


Figure 3-11: Surface scans of Ni/Au/TiB₂/Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature. The as-deposited sample is at top, that annealed at 800°C at center and that at 900°C at bottom .

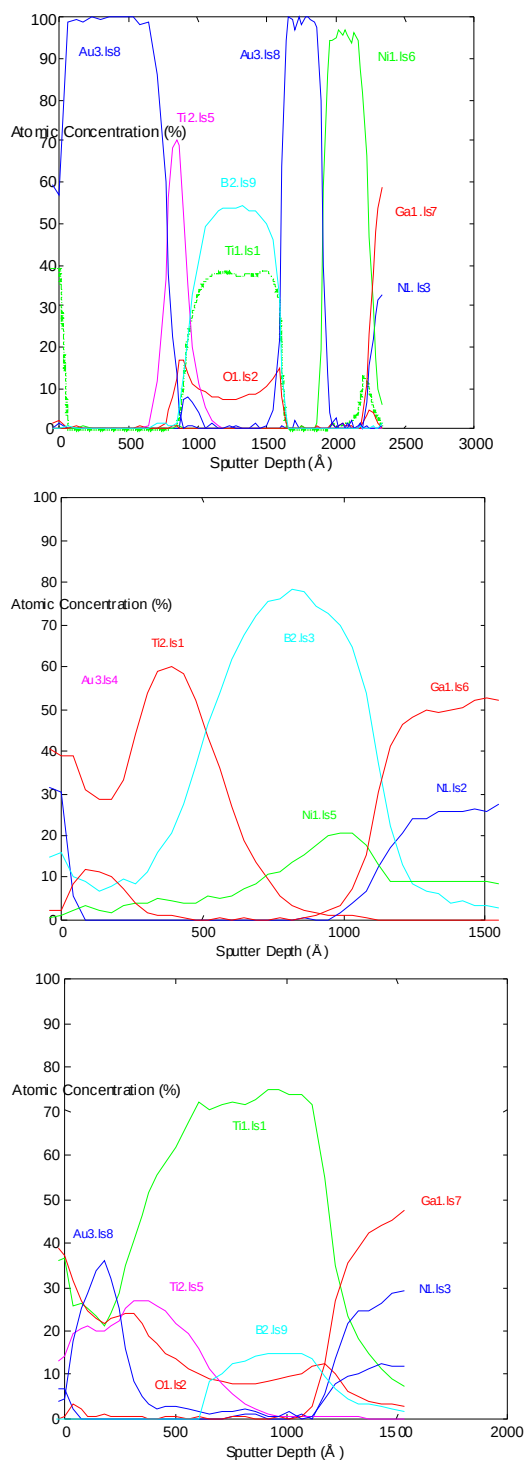


Figure 3-12: Depth profiles of Ni/Au/TiB₂/Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature. The as-deposited sample is at top, that annealed at 800 °C at center, and that at 900 °C at bottom.

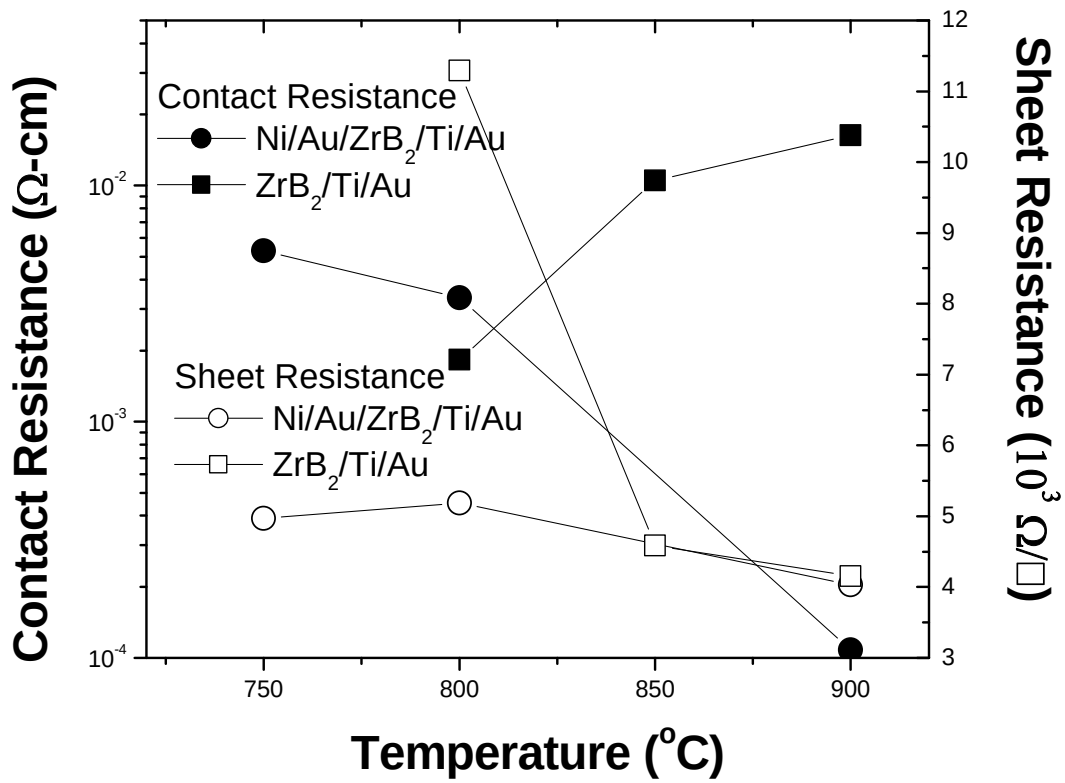


Figure 3-13: Specific contact resistance of Ni/Au/ZrB₂/Ti/Au and ZrB₂/Ti/Au Ohmic contacts and p-GaN sheet resistance under the contact as a function of annealing temperature.

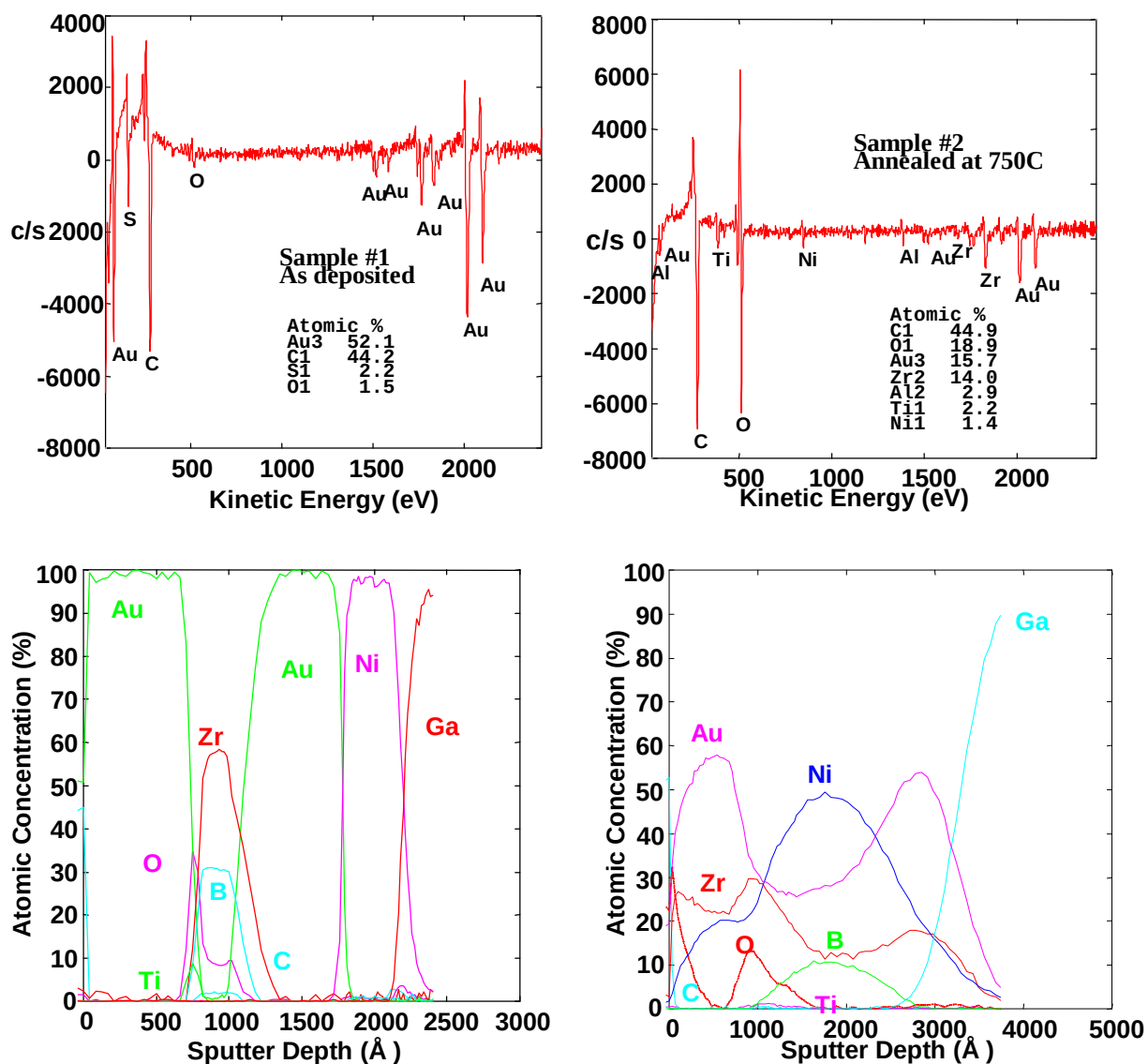


Figure 3-14: Surface scans and depth profiles of Ni/Au/TiB₂/Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature.

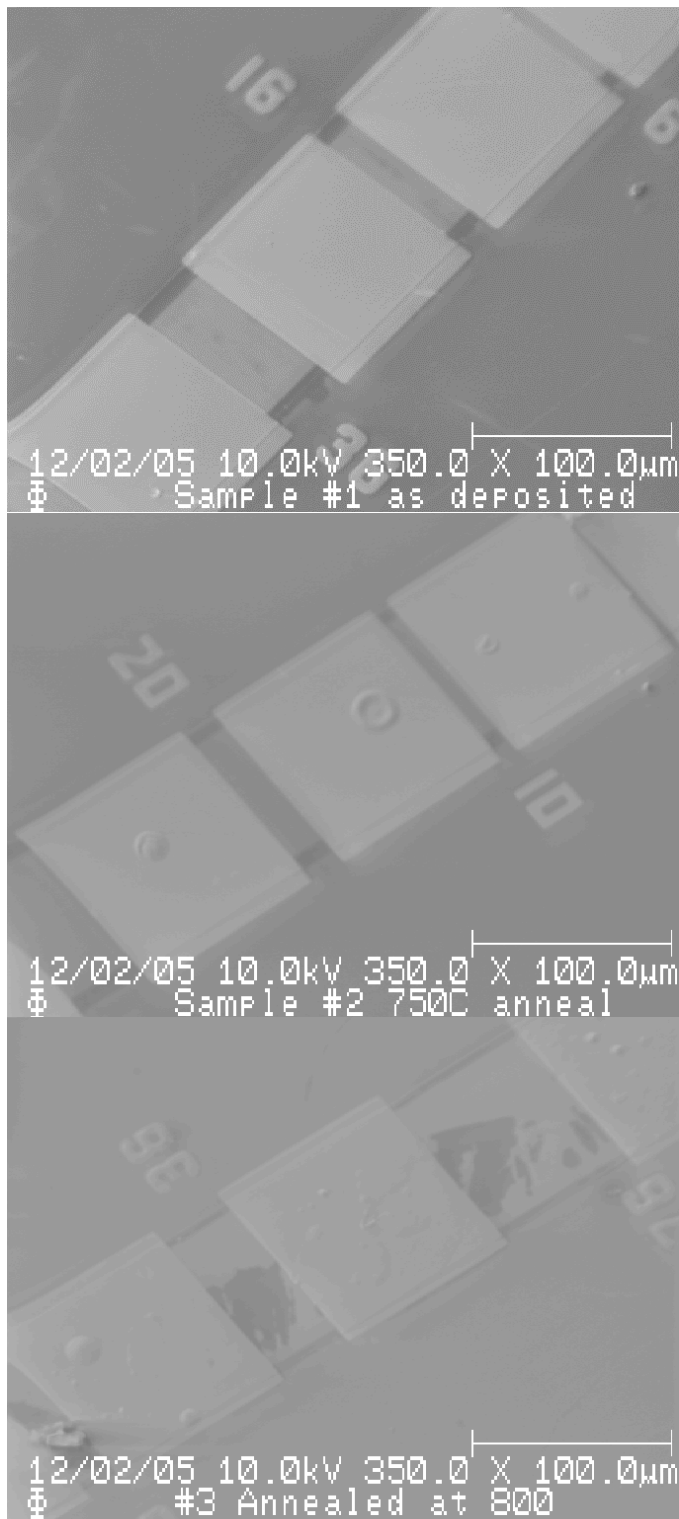


Figure 3-15: Scanning electron microscopy images of Ni/Au/TiB₂/Ti/Au contact pads on p-GaN as-deposited (top) or after annealing at either 750 (center) or 800°C (bottom).

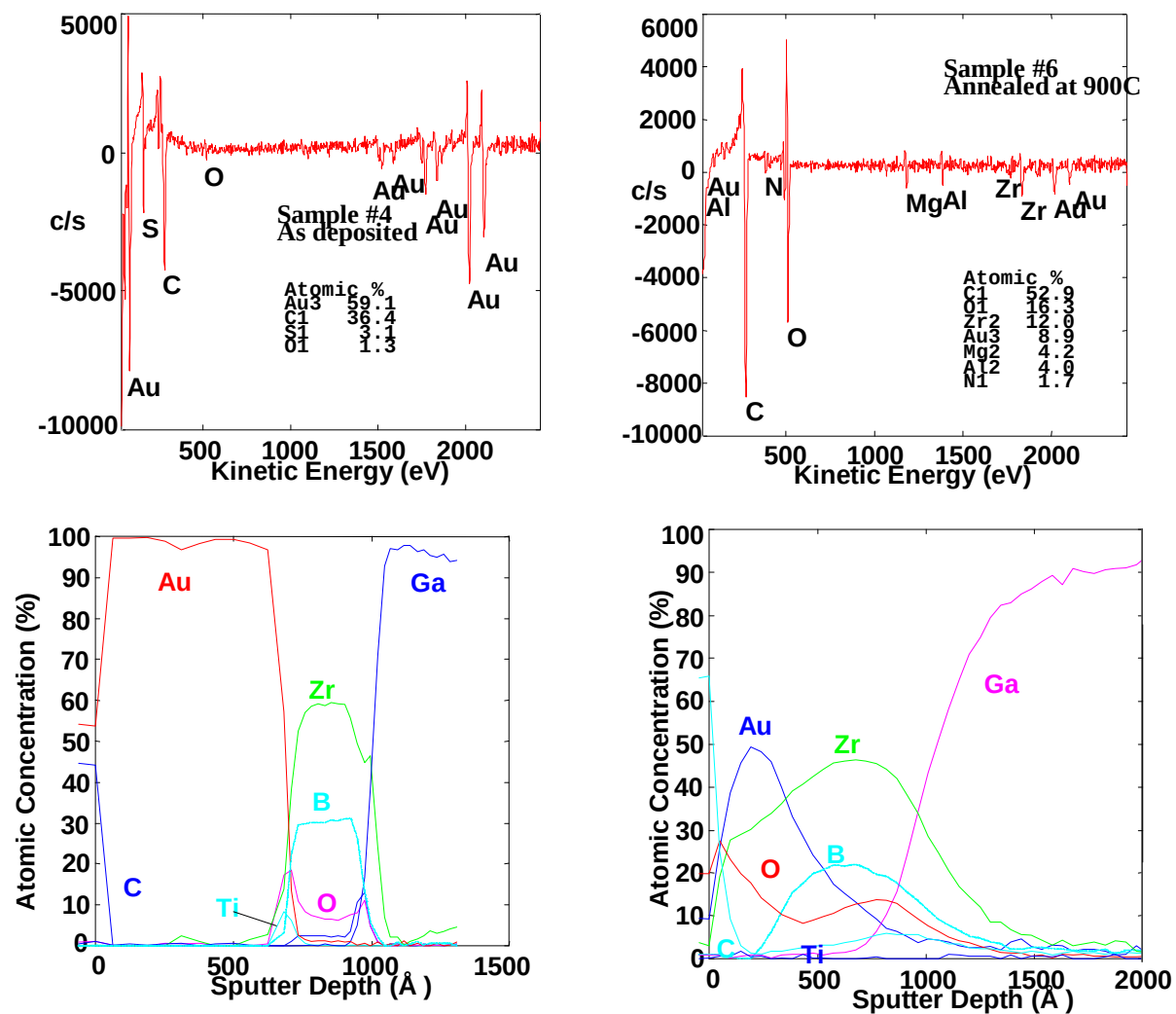


Figure 3-16: Surface scans and depth profiles of $\text{ZrB}_2/\text{Ti}/\text{Au}$ Ohmic contacts on p-GaN as a function of anneal temperature.

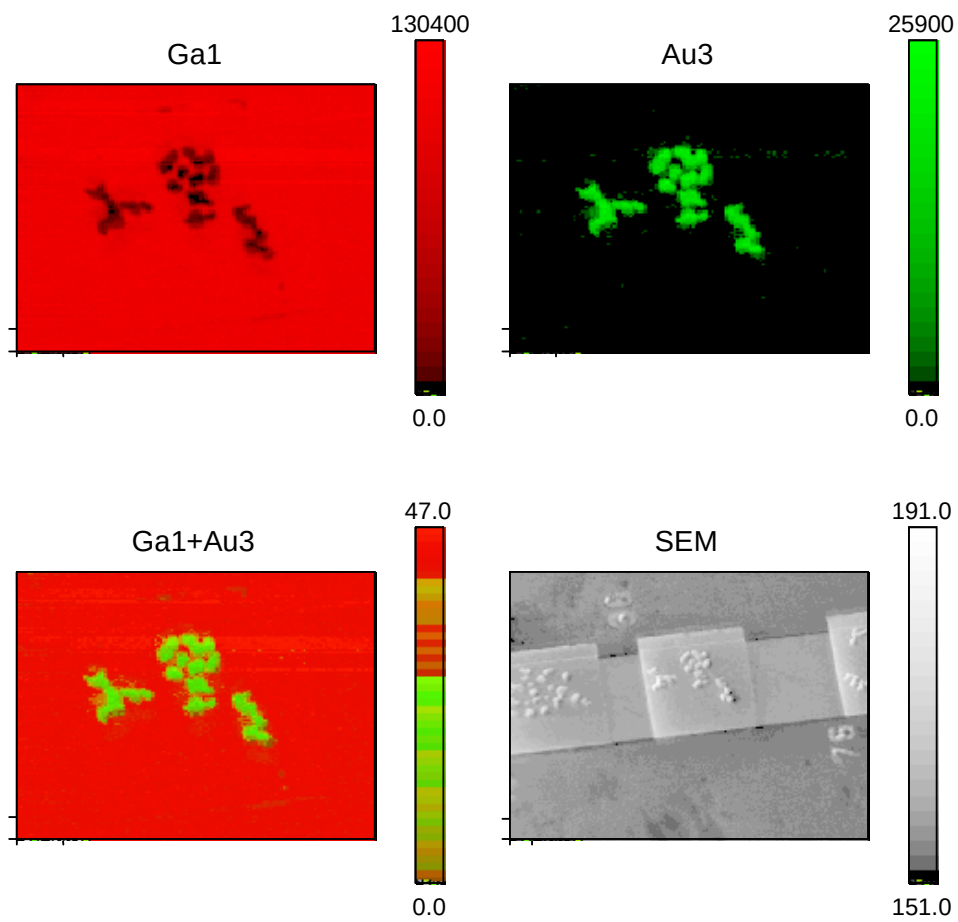


Figure 3-17: Elemental maps obtained from scanning AES of ZrB₂/Ti/Au Ohmic contacts pads on p-GaN.

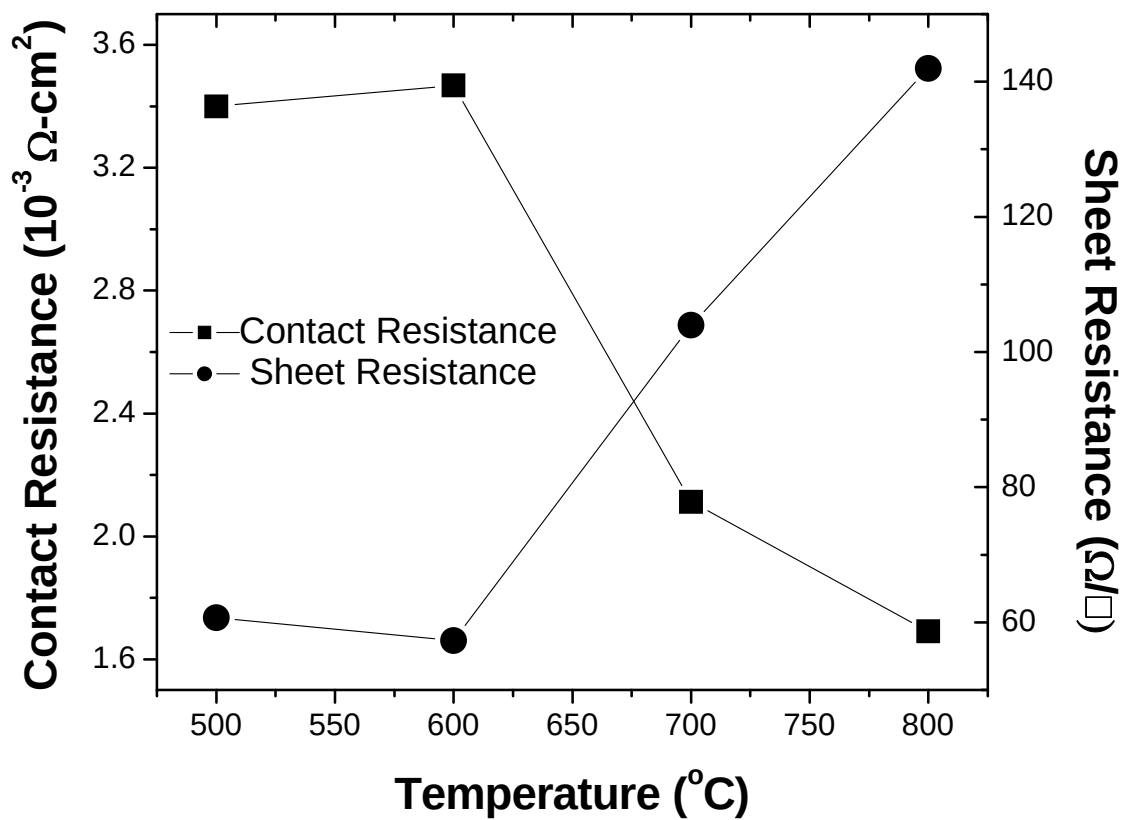


Figure 3-18: Specific contact resistivity of $\text{W}_2\text{B}/\text{Ti}/\text{Au}$ Ohmic contacts and measured p-GaN sheet resistance under the contact as a function of annealing temperature.

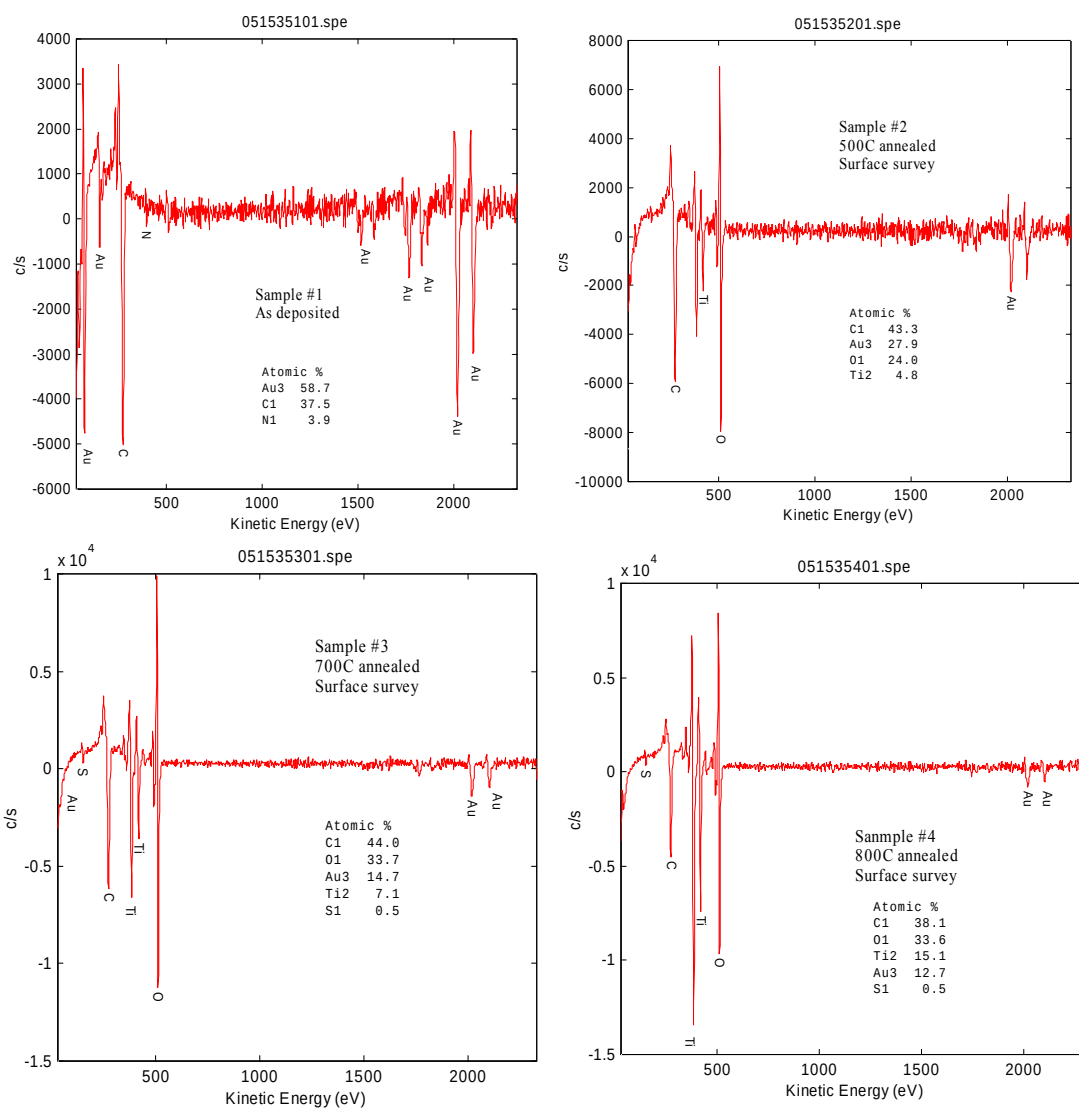


Figure 3-19: AES surface scans of W₂B/Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature.

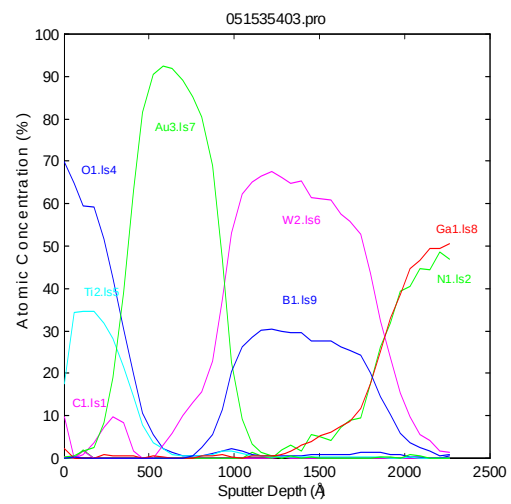
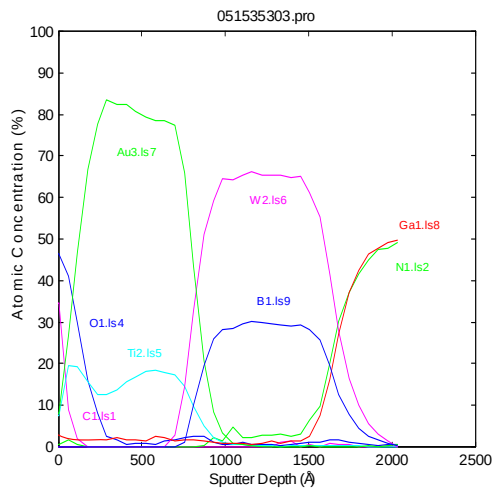
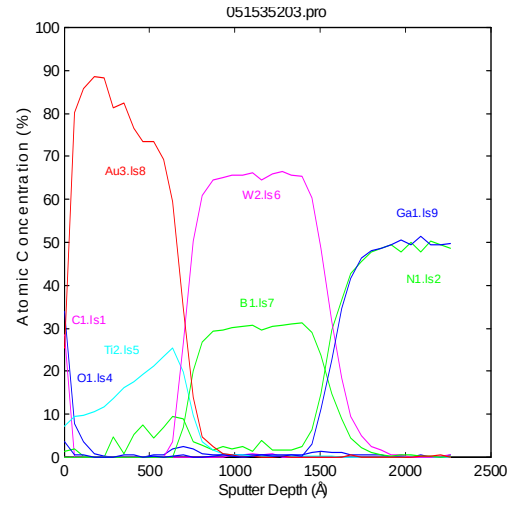
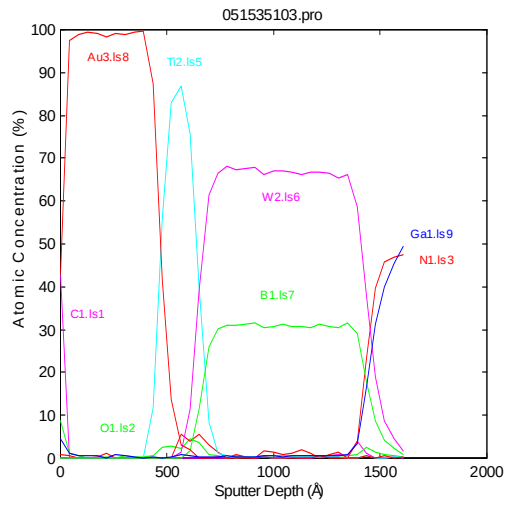


Figure 3-20: Depth profiles of W₂B/Ti/Au Ohmic contacts on p-GaN as a function of anneal temperature.

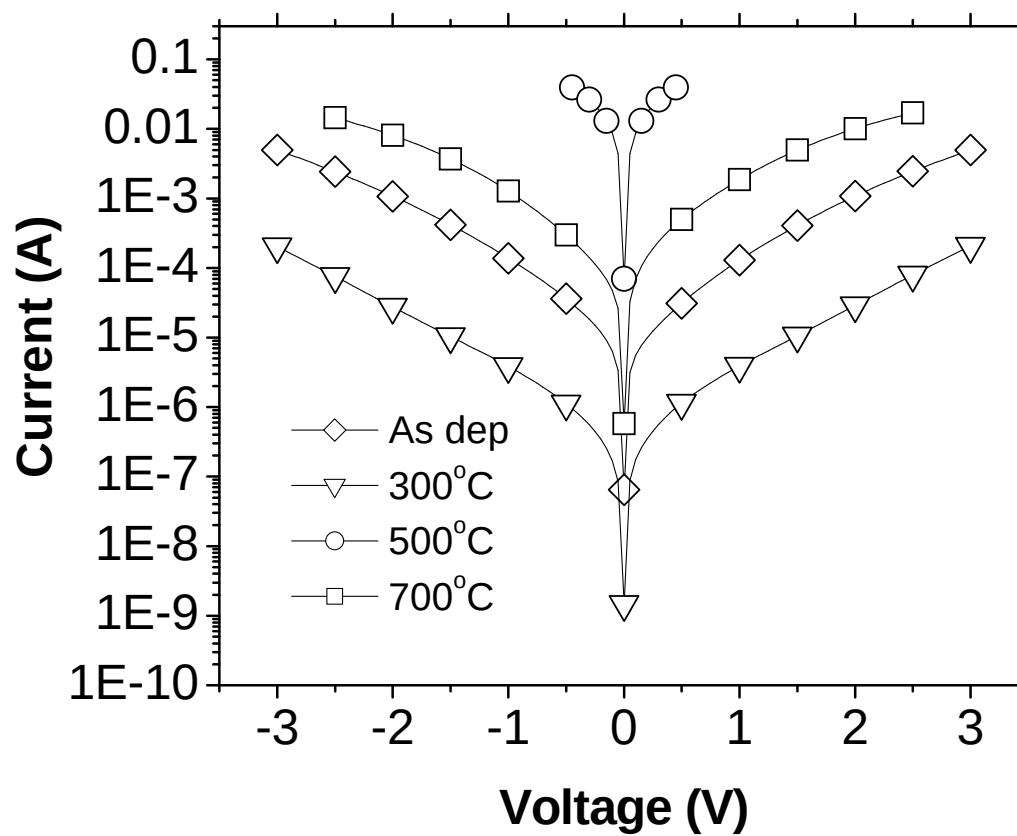


Figure 3-21: Current-voltage curves for Ni/Au/Ir/Au contacts.

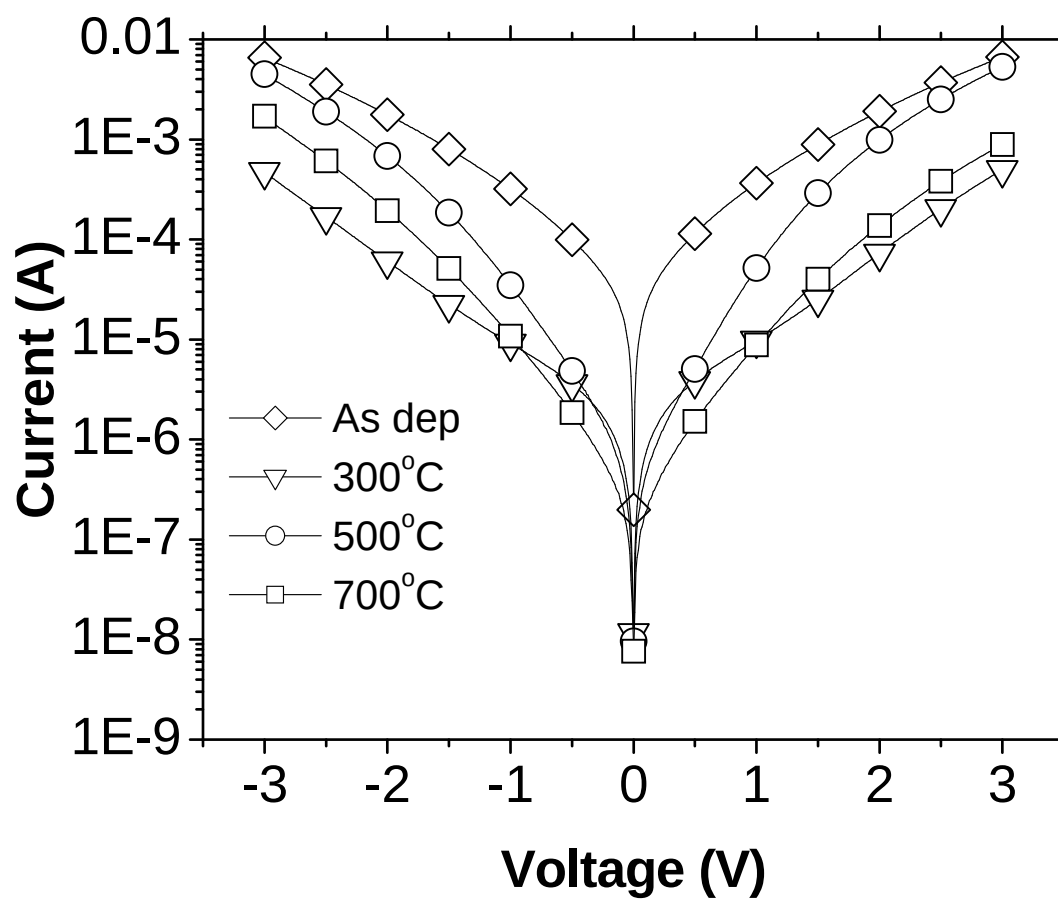


Figure 3-22: Current-voltage curves for Ni/Ir/Au contacts

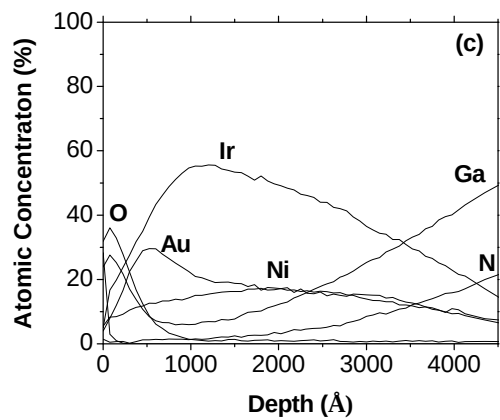
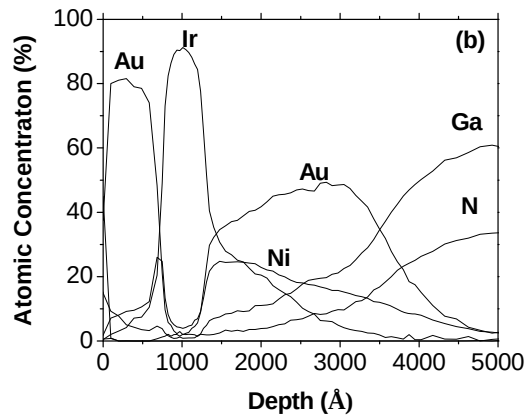
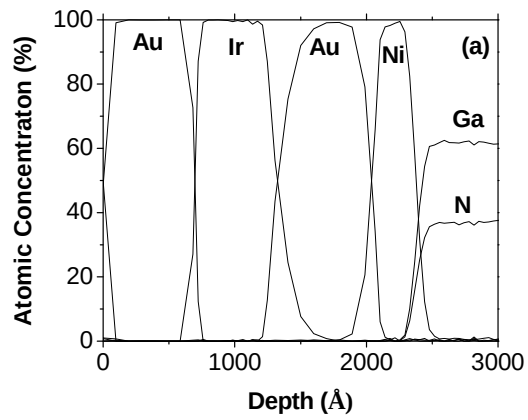


Figure 3-23: Depth profiles for Ni/Au/Ir/Au contacts (a) annealed at 300 °C (b) annealed at 500 °C and (c) annealed at 700 °C.

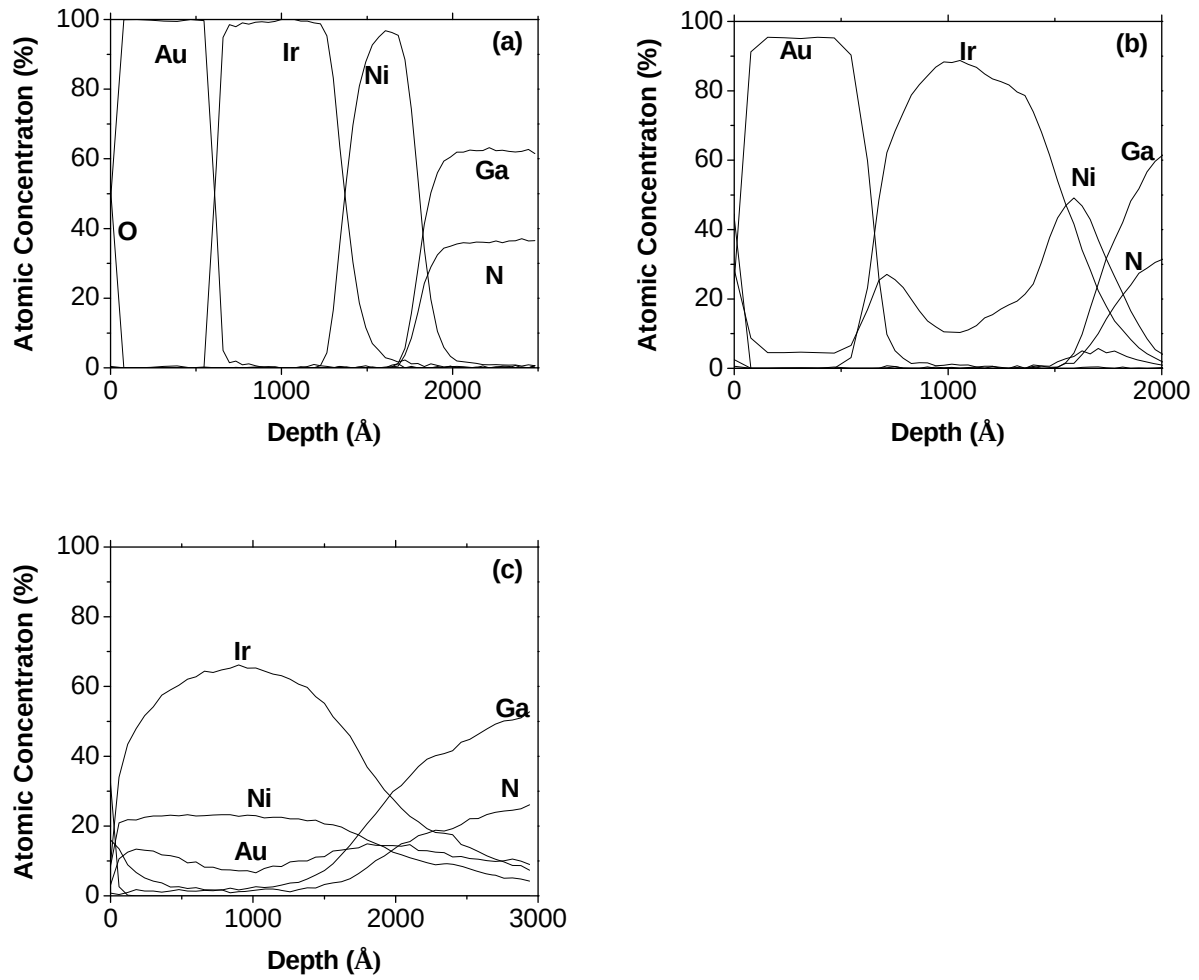


Figure 3-24: Depth profiles for Ni/Ir/Au contacts (a) annealed at 300 °C (b) annealed at 500 °C and (c) annealed at 700 °C.

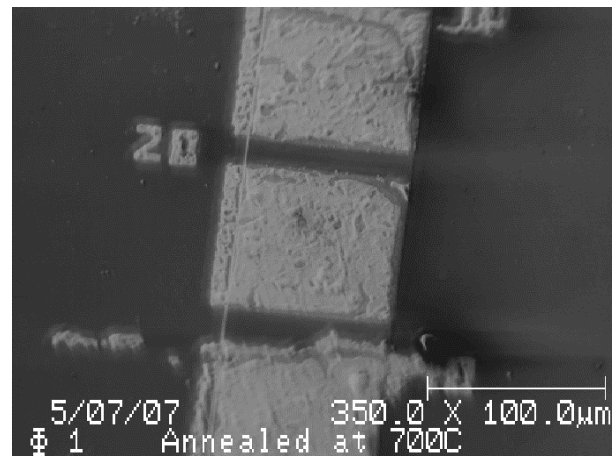
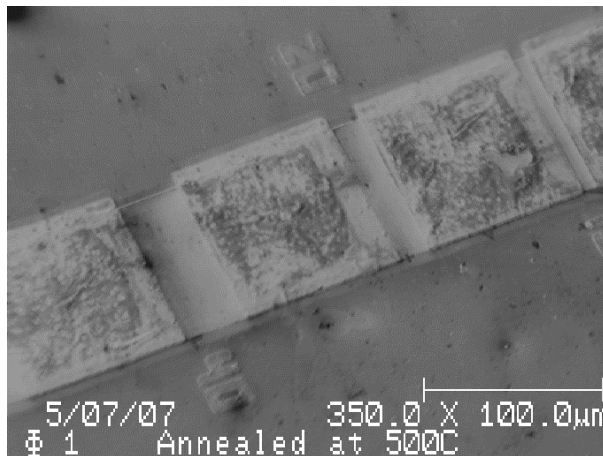
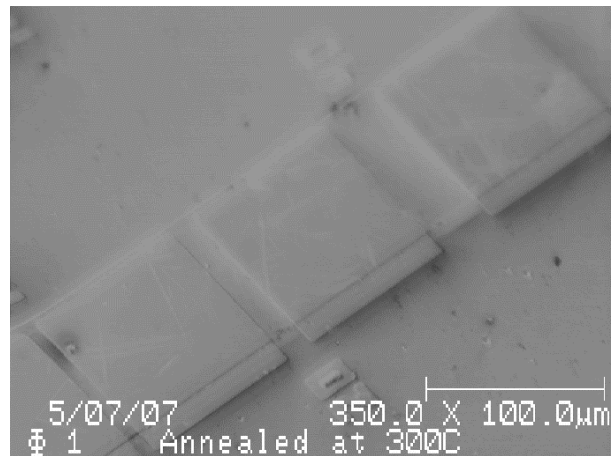
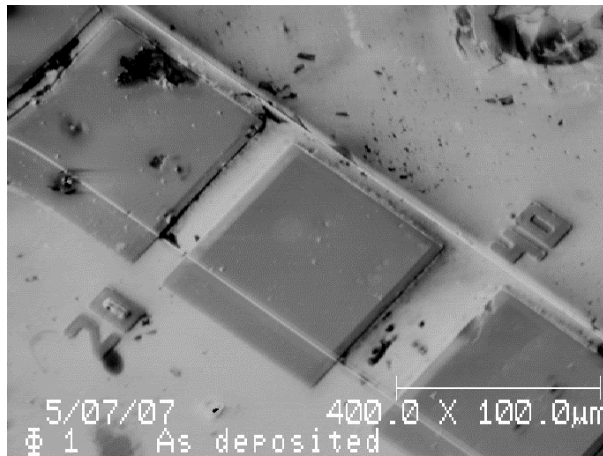


Figure 3-25: Scanning electron microscopy images of Ni/Au/Ir/Au contacts

CHAPTER 4

OHMIC CONTACTS TO N-GAN

In this chapter, we report results on Ohmic contacts based on these materials to n-GaN. Specific contact resistance has been studied as a function of annealing temperature, annealing time, and thermal aging for TaN, TiN, and ZrN diffusion barriers. All nitrides show comparable specific contact resistance to conventional Ti/Al/Pt/Au Ohmic contacts and display similar stability when aged at 350°C in air.

4.1 Experiment

The samples consisted of 3 μm thick Si-doped GaN grown by Metal Organic Chemical Vapor Deposition on c-plane Al_2O_3 substrates. From Hall measurements, the electron concentration was $\sim 3 \times 10^{17} \text{ cm}^{-3}$. Mesas 0.6 μm deep were formed by Cl_2/Ar inductively coupled plasma etching to provide for electrical isolation of the contact pads and to prevent current spreading. Deposition of a Ti (200 Å)/Al (800 Å)/X (500 Å)/Ti (200 Å)/Au (800 Å) metallization was performed by sputtering, where X is TaN, TiN, or ZrN. Sputtering was performed using a Ar plasma-assisted system at a pressure of 5 mTorr and rf (13.56 MHz) powers of 150-350W. For comparison, a Ti (200 Å)/Al (800 Å)/Pt (400 Å)/Au (800 Å) was deposited by e-beam evaporation. The contacts were patterned by lift off and annealed at 400-1000°C for 30-240s in a flowing N_2 ambient in a rapid thermal annealing (RTA) furnace.

Specific contact resistances were obtained using the linear transmission line (L-TLM) method. 100 μm x 100 μm pads with spacings of 80, 40, 20, 10, and 5 as well as 76, 36, 16, 6, and 1 μm were used. The total resistance is given by

$$R_T = 2R_C + R_s (L/W) \quad (4.1)$$

where R_C is the contact resistance, R_S the sheet resistance, L the pad spacing, and W the pad width. A plot of R_T vs pad spacing provides both R_C , from the y-intercept, and R_S , from the slope. The specific contact resistance is then calculated according to the equation

$$\rho_c = R_C^2 W^2 / R_S \quad (4.2)$$

All current-voltage plots were measured using an Agilent 4145B Parameter Analyzer.

Auger electron spectroscopy (AES) depth profiling of the contacts was performed with a Physical Electronics 660 scanning Auger microprobe. The electron beam conditions were 10 keV, 1 μ A beam current at 30° from the sample normal. For depth profiling, the ion beam conditions were 3 keV Ar^+ , 2.0 μ A, (3 mm)² raster. Before AES profiling, scanning electron microscopy images (SEMs) were acquired from the samples. The SEMs were obtained at magnifications of 125x and 1000x and were used to locate and document analysis area locations and the surface morphology. Quantification of elements was achieved using the elemental sensitivity factors.

4.2 Results and Discussion

Figure 4-1 shows the contact resistances as a function of anneal temperature for the nitride-based Ohmic contacts as well as the conventional Ohmic contact. As deposited, the contacts display slight curvature in the current-voltage curves. Upon annealing at 600-1000°C, the IV characteristics transform to Ohmic behavior. The specific contact resistances are stable up to 1000°C anneals, except for the TiN, which shows increased specific contact resistivity at 1000°C. The minimum specific contact resistance achieved was $\sim 6 \times 10^{-5} \Omega \cdot \text{cm}^2$ for the TiN-based contacts at an anneal of 800°C. This is likely due to diffusion of additional Ti to the surface to form the TiN phase. The ZrN-based contact appears to be the most stable with increased annealing temperature, maintaining a fairly constant value of $\sim 1 \times 10^{-4}$ for the range

600-900°C. These specific contact resistance values are expected for the moderately low doped samples used in this study. This is because the current transport mechanism for Ti/Al-based Ohmic contacts to n-GaN is tunneling and is governed by the relation

$$R_{SCR} \propto \exp \left[\frac{2\sqrt{\epsilon_S m_e^*}}{\hbar} \left(\frac{\phi_B}{\sqrt{N_D}} \right) \right] \quad (4.3)$$

Obviously, this relation shows a strong dependence on the doping of the n-GaN. For doping levels an order of magnitude higher, $3 \times 10^{18} \text{ cm}^{-3}$, we would expect a decrease in the contact resistance of approximately an order of magnitude.

Figure 4-2 shows the SEM images of the contacts as a function of anneal temperature. The as-deposited samples for TiN and ZrN show a smooth morphology while bubbles are present on the TaN as-deposited sample, possibly due to trapped sputter gases. At 600°C and 800°C anneals the contacts maintain a reasonable morphology. Furthermore, there appears to be little degradation of the surface even after aging at 350°C. All contacts show good edge acuity, a concern for devices with small contact separations.

Figures 4-3,4, and 5 show the AES depth profiles of the nitride-based contacts. As deposited, all contacts contain a significant amount of oxygen incorporation in the Ti and nitride layers. This is due to the relatively high base pressure of the sputtering system of $\sim 2 \times 10^{-6}$ Torr. Note that despite this, the contact resistances are not adversely affected when compared to the Ti/Al/Pt/Au contacts, which were deposited in an electron beam evaporation operating at a base pressure of $\sim 3 \times 10^{-7}$ Torr. As deposited, the metallic interfaces are sharp and there is little intermixing between the layers. Upon annealing at 600°C, Al has outdiffused to the surface and some Au has indiffused to the interface. At higher temperatures, the amount of interdiffusion increases. The amount of interdiffusion is much less than that seen with a standard metallic

diffusion barrier, such as Ni. Figure 4-6 shows a profile for a Ti/Al/Ni/Au contact annealed at 500°C. From the profiles, the nitrides appear to be breaking down somewhat, with TiN the least affected, as the location of the Zr and Ta peaks do not correspond precisely to those of the N. Little change in the contact structure is seen with long term aging even after greater than 20 days. Because there is only minimal intermixing of the layers, little of the viscous AlAu_4 phase has formed compared to conventional contact schemes.

Figure 4-7 shows the dependence upon anneal time at 800°C. Upon annealing for up to 180 seconds, an increase in contact resistance is seen in each of the contacts. The standard Ti/Al/Pt/Au contact exhibit the largest increase in contact resistance, while the contacts containing TaN and TiN display more moderate increases. The ZrN-based contact displays only a slight increase in contact resistance even upon annealing for 180 seconds.

Figure 4-8 displays the specific contact resistance as a function of long term thermal aging. Samples placed on a hot plate at 350°C display all display a gradual increase in the specific contact resistance throughout the period. Table 4-1 shows the percentage increase in specific contact resistance for each scheme. Compared to the Ti/Al/Pt/Au contacts, the ZrN and TaN contacts display better stability, with the specific contact resistance increasing only about 100%. The TiN contacts displayed a larger increase.

4.3 Conclusions

Ohmic contacts to n-GaN were fabricated using a Ti/Al/X/Ti/Au scheme, where X is either TaN, TiN, or ZrN. These contacts display similar specific contact resistances to the conventional Ti/Al/Pt/Au contacts deposited on the same wafer, $\sim 10^{-4}$ ohm-cm² over a wide range of annealing temperatures. In addition, the TaN and ZrN contacts display only about half the increase in specific contact resistance that is seen in the Ti/Al/Pt/Au contacts. The AES depth profiles confirm that little intermixing has occurred during the aging process. Because of this,

these contacts show promise for use in high temperature applications. While the contact resistance does not seem to be better than that of conventional contacts after aging, there is far less mixing between layers. This is a primary concern, due to the AlAu_4 phase, for devices with short spacings for high temperature applications. Further evaluation in devices such as HEMTs is needed in order to determine the potential of these contacts. In addition, the effect of oxygen incorporation in the nitride should be examined.

Table 4-1: Percent change in specific contact resistance during thermal aging

Contact	Percent Change
Ti/Al/Pt/Au	236%
Ti/Al/TaN/Ti/Au	107%
Ti/Al/TiN/Ti/Au	330%
Ti/Al/ZrN/Ti/Au	091%

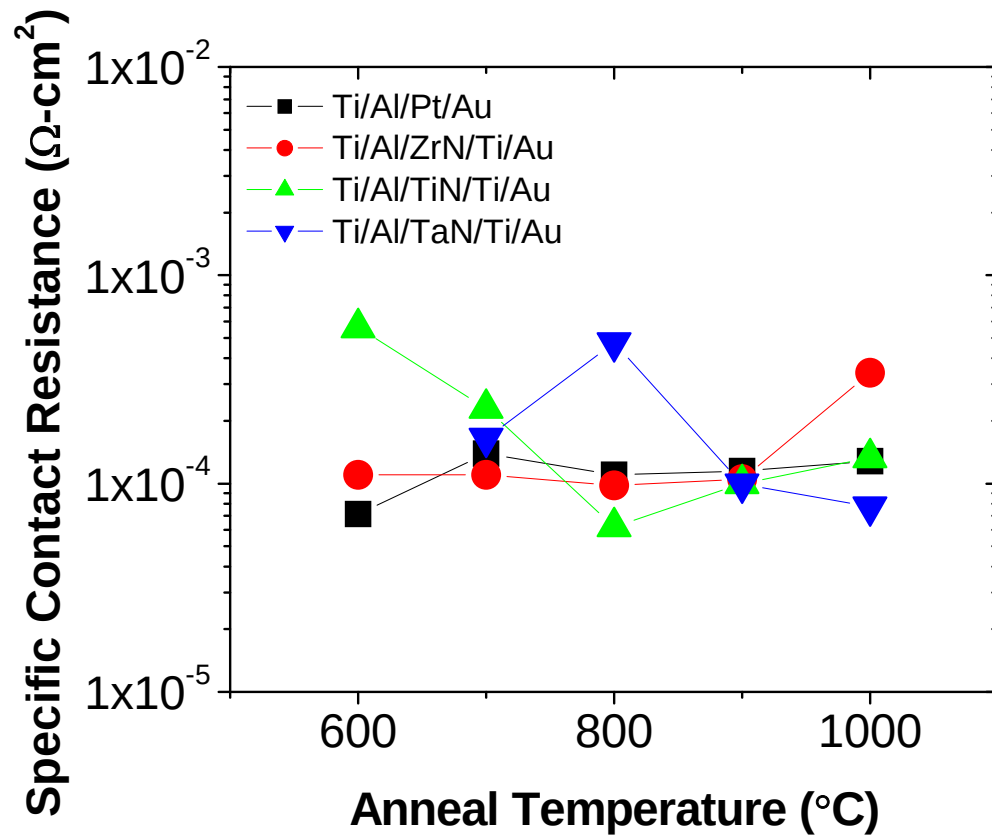


Figure 4-1: Specific contact resistance as a function of anneal temperature

TaN TiN ZrN

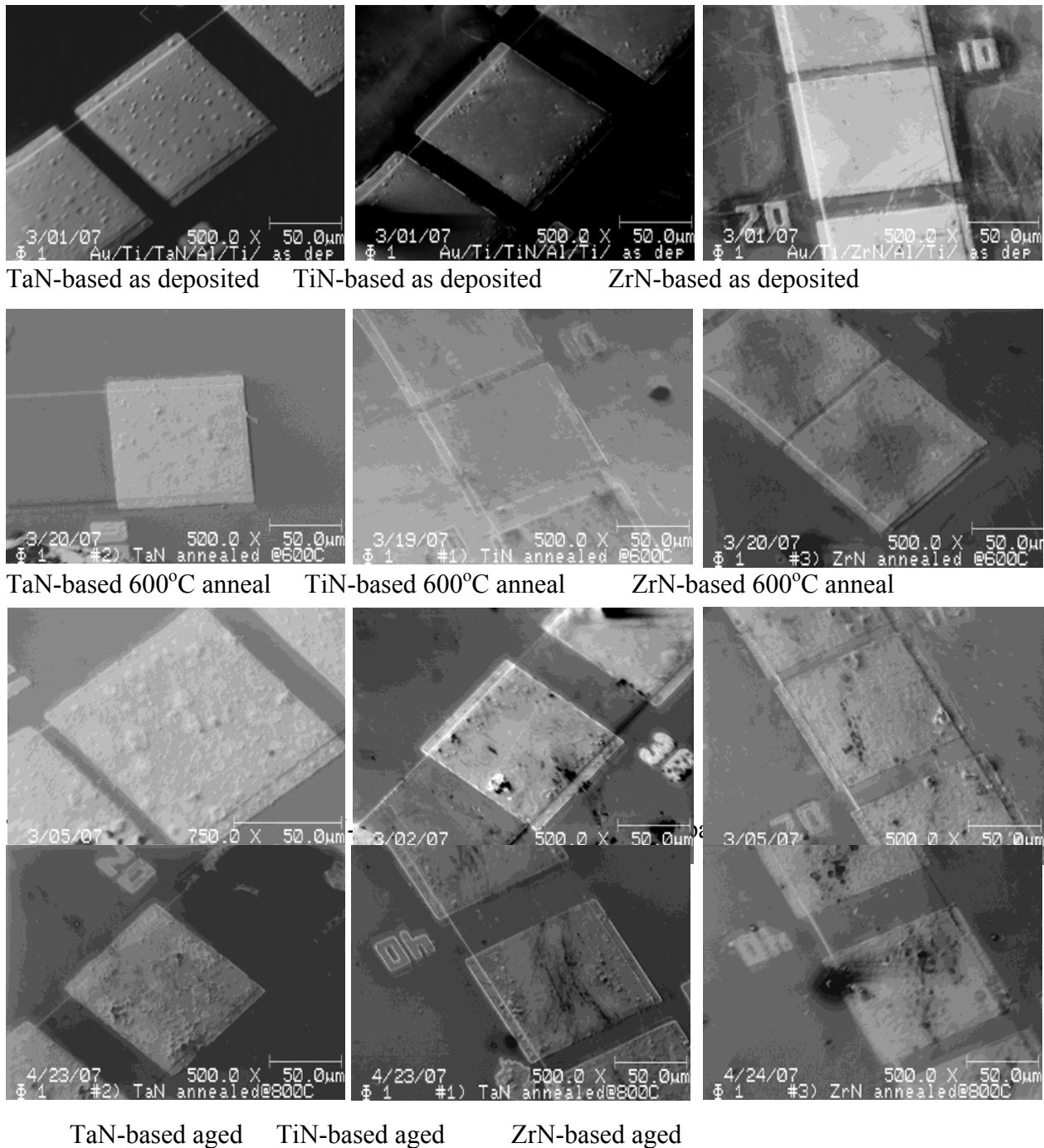


Figure 4-2: Scanning electron microscopy images of annealed contacts

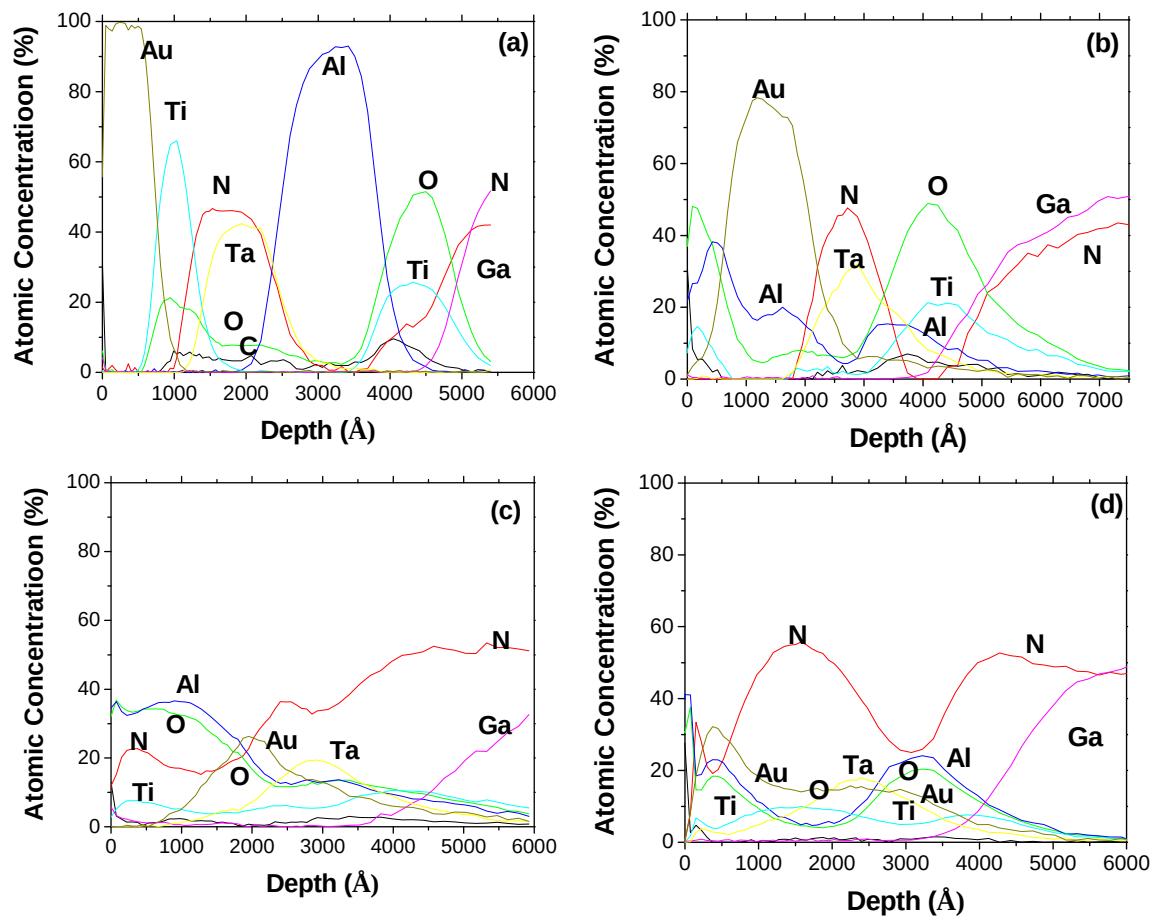


Figure 4-3: Depth profiles of Ti/Al/TaN/Ti/Au contacts (a) as deposited (b) annealed at 600°C. (c) annealed at 800°C and (d) annealed at 800°C and aged at 350°C.

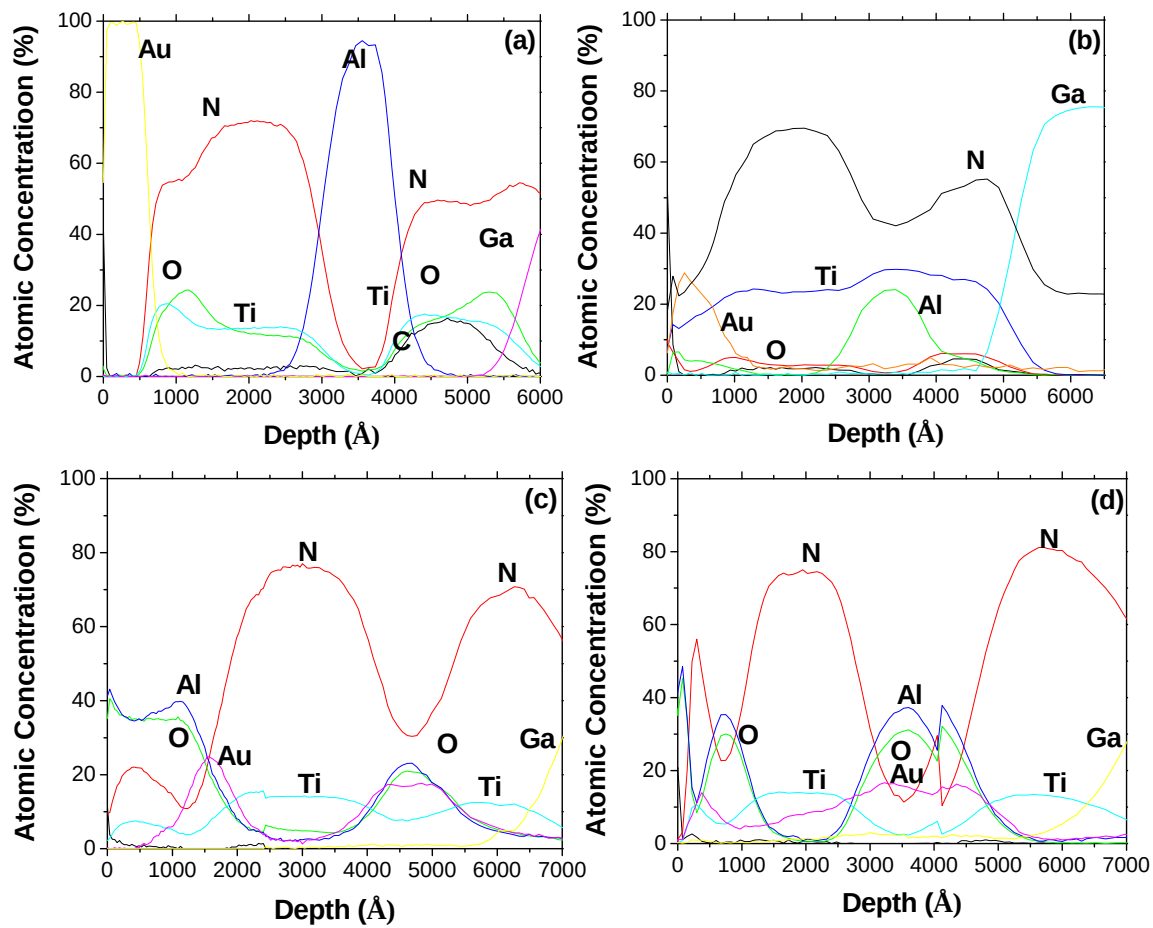


Figure 4-4: Depth profiles of Ti/Al/TiN/Ti/Au contacts (a) as deposited (b) annealed at 600°C. (c) annealed at 800°C and (d) annealed at 800°C and aged at 350°C.

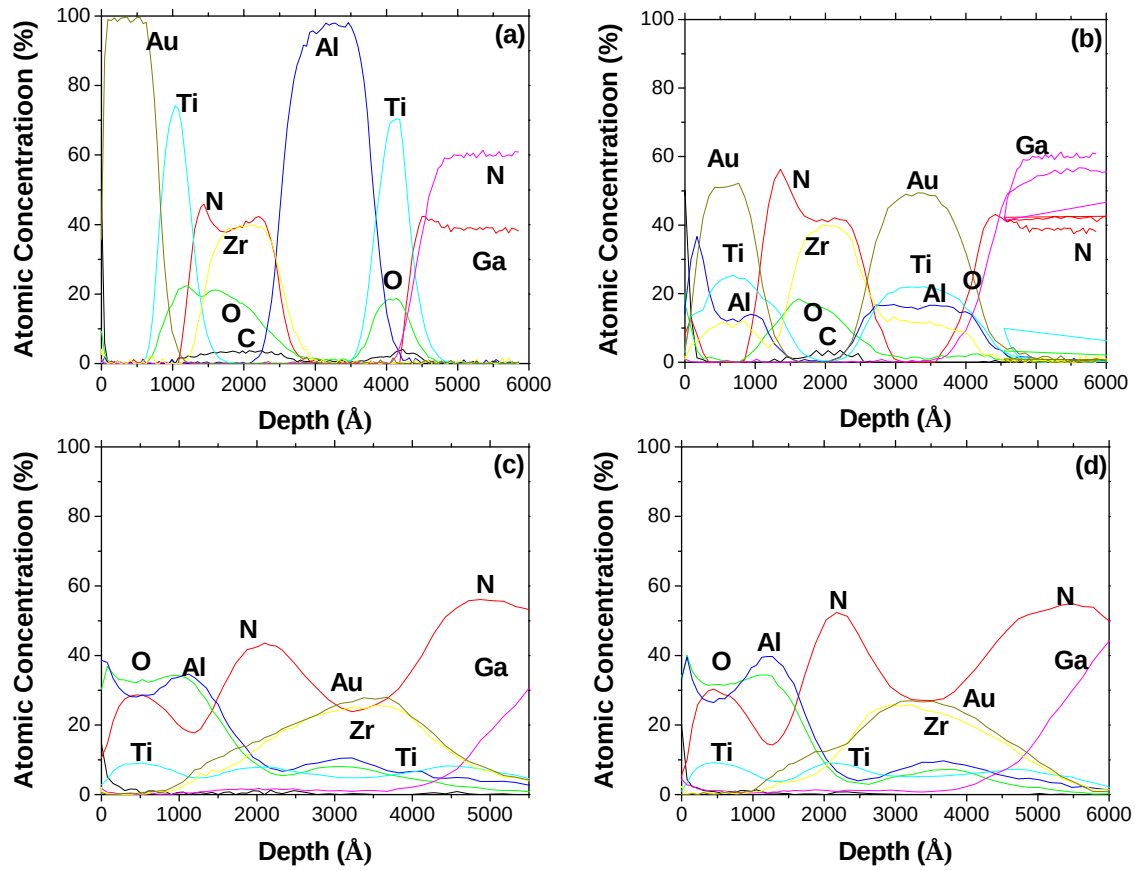


Figure 4-5: Depth profiles of Ti/Al/ZrN/Ti/Au contacts (a) as deposited (b) annealed at 600°C. (c) annealed at 800°C and (d) annealed at 800°C and aged at 350°C.

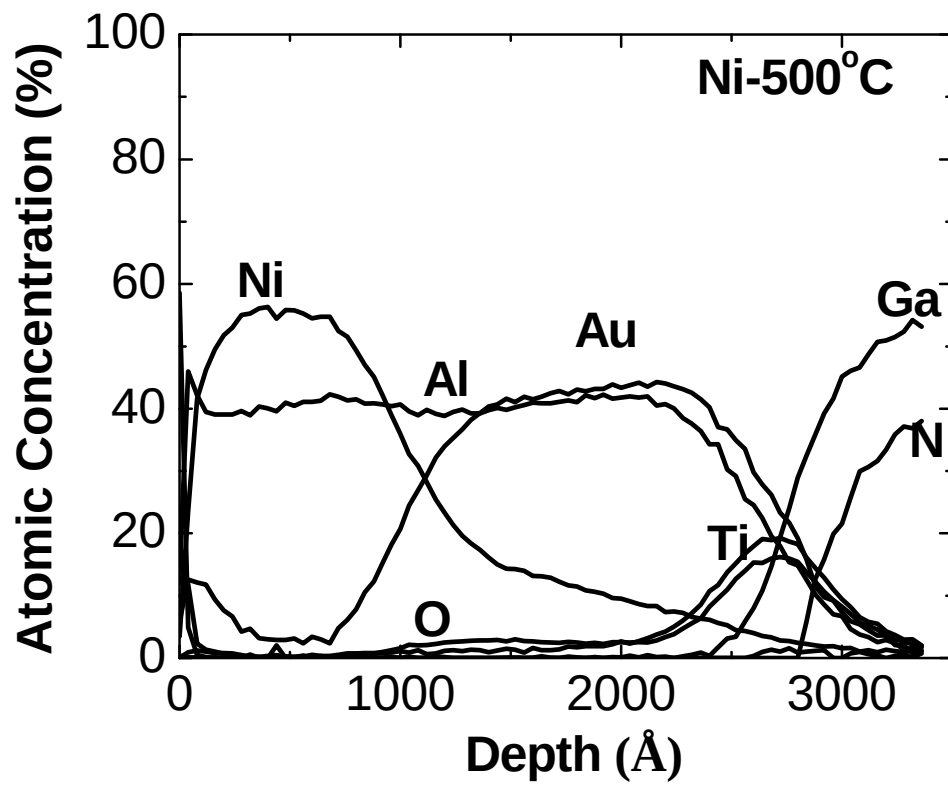


Figure 4-6: Depth profile of Ti/Al/Ni/Au contact annealed at 500°C.

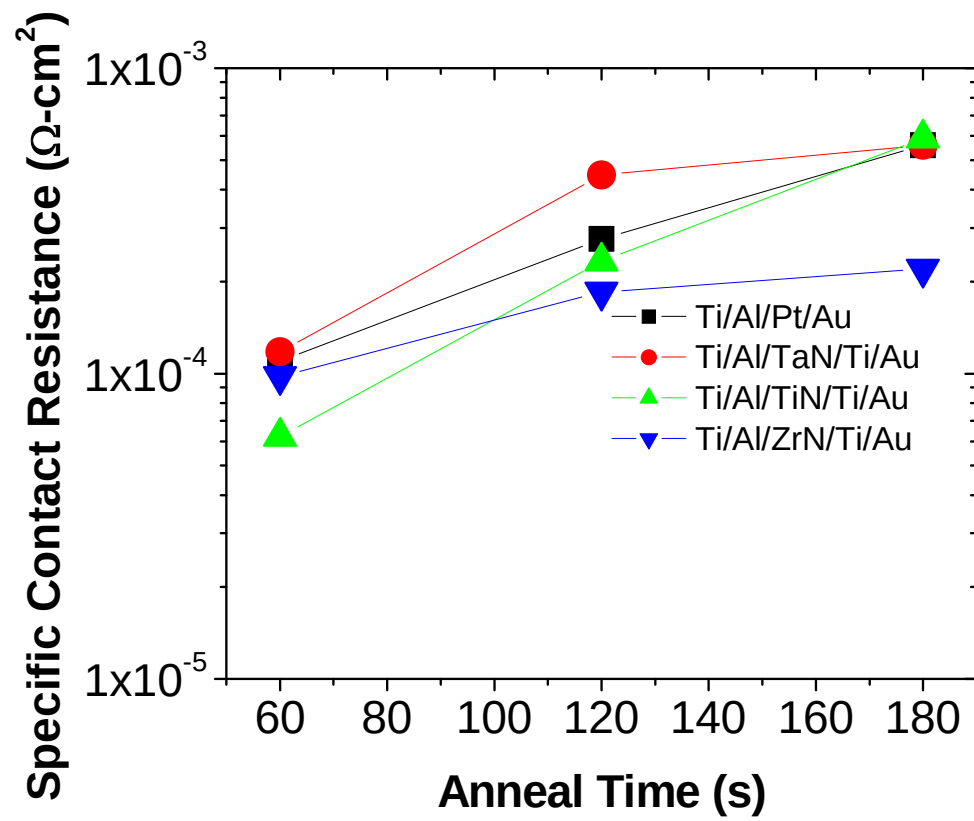


Figure 4-7: Specific contact resistance as a function of anneal time.

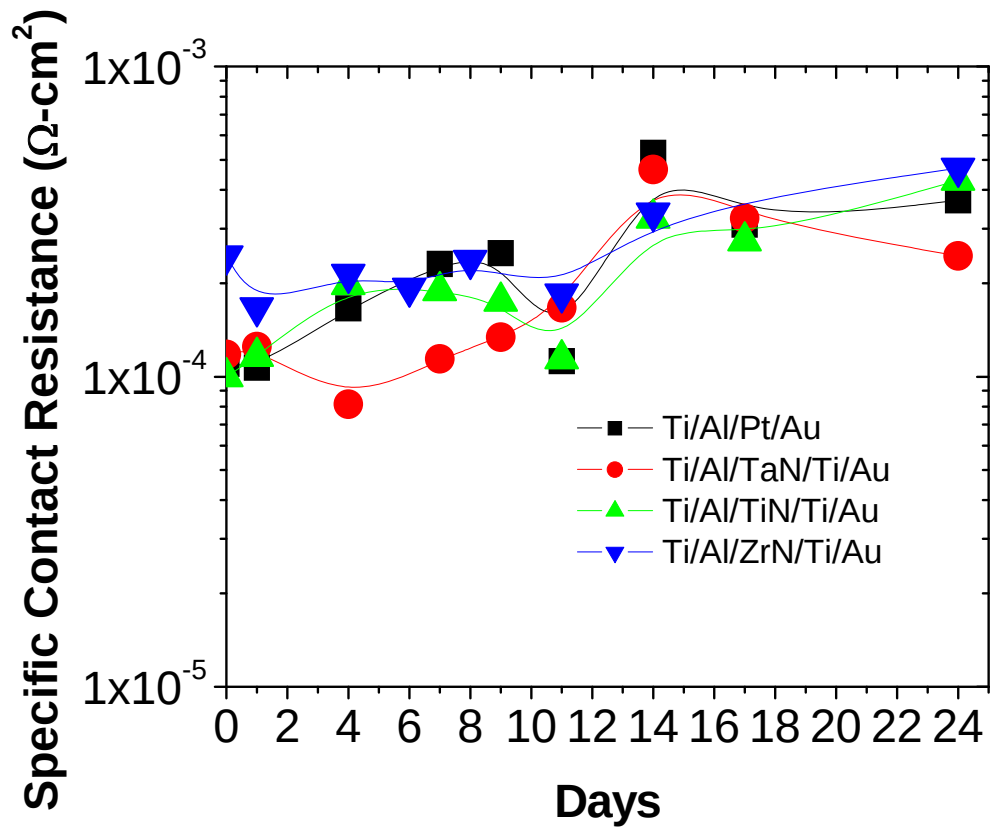


Figure 4-8. Specific contact resistance as a function of long term thermal aging.

CHAPTER 5 BORIDE-BASED SCHOTTKY CONTACTS TO P-GAN

5.1 Introduction

The unique combination of wide bandgap, high breakdown field, high saturation velocity, and ability to form high-quality heterostructures with good transport properties make GaN an ideal candidate for several device applications including light emitting diodes (LEDs) for displays, laser diodes for data storage, and high electron mobility transistors (HEMTs) for high-power and high frequency electronics. An important aspect for improved reliability of GaN-based devices is the development of more thermally stable Ohmic and Schottky contacts to both n-type and p-type GaN. This aspect has been one of the major issues in the operating lifetime of III-nitride lasers and LEDs and it is yet to be overcome completely. Another example is AlGaIn/GaN HEMTs in advanced power amplifiers and converters for which the development of Ohmic and Schottky contacts ensuring long-time operation under uncooled and high temperature conditions without metal spiking or loss of edge acuity remains a challenge. One approach that has proven promising for contact formation on n-GaN is the use of very high melting temperature metals like W and WSi₆ [24,68,71-74]. Recently, other promising metallurgies based on transition metal borides like W₂B, W₂B₅, ZrB₂, CrB₂, and TiB₂ have also been proposed [75-78]. The interest in borides is due to their high melting temperature (e.g. 3200°C for ZrB₂) and high thermodynamic stability. For p-GaN, most rectifying contact studies have been performed with simple metals such as Ni, Pd, Ti, Cr, and Pt, [17, 54-66] and studies on boride-based metallurgies are still in their infancy.

In this work, we report on the annealing and measurement temperature dependence of W₂B and W₂B₅-based rectifying contacts to p-GaN. The barrier heights determined by X-Ray Photoelectron Spectroscopy (XPS) are in the range 2.7-2.9 eV. These contacts are found to be

reasonably stable upon annealing to $\sim 600\text{-}700^\circ\text{C}$. While current-voltage characteristics as a function of measurement temperature suggest thermionic field emission (TFE) over a Schottky barrier as the most dominant mechanism of forward current flow, the bias and measurement temperature dependence of the reverse-bias current indicates that leakage must originate from surface leakage or generation in the depletion layer.

5.2 Experimental Details

The p-GaN samples were 1 μm -thick Mg-doped GaN layers grown by metal organic chemical vapor deposition (MOCVD) on 1 μm -thick undoped buffers on c-plane Al_2O_3 substrates. The hole concentration obtained from Hall measurements after acceptor activation annealing was $\sim 10^{17} \text{ cm}^{-3}$. The surface was cleaned by sequential rinsing in acetone, ethanol and 10:1 $\text{H}_2\text{O}:\text{HCl}$ prior to insertion in the deposition chamber. Boride(500Å)/Pt(200Å)/Au(800Å), where the boride was either W_2B or W_2B_5 , was used as the Schottky metallization scheme. Au was added to lower the contact sheet resistance while Pt is a diffusion barrier. All metals or compounds were deposited by Ar plasma-assisted rf (13.56 MHz) sputtering at a pressure of 15 mTorr and rf powers of 250-400 W. The contacts were patterned by liftoff of lithographically-defined photoresist and annealed at temperatures up to 700°C for 1 min in a flowing N_2 ambient in a RTA furnace. For Ohmic contacts, we used Pt/Au annealed at 500°C in O_2 for 30s prior to deposition of the Schottky metallization. Ring contact geometry for the diodes was employed, with the Schottky contacts surrounded by the Ohmic contacts. The Schottky contact dots were 40 μm in diameter, the surrounding was 60 μm in inner diameter and 70 μm in outer diameter.

XPS, current-voltage (I - V), and auger electron spectroscopy (AES) were used to characterize boride-based rectifying contacts. XPS measurements were taken with a Physical Electronics 5100LSci spectrometer with an aluminum x-ray source (energy 1486.6 eV). High-

resolution spectra were acquired to determine the binding energy (i.e. chemical state) and concentration of specific elements observed in the survey spectra. Charge correction was performed by using the known position of the C-(C,H) line in the C 1s spectra at 284.8 eV. The SBH was determined from the binding energy of the Ga 3d core level E_B and the energy difference between that core level and the valence band maximum E_{VC} according to

$$\phi_B = E_B - E_{VC}. [62,79]$$

The I -Vs were recorded over the temperature range 25-200°C using a probe station and an Agilent 4145B parameter analyzer. For the relatively high doped p-GaN samples investigated in this work, TFE over a Schottky barrier is expected to be the dominant mechanism of forward current flow [56,57,62,63,80]. We fit the forward I - V characteristics to the relation for TFE over a barrier [81]

$$J_F = J_0 \exp\left(\frac{eV}{E_0}\right) (5.1)$$

where J_F is the current density, e is the electronic charge, and V is the applied voltage. In Eq. (1), $E_0 = E_{00} \coth(E_{00}/k_B T)$ is the characteristic energy related to the tunneling probability, k_B and T being the Boltzmann's constant and absolute temperature, respectively. For p-GaN, $E_{00} (eV) \approx 7.75 \times 10^{-12} \sqrt{N_A (cm^{-3})}$, [56,62] N_A being the density of acceptors. The saturation current density J_0 is given by

$$J_0 = \frac{A^* T [\pi E_{00} q (\phi_B - V - \xi)]^{0.5}}{k_B \cosh(E_{00}/k_B T)} \exp\left(-\frac{e\xi}{k_B T} - \frac{e(\phi_B - \xi)}{E_0}\right) (5.2)$$

where $A^* = 103.8 \text{ A cm}^{-2} \text{ K}^{-2}$ is the effective Richardson's constant for p-GaN, [82] ϕ_B is the barrier height, and $\xi = (E_F - E_V)/e$ is the difference between the valence band maximum and the position of the Fermi level. This parameter depends on the doping level, but, as will be shown

later, it only slightly influences the SBH of W_2B and W_2B_5 -based rectifying contacts to p-GaN. Nakayama *et al.* [83] have suggested that a hole concentration of $2 \times 10^{17} \text{ cm}^{-3}$ in p-GaN samples leads to $\xi = 0.13 \text{ V}$. This hole concentration is very close to that achieved in the present study so that we also assume $\xi = 0.13 \text{ V}$.

Auger electron spectroscopy (AES) was used to analyze the depth profiles. A Physical Electronics 660 Auger Microprobe Electron Beam at 10 keV, 0.3 μA , 30° from sample normal was used for the data collection while for profiling the ion beam conditions were 3 keV Ar^+ , 2.0 μA , $(4 \text{ mm})^2$ raster with sputter-etch rates of 80, 40, and 104 $\text{\AA}/\text{min}$ for the boride, Pt and Au layer respectively. A survey spectrum (a plot of the first derivative of the number of electrons detected as a function of energy) was used to determine the composition of the outer few nanometers of each sample. Quantifications were accomplished by using elemental sensitivity factors.

5.3 Results and Discussion

Figure 5-1 presents an example of the Ga 3d core level and the valence band spectrum collected on a p-GaN surface without a boride overlayer. From Figure 5-1, we find $E_{VC} = 17.54 \text{ eV}$, which is in reasonable agreement with the value of 17.8 eV reported previously. [62,84] After W_2B deposition, Figure 5-1 shows that the binding energy of the Ga 3d core level is $E_B = 20.25 \text{ eV}$, thereby yielding $\phi_B = 2.71 \text{ eV}$. Similarly, we find $E_B = 20.41 \text{ eV}$ for W_2B_5 , which gives $\phi_B = 2.87 \text{ eV}$. These results are similar to the 2.68-2.78 eV values reported by Yu *et al.* [56] for Ni/p-GaN. Based on the Schottky-Mott model [52], the SBHs for n-GaN and p-GaN should add up to the GaN band gap 3.4 eV. For W_2B and W_2B_5 -based rectifying contacts to n-GaN, Khanna *et al.* [76,77] have reported $\phi_B \sim 0.55 \text{ eV}$, thereby suggesting $\phi_B \sim 2.85 \text{ eV}$ for p-GaN. Our XPS results are clearly in excellent agreement with the predictions of this model.

The I - V characteristics as a function of the measurement temperature for the W_2B -based diodes are shown in Figure 5-2. All $\log I$ vs V curves measured between 25 and 200°C exhibit a linear region at low forward bias (up to ~ 2.0 V) and a less steep region at higher voltages. Furthermore, all $\log I$ vs V curves are parallel. As noted in refs. [56,57,62,63] for p-GaN samples with relatively high doping levels ($>10^{17} \text{ cm}^{-3}$), this latter result is inconsistent with the thermionic emission model but typical for carrier transport with a dominant tunneling component. Note that Shirojima *et al.* [61] have reported accurate determination of the SBH using the TE model. However, the acceptor concentration in their p-GaN samples was relatively low ($\sim 10^{16} \text{ cm}^{-3}$). In our case, the Mg concentration is expected to be in the 10^{19} cm^{-3} range, thus confirming that the forward current cannot be analyzed using the thermionic emission model.

Figure 5-3 displays the I - V characteristics obtained from the diodes annealed at different temperatures. The extracted characteristic energy related to the tunneling probability as a function of annealing temperature is shown in Figure 5-4. For W_2B , the value of E_0 is seen to remain stable in the 120 meV range and then increases beyond $\sim 500^\circ\text{C}$. This value of E_0 corresponds to an acceptor density of about $2 \times 10^{20} \text{ cm}^{-3}$, which is higher than that expected from the Mg concentration alone ($E_0 \sim 25 \text{ meV}$ for $N_A \sim 10^{19} \text{ cm}^{-3}$). This can probably be attributed to the presence of acceptor-like deep level defects induced by both the high Mg doping [63,85,86] and the sputter-deposition process [29,87]. In the case of W_2B_5 , a slight decrease of E_0 is observed at intermediate annealing temperature which can probably be attributed to the annealing of sputter-damage [29,87].

The influence of annealing on the SBH derived from the I - V measurements of $W_2B/\text{Pt}/\text{Au}$ and $W_2B_5/\text{Pt}/\text{Au}$ contacts is presented in Figure 5-5. Over the whole range of temperatures investigated, the SBH only slightly decreases with increasing annealing temperature. However,

these values are unphysical, being larger than the GaN band gap, and are inconsistent with both our XPS measurements and the predictions of the Schottky-Mott model. One may argue that this discrepancy results from the value of ξ used in our calculations. However, it is shown in Figure 5-6 that over the wide range of ξ values investigated, this parameter only slightly influences the SBH. The discrepancy between XPS and *I-V* measurements is more likely related to the presence of an interfacial defect layer or due to the presence of an interfacial oxide layer. Indeed, it was shown by Shiojima *et al.* [88] using high-temperature isothermal capacitance transient spectroscopy that the defects induced by the high Mg doping in p-GaN are essentially located at the surface vicinity and that this region acts as a series capacitance [88,89]. Therefore, when such defect or oxide layer is present, the carriers have to tunnel through an additional barrier, thus resulting in an apparent SBH given by $\phi_B = \phi_B^0 + \Delta\phi_B$, where ϕ_B^0 is the true SBH between the contact metal and p-GaN and where $\Delta\phi_B$ is the increment of the SBH due to the presence of the thin defect or oxide layer. Our separate capacitance-voltage measurements (*C-V*) have indeed shown that by accounting for such defect layer, the SBH obtained from the *C-V* characteristics becomes similar to that determined by XPS [80]. We have calculated a corrected junction capacitance C_{corr} for W₂B/p-GaN from the equivalent circuit using the simple relation $(1/C_{corr}) = (1/C_m) - (1/C_{ox})$, where C_m and C_{ox} are the as-measured and oxide capacitances respectively. From our XPS measurements, the true SBH for W₂B/p-GaN is $\phi_B^0 \sim 2.7$ eV. Using our *C-V* measurements, Figure 5-7 shows that the value of C_{ox} required to obtain a SBH similar to that determined by XPS is $C_{ox} \sim 0.70$ nF. Assuming a contact area of $\sim 2 \times 10^{-9}$ m² and a relative permittivity of ~ 10 for the oxide layer [90], we estimate an oxide layer thickness of ~ 0.25 nm, i.e. about one monolayer. For 20 μ m-diameter diodes, the value of C_{ox} required to fit the XPS

data was 4 times lower than that for 40 μm -diameter diodes, as expected from the surface area ratio. In addition, the density of acceptors obtained from the corrected C - V s was $1.8 \times 10^{20} \text{ cm}^{-3}$, which is very similar to the value determined above from the I - V s. Table 5-1 summarizes the calculated barrier heights from XPS, IV with both thermionic and thermionic field emission, and CV measurements.

Figure 5-8 presents the influence of the measurement temperature on the reverse-bias current for the W_2B -based diodes. All $\log I$ vs V curves measured between 25 and 200°C exhibit a linear region at high reverse bias and a steeper variation at lower reverse voltages. In addition, as the measurement temperature increases, the reverse leakage current also increases. Given the large barrier height typical for rectifying contacts to p-GaN, one can assume that thermionic emission over the Schottky barrier makes only a negligible contribution to the reverse-bias current flow. This assumption is further supported by the fact that all $\log I$ vs V curves in Figure 5-8 are parallel, which is clearly inconsistent with the thermionic emission model. On the other hand, in the tunneling approach, the reverse current density J_L is given by the Fowler-Nordheim tunneling expression $J_L = CE_b^2 \exp(E_b/D)$, where $C=C(\phi_B)$ and $D=D(\phi_B)$ are parameters independent of the measurement temperature [91-93]. For tunneling, the reverse-bias current is thus independent of the measurement temperature, which again is inconsistent with the experimental data displayed in Figure 5-6. Leakage must therefore originate from other mechanisms such as generation in the depletion layer or surface leakage. The large band gap of GaN makes the intrinsic carrier concentration in a depletion region very small, suggesting that contributions to the reverse-bias leakage from generation in the depletion layer are negligible. However, given the large number of deep-level defects located at the surface vicinity [88] as a result of both the high Mg doping [29,85,86] and the sputter-deposition process [29,87], one may

expect these defects to act as generation centers when the carrier density is below its equilibrium value as in the reverse-bias regime of a Schottky diode.

The breakdown voltage, V_B , of the boride-based rectifying diodes as a function of annealing temperature is shown in Figure 5-9. V_B shows the opposite trend to the characteristic energy related to the tunneling probability displayed in Figure 5-4, decreasing where E_0 increases. As E_0 is directly related to the density of acceptor-like deep-level defects, this observation is consistent with our expectations that leakage essentially results from a defect-mediated mechanism. As observed for boride-based rectifying contacts to n-GaN [75,76], the improvement of breakdown voltage at intermediate annealing temperatures is likely to result from the annealing of sputter-damage in the near-surface region of GaN. At high annealing temperature, V_B is seen to decrease, indicating that the diodes become very leaky.

AES depth profiles of the as-deposited and annealed contacts are shown in Figure 5-10. For both diodes, the as-deposited layers exhibit relatively sharp interfaces, consistent with the featureless surface morphology observed with both optical and scanning electron microscopy. After high-temperature annealing, W_2B -based contacts show the onset of metallurgical reaction in the contact scheme whereas W_2B_5 presents significant interdiffusion of layers.

5.4 Conclusions

In summary, our XPS measurements have shown that W_2B - and W_2B_5 -based rectifying contacts to p-GaN produce barrier height in the 2.7-2.9 eV range, in excellent agreement with the predictions of the Schottky-Mott model. By comparison, the SBH determined from the I - V s using the TFE model are unphysically large and much higher than those deduced from XPS due to the presence of a defect layer acting as an additional barrier to carrier transport. The apparent SBH only slightly decreases upon annealing to 600-700°C due to the onset of metallurgical

reaction with the GaN. This suggests that that the boride-based metallurgies may be promising for rectifying contacts to p-GaN where thermal stability is a critical issue. The bias and measurement temperature of the reverse leakage current indicates that leakage must originate from surface leakage or generation in the depletion region through deep-level defects.

Table 5-1: Comparison of different barrier height calculations

XPS	TE	TFE	C-V
$\phi_B = 2.7 \text{ eV}$	$\phi_B = 1.2 \text{ eV}$ $n = 4.4$	$\phi_B = 3.8 \text{ eV}$ $E_0 = 110 \text{ meV}$	$\phi_B = 4.1 \text{ eV}$

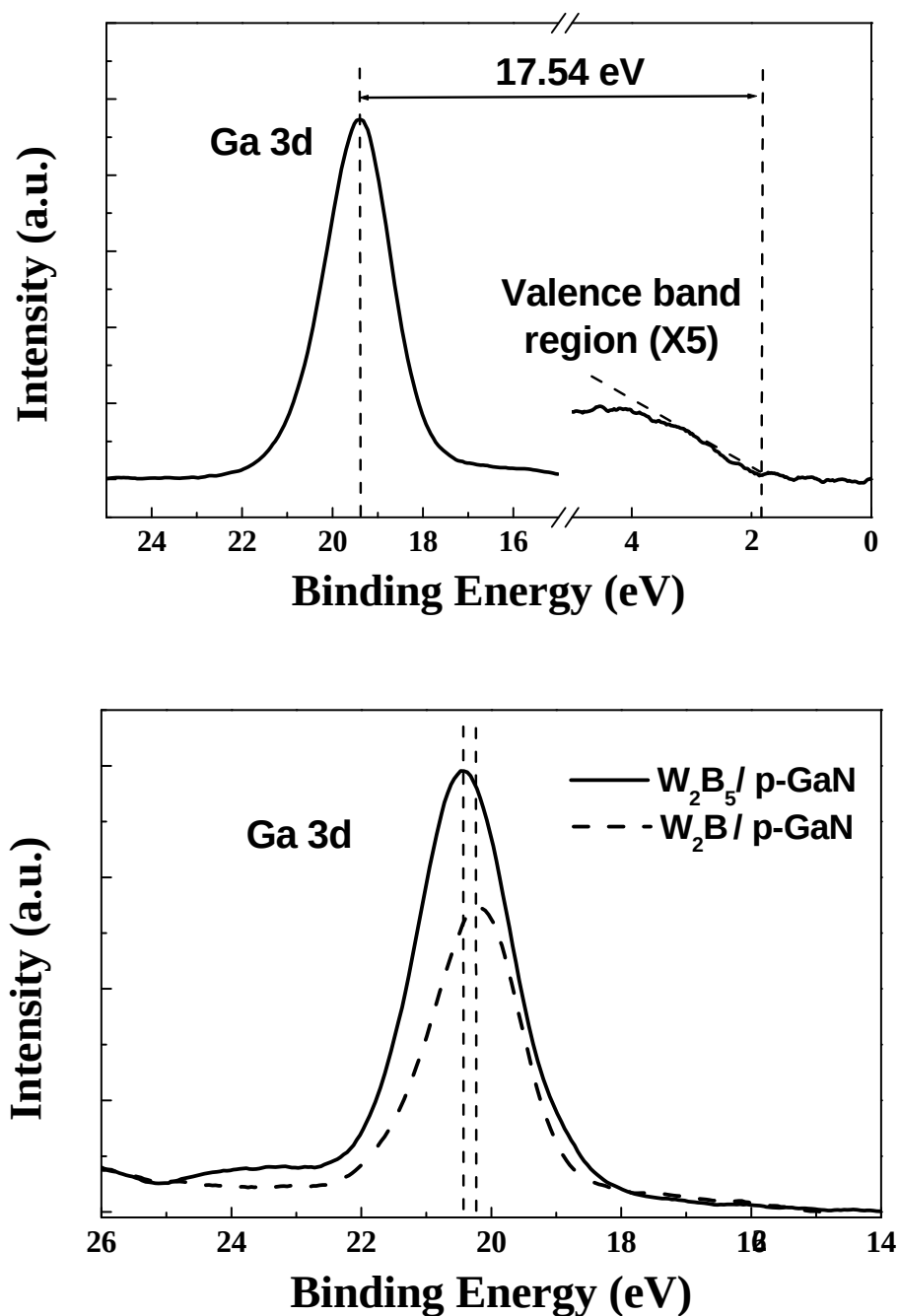


Figure 5-1: XPS spectra without (top) and with (bottom) a boride overlayer. The left-hand spectrum in the top figure corresponds to the Ga 3d core level whereas the right-hand panel presents the spectrum of the valence band region.

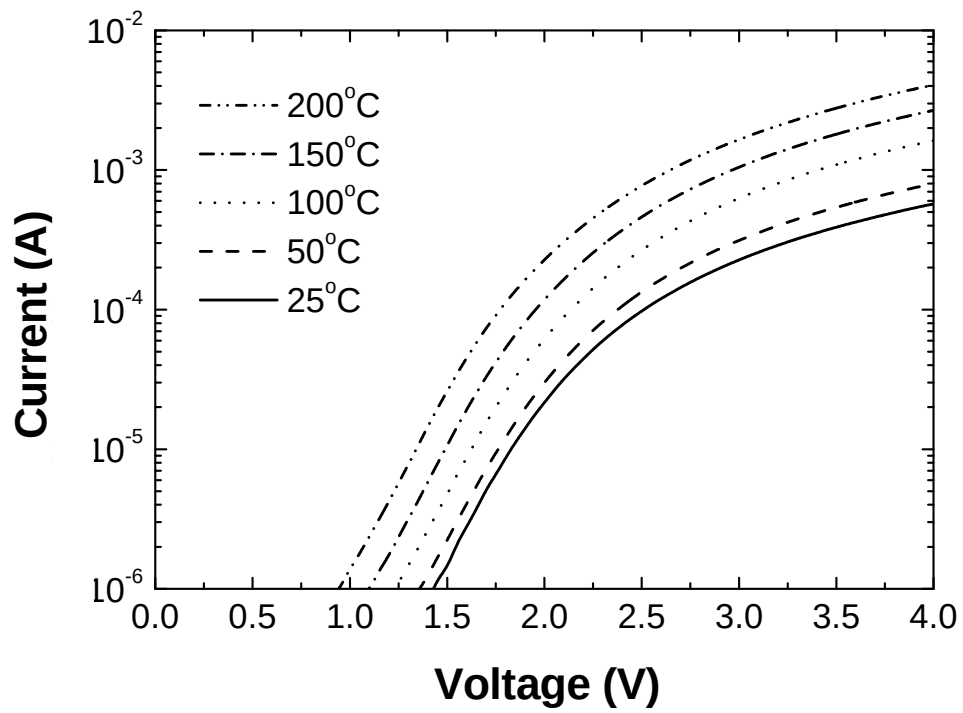


Figure 5-2: Forward current-voltage characteristic of W₂B-based Schottky diodes as a function of measurement temperature.

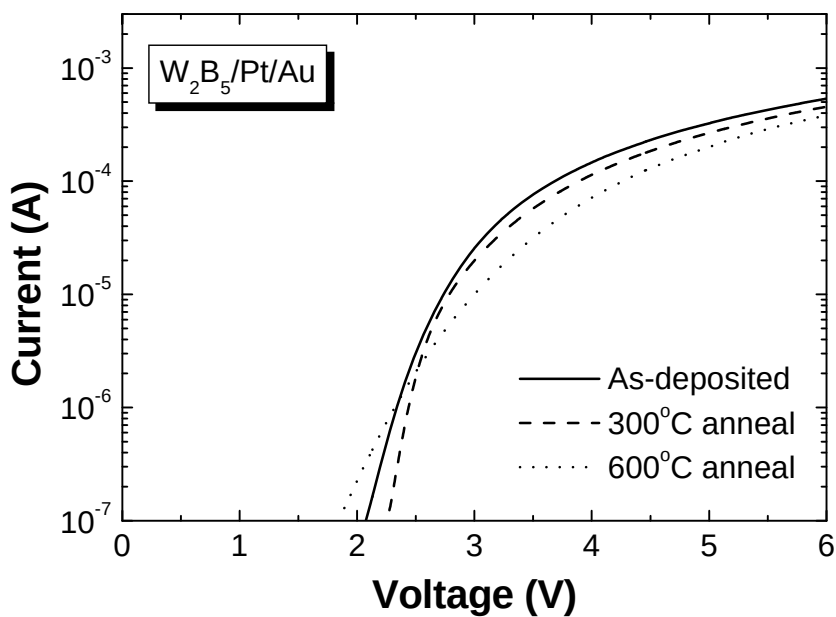
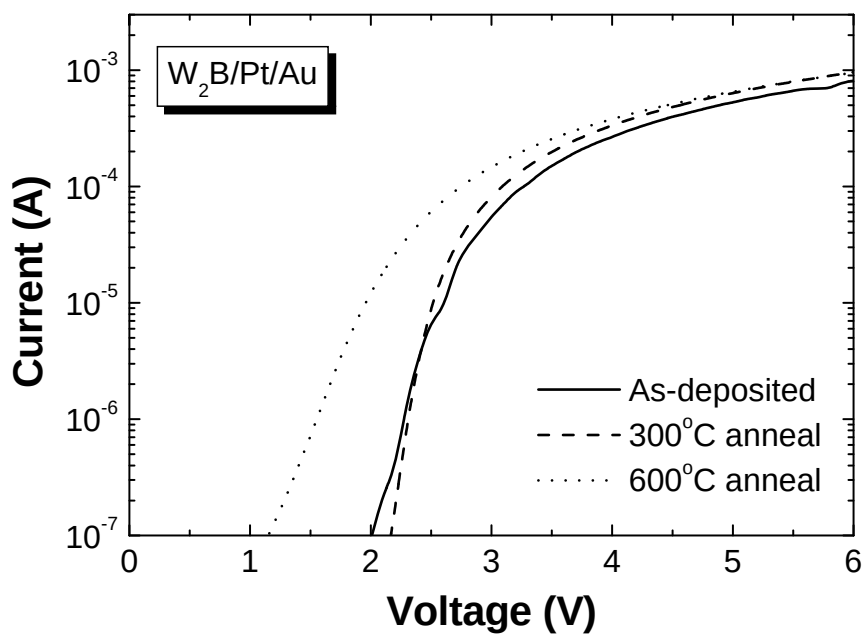


Figure 5-3: Forward current-voltage characteristic of W_2B -based (top) and W_2B_5 -based (bottom) Schottky diodes as a function of annealing.

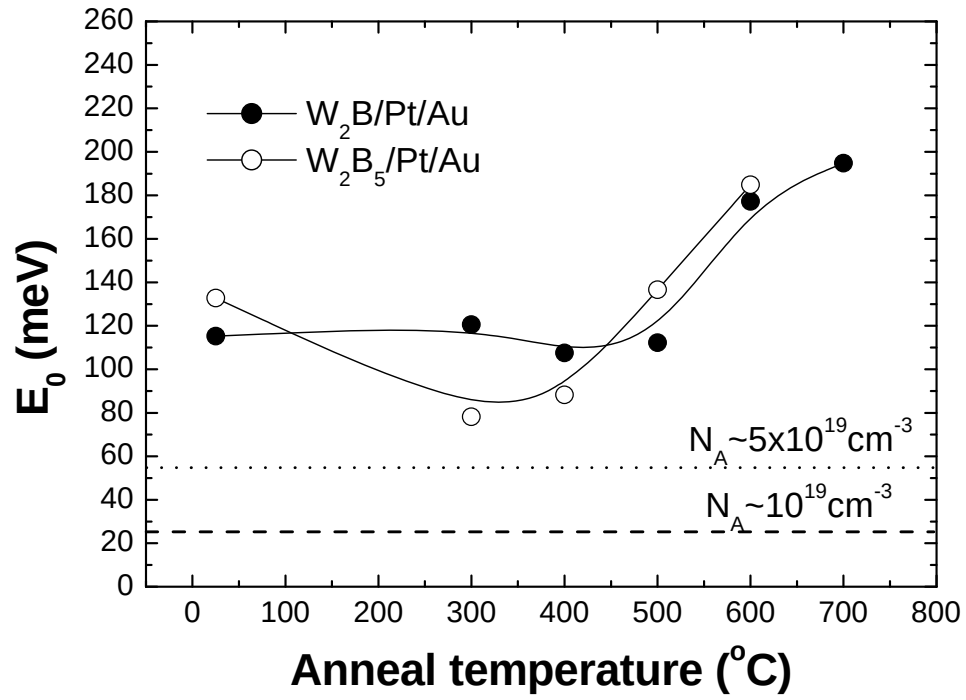


Figure 5-4: Influence of the annealing temperature on the characteristic energy related to the tunneling probability. Dashed and dotted lines correspond to the values of E_0 for $N_A \sim 10^{19}$ and $5 \times 10^{19} \text{ cm}^{-3}$ respectively.

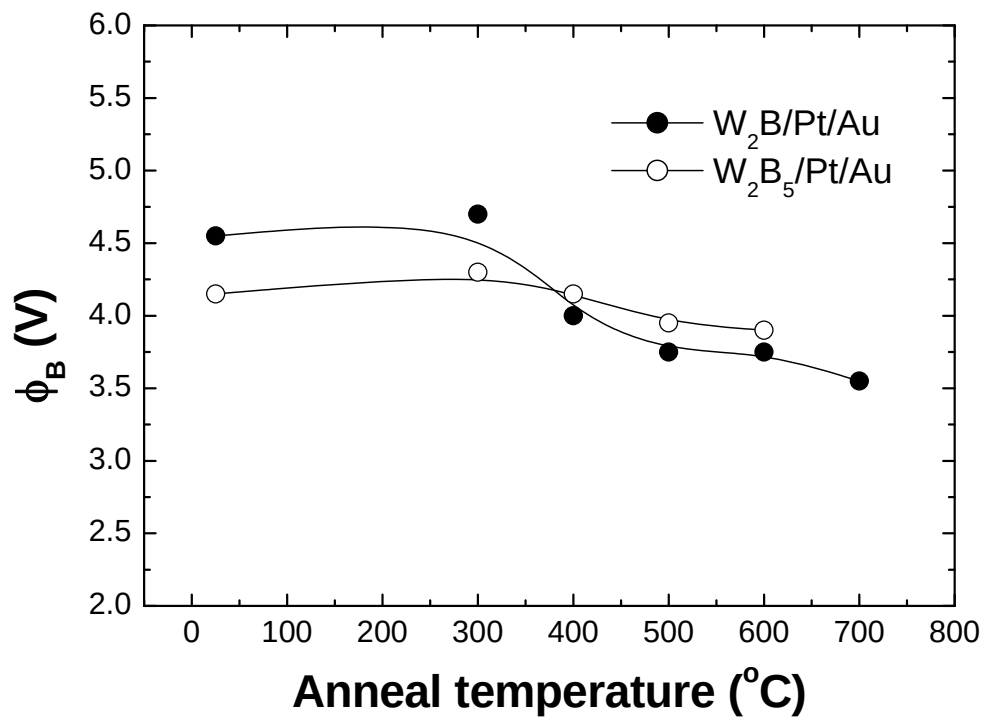


Figure 5-5: Influence of the annealing temperature on the apparent Schottky barrier height derived from IV measurements.

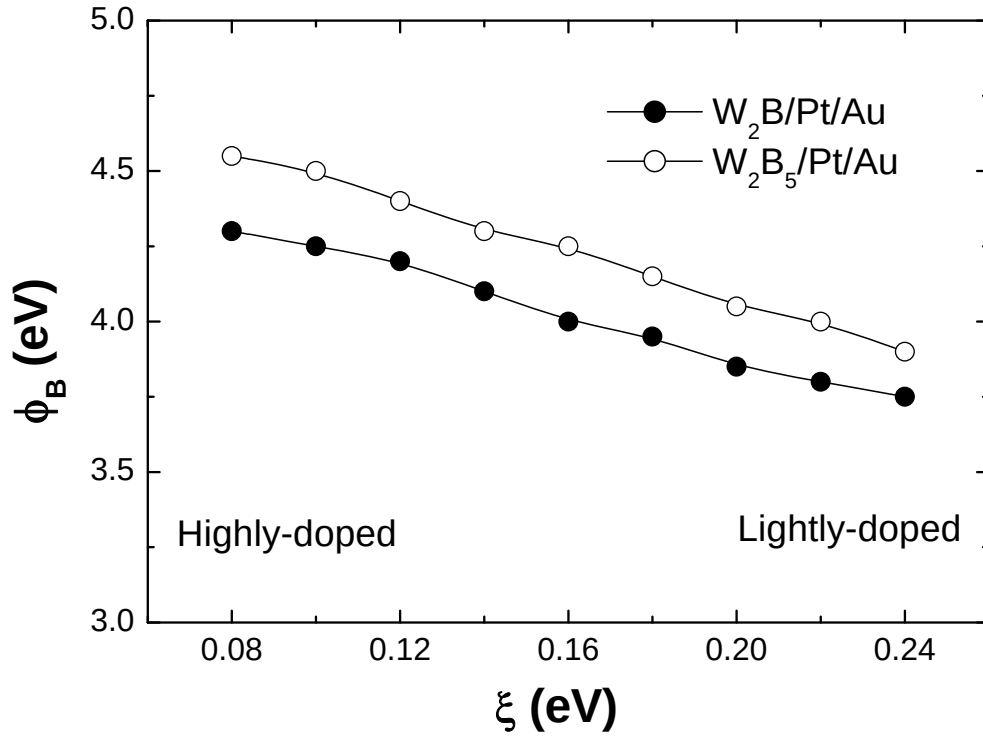


Figure 5-6: Dependence of the apparent Schottky barrier height on the parameter ξ defined as the difference between the valence band maximum and the position of the Fermi level. Low and high

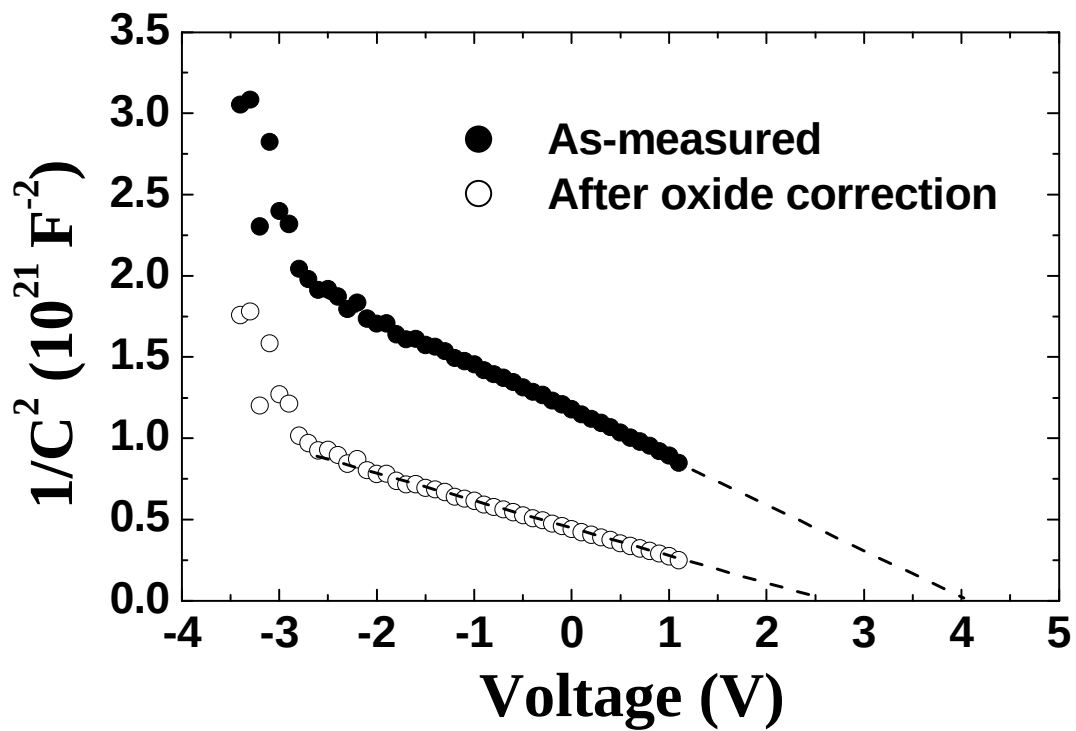


Figure 5-7: As-measured and after oxide correction dependence of C^{-2} versus V of Au/Pt/W₂B/p-GaN Schottky diodes. The measurement frequency was set to 1 kHz.

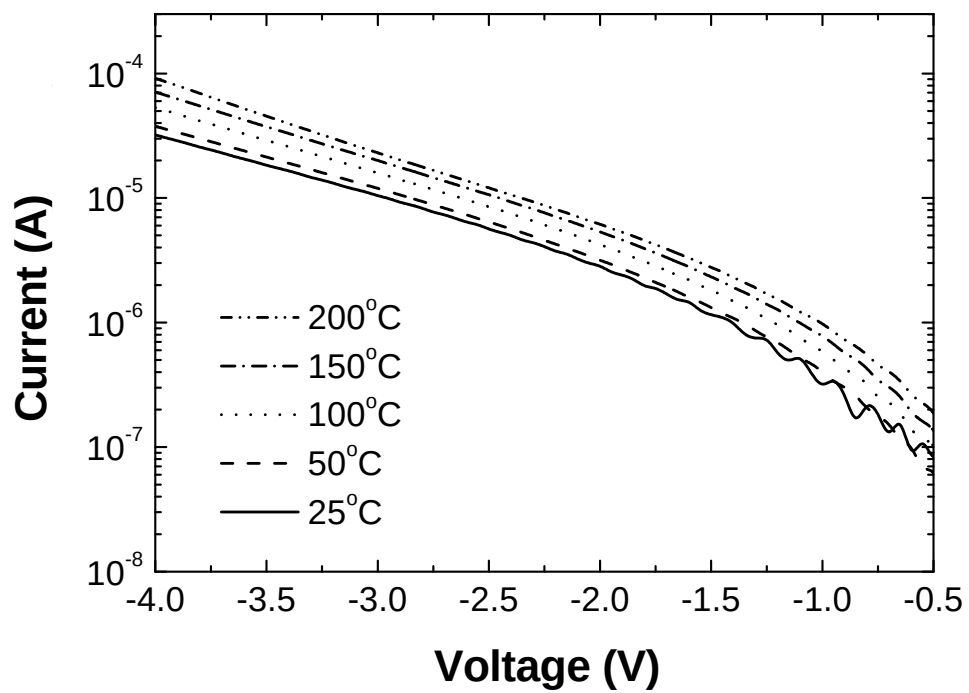


Figure 5-8: Reverse current-voltage characteristic of W₂B-based Schottky diodes as a function of measurement temperature.

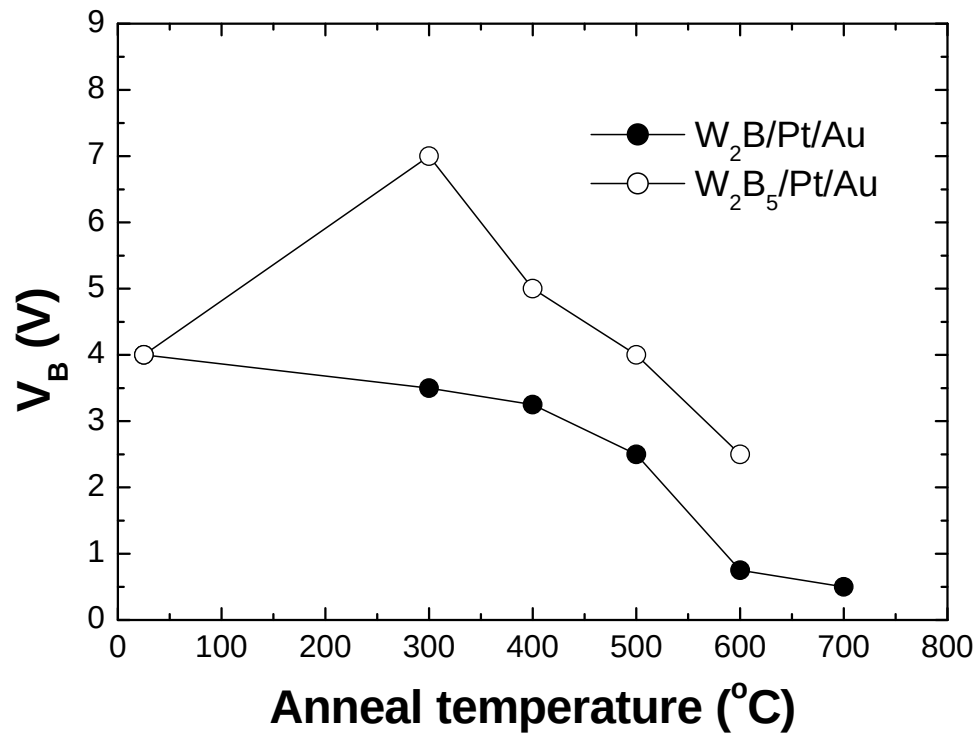
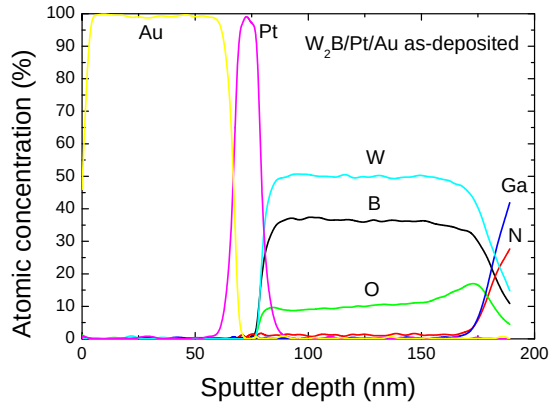
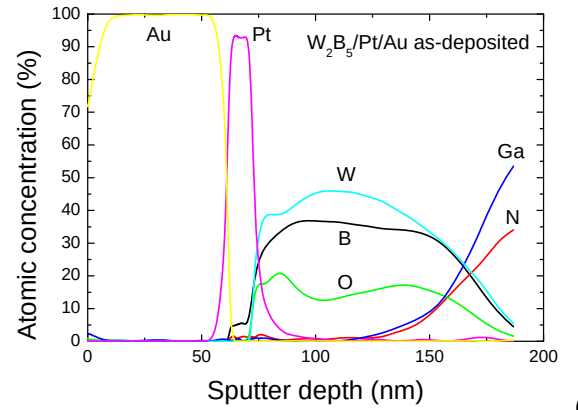


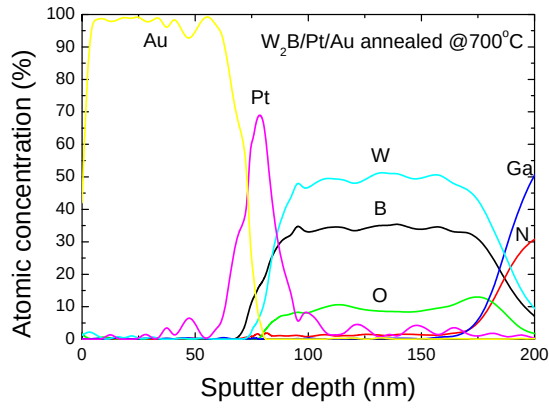
Figure 5-9: Influence of the annealing temperature on the breakdown voltage.



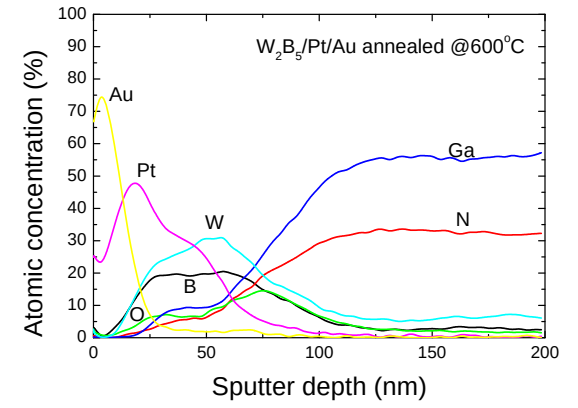
(a)



(b)



(c)



(d)

Figure 5-10: Depth profiles of W₂B/Pt/Au contacts and W₂B₅/Pt/Au rectifying contacts (a,b) before and (c,d) after annealing at 600°C.

CHAPTER 6 BORIDE AND IR BASED CONTACTS FOR LIGHT EMITTING DIODES

6.1 Introduction

InGaN/GaN multiple quantum well light-emitting diodes (MQW-LEDs) are commercially available in a broad range of wavelengths for use in applications such as full color displays, traffic signals, and exterior lighting. There is also interest in shorter wavelength LEDs with AlGaIn active regions to excite down conversion phosphors for white light [94]. Nevertheless, to compete with fluorescent and other high-efficiency lighting sources, it is essential to drive GaN-based LEDs at very high current densities to maximize light output. One drawback of the high current densities is self-heating of the heterostructure which can produce Ohmic contact degradation and generation of non-radiative recombination centers [95-98]. Cao *et al.* [99-101] demonstrated improved heat dissipation and current spreading by reducing the density of dislocations in the heterostructure through the use of free-standing GaN instead of the more common sapphire substrates. Further reduction of self-heating effects and improved efficiency and operating lifetime can be obtained through the use of low-resistance and thermally stable Ohmic contacts to the p-GaN layer. Indeed, power dissipation by Joule heating across the p-GaN/metal interface at high current injection levels was found to produce indiffusion of the Ohmic contact elements along dislocations in the III-nitride-based epilayers, leading to an electrical short of the pn junction. [102,103]

The conventional metallization schemes used for making Ohmic contacts to p-GaN for InGaIn/GaN LEDs are based on high work function metals such as Ni, Pd, Cr or Pt with an overlayer of Au to reduce the sheet resistance. Specific contact resistances of $\sim 10^{-2}$ - $10^{-4} \Omega \cdot \text{cm}^2$ are obtained by annealing at 450-650 °C [106,107]. These contacts have stability problems at high temperature. For example, the initial Au/Ni/GaN structure transforms to Ni/Au/GaN with a

rough Ni surface after annealing at 600°C [44,108]. A way to prevent excessive intermixing and contact morphology degradation is to use a high-melting-point diffusion barrier in the contact stack [109-111]. TiB₂, with a melting temperature of ~3000°C, reasonable electrical resistivity (28 μΩ.cm) and thermal conductivity (26 W.m⁻¹.K⁻¹), and heat of formation comparable to those for silicides or nitrides [112], shows promise as a diffusion barrier.

In this letter, we report on the long-term annealing characteristics at 200-350°C of InGaN/GaN MQW-LEDs with TiB₂- and Ir-based p-Ohmic contacts. This high-temperature stress stimulates accelerated aging of GaN-based LEDs and gives an idea of the expected reliability of the Ohmic contacts. The use of TiB₂ or Ir as a diffusion barrier in Ni/Au-based contacts is found to produce superior long-term stability of turn-on voltage, leakage current and output power.

6.2 Experimental

The MQW-LED structures were grown by metal organic chemical vapor deposition on c-plane sapphire substrates. The layer structure consisted of a low-temperature GaN buffer, 3 μm-thick n-GaN, 0.1 μm n-AlGaIn clad, three period undoped InGaIn/GaN MQW active, 0.1 μm p-AlGaIn clad, and 0.3 μm p-GaN layer. 1 μm-deep mesas were fabricated using Cl₂/Ar inductively coupled plasma etching. Ohmic contacts to n-GaN were formed by lift-off of e-beam deposited Ti (20 nm) / Al(80 nm) / Pt(40 nm) / Au(80 nm) subsequently annealed at 800°C for 1 min in a flowing N₂ ambient in a rapid thermal annealing (RTA) furnace. The first p-metallization scheme investigated consisted of Ni (50 nm) / Au (80 nm) / Ir (50 nm) / Au (80 nm). The second contact scheme was Ni (50 nm) / Au (80 nm) / TiB₂ (50 nm) / Ti (20 nm) / Au (80 nm). Ti was added to improve the adherence of Au on TiB₂. The Ni/Au layers were deposited by e-beam evaporation while the Ir/Au and TiB₂/Ti/Au overlayers were deposited by

Ar plasma-assisted rf magnetron sputtering. For comparison, devices with Ni/Au contacts were also fabricated using the same wafer. All contacts were patterned by liftoff of lithographically-defined photoresist and annealed at 600°C for 1 min in a flowing N₂ ambient. Prior to their insertion in the e-beam chamber, the surface of both n- and p-type GaN were cleaned in a 1HCl:10H₂O solution for 1 minute. Figure 6-1 shows a typical optical micrograph of as-fabricated MQW-LEDs with Ni/Au/TiB₂/Ti/Au Ohmic contacts. Similar contact morphology was achieved using the other metallization schemes. All devices were first aged for a period of 10 days at 200°C on a heater plate in air. The samples were then removed from the heater block, allowed to cool to room temperature, and characterized before being returned for further 35 days aging at 350°C. MQW-LEDs were analyzed by luminescence-current-voltage (*L-I-V*) measurements using a probe station and an Agilent 4145B parameter analyzer. The light output power was measured using a Si photodetector located at ~2 cm from the sample surface. Electroluminescence (EL) spectra were acquired by a fiber optic spectrometer.

6.3 Results and Discussion

Figure 6-2 presents the 300 K *L-I* characteristics from each as-fabricated device. Typical EL spectra measured for different forward currents are also shown in the inset. For an injected current of 500 μ A, the EL peak wavelength of the InGaN/GaN MQW-LEDs is 459 nm with a full width at half maximum (FWHM) of 26 nm. As the injected current increases, the peak exhibits a blue shift while the FWHM remains fairly constant. This behavior results from the decrease by carrier screening of the quantum-confined Stark effect induced by the built-in piezoelectric field in the strained InGaN/GaN QWs [113]. The *L-I* characteristics are similar for all metallization schemes investigated, showing that the TiB₂/Ti/Au or Ir/Au overlayers did not reduce the light output with respect to the more conventional Ni/Au contacts. The non-linear

increase and relatively low output power can probably be attributed to enhanced current crowding and self-heating effects [114,115]. These effects are expected to be particularly important for the LED structures investigated in this work due to the high density of dislocations in InGaN and GaN epilayers grown on sapphire as well as the low thermal conductivity of sapphire [99-101]. As the dislocation density or LED junction temperature increases, confinement in the MQW becomes less efficient, leading to premature saturation of the emission power.

I-V characteristics from MQW-LEDs with Ni/Au, Ni/Au/TiB₂/Ti/Au, and Ni/Au/Ir/Au Ohmic contacts to the p-GaN layer are shown in Figure 6-3. For all diodes, the ideality factor was >2 , consistent with other data reported previously [95-101,116,117]. There is still no agreement whether such high values result from tunnelling [101,117], recombination in the depletion layer [117], or rectifying junctions present in heterostructure diodes [118]. The turn-on voltage (voltage at which the current reaches 0.05 mA) and reverse leakage current (measured at -5V) are given in Table 6-1. The uncertainty on each value was estimated from the deviation between different devices on the same wafer. For as-fabricated devices, the turn-on voltage was 3.2-3.6V and the reverse leakage current was $\sim 10^{-6}$ A. Such high leakage currents are commonly observed in GaN-based LEDs grown on sapphire substrates and essentially result from the high density of dislocations in such samples [101]. After 10 days aging at 200°C, an increase of the turn-on voltage to ~ 4.1 V and a decrease of the leakage current to $\sim 10^{-9}$ was observed for all devices. After aging at 350°C for an additional 30 days, MQW-LEDs with TiB₂- and Ir-based Ohmic contacts show turn-on voltage and leakage current similar to those in the as-deposited state whereas there was serious degradation in LEDs fabricated with Ni/Au contacts. This reduction of injected current at a given forward voltage had a large impact on the EL output as

shown in Figure 6-4. While the brightness of MQW-LEDs with Ni/Au Ohmic contacts at 10 V ($I = 80 \mu\text{A}$) was low, optical images of aged MQW-LEDs with boride-based Ohmic contacts show much stronger emission, even at a lower applied voltage of 4.5 V ($I = 300 \mu\text{A}$).

Several mechanisms can be invoked to explain the drastic degradation of Ni/Au contacts upon aging, including formation of an islanded contact morphology, formation of reactions with the GaN resulting in a modification of the doping profile, and excessive intermixing of Ni and Au leading to oxidation on the rough Ni surface and an increase of the series resistance [44,109,119]. Although the dominant degradation mechanism remains unknown, the use of TiB₂/Ti/Au or Ir/Au overlayers on the Ni/Au-based Ohmic contacts clearly improves the long-term thermal stability of InGaN/GaN MQW-LEDs.

6.4 Conclusions

In conclusion, TiB₂ and Ir diffusion barriers in p-Ohmic contacts on GaN LEDs produced less change in turn-on voltage, leakage current, and output power after long-term annealing at 200°C and 350°C for 45 days. These schemes look promising for high temperature applications where improved stability over Ni/Au is mandatory.

Table 6-1: Influence of long-term aging at 200°C and 350°C on the turn-on voltage and reverse current of InGaN/GaN MQW-LEDs.

Contact to p-GaN	Turn-on voltage (V)			Reverse current @ -5V (A)		
	Day 0	Day 10 @ 200°C	Day 45 @ 350°C	Day 0	Day 10 @ 200°C	Day 45 @ 350°C
Ni/Au	3.3±0.3	4.9±0.4	9.1±0.5	$(2\pm1)\times10^{-6}$	$(6\pm2)\times10^{-9}$	$(5\pm3)\times10^{-5}$
Ni/Au/TiB ₂ /Ti/Au	3.5±0.2	4.1±0.5	4.0±0.2	$(5\pm2)\times10^{-6}$	$(2\pm1)\times10^{-9}$	$(2\pm1)\times10^{-8}$
Ni/Au/Ir/Au	3.3±0.2	4.3±0.3	3.9±0.3	$(3\pm1)\times10^{-6}$	$(2\pm1)\times10^{-9}$	$(3\pm2)\times10^{-7}$

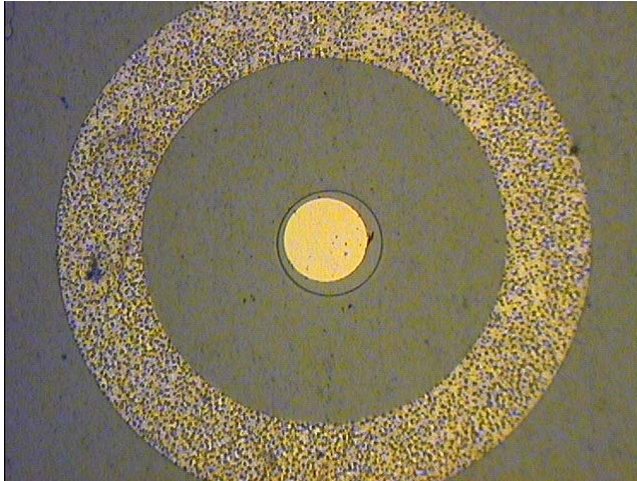


Figure 6-1: Optical micrograph of an as-fabricated MQW-LED. The p-contact at the center of the diode is 80 μm in diameter.

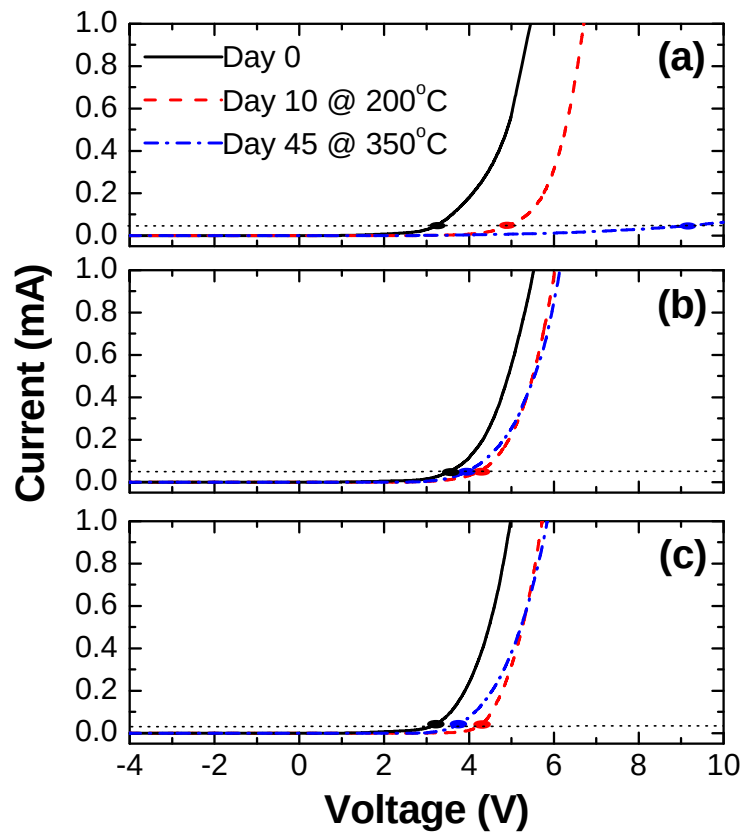


Figure 6-2 : I - V characteristics of MQW-LEDs with Ni/Au, Ni/Au/TiB₂/Ti/Au, and Ni/Au/Ir/Au p-Ohmic contacts. The inset shows emission spectra from as-fabricated LEDs at various injection currents.

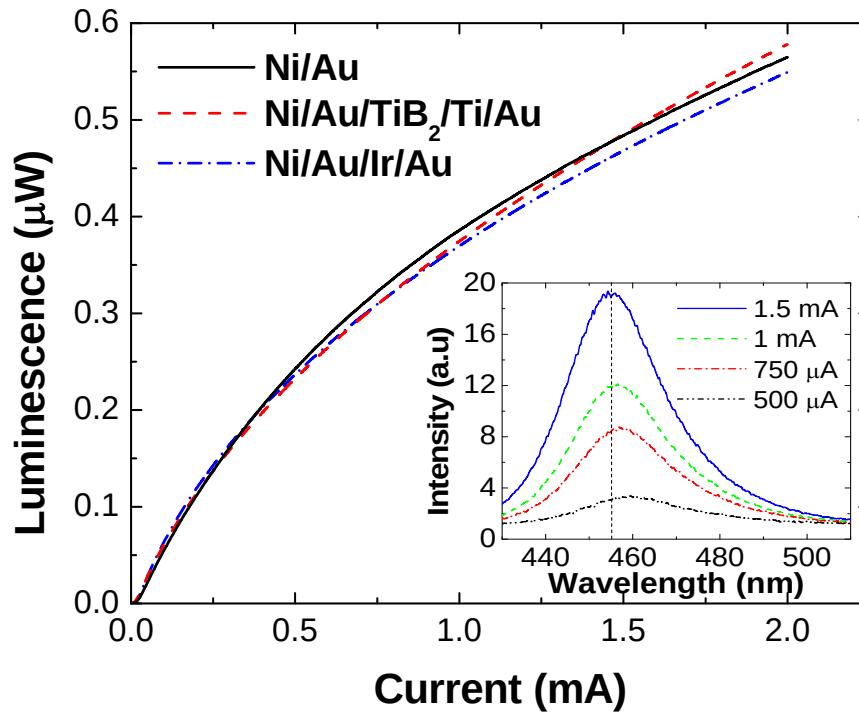


Figure 6-3: Influence of long-term aging at 250°C and 350°C on the I-V characteristics of LEDs with (a) Ni/Au, (b) Ni/Au/TiB₂/Ti/Au, and (c) Ni/Au/Ir/Au p-Ohmic contacts.

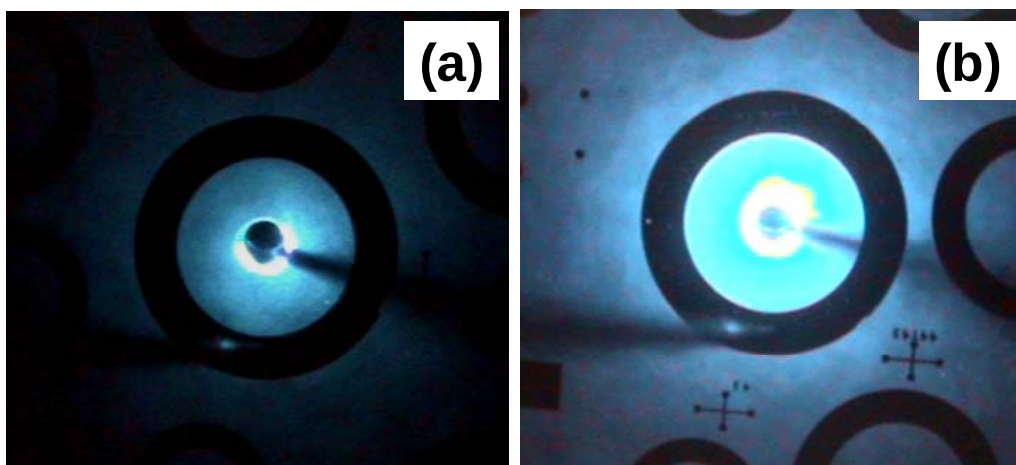


Figure 6-4: Image of aged LEDs with (a) Ni/Au and (b) Ni/Au/TiB₂/Ti/Au p-Ohmic contacts. In (a), the picture was taken for a forward bias of 10 V ($I = 80 \mu\text{A}$), while the forward voltage in (b) was 4.5 V ($I = 300 \mu\text{A}$).

CHAPTER 7 CONCLUSION

Improved device processing is necessary in order to realize the full potential of GaN based electronics and optoelectronics. While improved material quality is critical, especially for p-GaN as well as related alloys such as InGaN to increase the efficiency of green emitting devices, it is not the only challenge. Developing reliable, stable, low resistance Ohmic and Schottky contacts to both n- and p-type GaN is still a challenge and hence remains of interest to the GaN community at large. Without contacts that can withstand elevated temperatures and other harsh environments, many of the properties that make GaN a unique and desirable semiconductor mean nothing.

The goal of this work was to develop such contacts to both n- and p-GaN. In order to improve upon existing contact schemes, it is necessary to achieve at least comparable contact resistances or barrier heights. In addition, the contacts should be able to withstand more stressful processing conditions, such as elevated annealing temperatures, while maintaining predictable and stable characteristics. Perhaps the most critical factor is the ability of the contacts to withstand long periods in a harsh environment, simulated here by placement on a hot plate at temperatures of 200°C and 350 °C. A final consideration is the amount of intermixing of the contact layers, especially in Ohmic contacts to n-GaN, as large amounts of intermixing can lead to undesirable phases, such as AlAu₄ and issues with lateral flow. In addition, if any undesirable phases may form at device operation temperatures, or if the contacts themselves interact with the GaN at these temperatures, devices will prove unreliable during prolonged operation. To tackle these issues, three separate materials systems were examined: borides, nitrides, and Ir.

The first section of this dissertation involved the fabrication of Ohmic contacts to p-type GaN. All three material systems mentioned were examined for this use. Contacts were fabricated of the following structures:

1. Nickel / Gold / X / Titanium / Gold, where X is a chosen boride or nitride
2. X / Titanium / Gold, where X is a chosen boride or nitride
3. Nickel / Gold / Ir / Gold
4. Nickel / Ir / Gold

Each of these was then subjected to annealing at temperatures ranging from 300°C to 1000°C in a flowing N₂ ambient for 60 s. Schemes 1 and 3 consistently produced Ohmic contacts in the range of 500-1000 °C, 2 only inconsistently at specific temperatures, 3 at only 500°C and 4 not at all. Schemes 1 and 3 produced specific contact resistance values similar to those reported for Nickel / Gold contacts in the literature. Contacts of scheme 1 were subjected to long term thermal aging on a hot plate at both 200°C and 350°C. Nitride-based contacts failed early in aging, however boride based contacts displayed stable specific contact resistances throughout. Auger Electron Spectroscopy showed breakdown of the nitride structure during aging due to severe intermixing with the GaN. The borides showed minimal intermixing with the GaN, accounting for their stability. AES depth profiles of scheme 3 revealed severe intermixing of the contacts with the GaN at anneal temperatures above 500°C, accounting for their failure at elevated anneal temperatures. Contacts fabricated with scheme 4 were not Ohmic due to the absence of Au at the surface to promote increased hole concentration as well as severe intermixing at high temperatures.

The second section of the work dealt with the examination of nitride based contacts to n-GaN. Contacts using the borides and Ir have previously been examined. Contacts of the

structure Titanium / Aluminum / X / Titanium / Gold were fabricated using standard semiconductor processing procedures, where X is either TaN, TiN, or ZrN. For comparison, conventional contacts of the form Titanium / Aluminum / Platinum / Gold were fabricated as well. The contacts were then subjected to a range of anneal temperatures between 500°C and 1000°C in a flowing N₂ ambient for 60 s, as well as anneals at 800°C for up to 180 s, in order to determine if the nitrides would allow for an increased thermal budget. Contacts were also aged on a hot plate at 350°C and aged for a period of 24 days. Current-voltage measurements, Auger Electron Spectroscopy, and Scanning Electron Microscopy were used to characterize the contacts. Current-voltage measurements of the nitride contacts did not show any improvement over the performance offered by the conventional Pt-barrier contacts in any of the experiments. However, AES depth profiles revealed that the nitride based contacts displayed far less intermixing than Ni-barrier contacts, even when the nitrides were annealed at higher temperatures. Further, the profiles of thermally aged nitride contacts displayed no noticeable difference from unaged contacts. Thus, while electrical performance of these contacts was essentially unchanged from that of the conventional ones, they do offer the benefit of dramatically reducing the amount of intermixing between layers even after being subjected to harsh long term aging. This is significant, as one of the sources of failure for small gate width GaN devices is lateral flow arising due to the mixing of the Al underlayer and Au overlayer, leading to the formation of the viscous AlAu₄ phase. This leads to short circuiting and thus failure of devices.

Chapter five dealt with the fabrication of Schottky contacts to p-GaN. For this purpose, W₂B and W₂B₅ sputter targets were chosen. Nitrides were ignored due to the severe intermixing expected between them and the GaN. It is also expected Ir would diffuse a great deal into the

GaN at elevated annealing temperatures, also making it unsuitable for use as a Schottky contact. Contacts were fabricated with the scheme X / Platinum / Gold, where X is the boride. Platinum was chosen as the adhesive layer instead of Titanium in order to eliminate formation of TiN_x phases. Current-voltage measurements were used to evaluate the barrier height of the contacts. Because IV curves measured at different temperatures were parallel, it was determined that the current transport mechanism present was thermionic field emission. Unphysical barrier heights of approximately 4 eV were observed for anneals up to 700°C, with good stability. A slight decrease is seen at increased annealing temperatures. This likely was the result of either an increased near surface defect concentration due to sputtering or due to incorporation of an interfacial oxygen layer between the GaN and the contact. X-ray Photoelectron Spectroscopy measurements of thin boride layers on GaN reveal a true barrier height of 2.85 eV, in close agreement with that predicted by the Schottky-Mott model. Capacitance-voltage measurements confirm the large barrier height in agreement with the IV results, but if an interfacial layer of 1-2 monolayers is included the corrected barrier height would be in agreement with XPS measurements.

Chapter six deals with the application of boride and Ir-based Ohmic contacts to p-GaN for light emitting diodes. Contacts to LEDs were fabricated with the structures Nickel / Gold, Nickel / Gold / Titanium Boride / Titanium / Gold, and Nickel / Gold / Iridium / Gold. They were then annealed at 500°C, in order to prevent damage of the LED structure as well as metal spiking into the active layers. Initial IV and photoluminescence measurements revealed all contacts to have similar properties and performance. Contacts were then aged initially at 200°C, after which all displayed a slight degradation of performance. After further aging at 350°C, the

Ni/Au contacts had degraded severely while the TiB₂ and Ir-based contacts maintained good performance. This increased device stability confirms the earlier work.

In conclusion, contacts to n- and p-GaN were fabricated. Nitride diffusion barrier contacts to n-GaN show much less intermixing than that present with a Ni diffusion barrier, although no improvement in the IV characteristics either as a function of annealing or during long term aging. Ohmic contacts to p-GaN using the borides displayed both the ability to withstand a wide range of anneal temperatures, indicating their increased thermal budget as compared to conventional Ni/Au contacts, as well as far superior long term aging characteristics due to the stability of the borides on GaN. This has implications for processing of devices using p-GaN which may be used at elevated temperatures. While the specific Ohmic contacts may not be completely suitable for immediate use in light emitting applications due to their poor reflectivity and opacity, they show great promise. Development of transparent contacts using very thin layers of these borides may be possible, as are improvements in the reflectivity by experimenting with different metallization schemes and low anneal temperatures. In addition, if MOSFETs are to be achieved using GaN, low resistance, stable Ohmic contacts will be necessary and these may fit the requirements.

LIST OF REFERENCES

1. S. A. Campbell, The Science and Engineering of Microelectronics Fabrication 2nd ed., Oxford University Press, Oxford, UK, 2001.
2. J. C. Bean, in High-Speed Semiconductor Devices, edited by S.M. Sze, John Wiley & Sons, New York, NY, 1990.
3. S. M. Sze, Physics of Semiconductor Devices, John Wiley & Sons, New York, NY, 1981.
4. D.C. Look, Mater. Sci. Eng. B80, 383 (2001).
5. J. Sun, H. Fatima, A. Koudymov, A. Chitnis, X. Hu, H.-M. Wang, J. Zhang, G. Simin, J. Yang, and M.A. Khan, IEEE Electron Dev. Lett., 24, 375 (2003).
6. A. P. Zhang, L. B. Rowland, E. B. Kaminsky, J. W. Kretchmer, R. A. Beaupre, J. L. Garrett, J. B. Tucker, B. J. Edward, J. Foppes and A. F. Allen, Solid-State Electron 47 821(2003).
7. A. P. Zhang, L. B. Rowland, E. B. Kaminsky, V. Tilak, J. C. Grande, J. Teetsov, A. Vertiatchikh and L. F. Eastman, J. Electron. Mater. 32 388(2003).
8. V. Kumar, L. Zhou, D. Selvanathan, and I. Adesida, J. Appl. Phys. 92, 1712 (2002)
9. A. Motayed, R. Bathe, M.C. Wood, O.S. Diouf, R. D. Vispute, and S. Noor Mohammad, J. Appl. Phys. 93, 1087 (2003)
10. J. Burm, K. Chu, W. A. Davis, W. J. Schaff, L.F. Eastman, and T. J. Eustis, Appl. Phys. Lett. 70, 464 (1997)
11. M. E. Lin, Z. Ma, F. Y. Huang, Z. F. Fan, L. H. Allen, and H. Morkoç, Appl. Phys. Lett. 64, 1003 (1994).
12. B. P. Luther, S. E. Mohny, T. N. Jackson, M. Asif Khan, Q. Chen, and J. W. Yang, Appl. Phys. Lett. 70, 57 (1997).
13. Z. Fan, S. N. Mohammad, W. Kim, Ö. Aktas, A. E. Botchkarev, and H. Morkoç, Appl. Phys. Lett. 68, 1672 (1996)
14. S. Ruvimov, Z. Liliental-Weber, J. Washburn, D. Qiao, S. S. Lau, and Paul K. Chu, Appl. Phys. Lett. 73, 2582 (1998).
15. A. N. Bright, P. J. Thomas, M. Weyland, D. M. Tricker, C. J. Humphreys, and R. Davies, J. Appl. Phys. 89, 3143 (2001).
16. N. A. Papanicolaou, M. V. Rao, J. Mittereder, and W. T. Anderson, J. Vac. Sci. Technol. B 19, 261 (2001).
17. Q. Z. Liu and S. S. Lau, Solid-State Electronics, 42, 677-691 (1998).

18. R. Li, S. J. Cai, L. Wong, Y. Chen, K. L. Wang, R. P. Smith, S. C. Martin, K. S. Boutros, J. M. Redwing, IEEE Electron Device Letters, 20, 323 (1999).
19. S. T. Sheppard, K. Doverspike, W. L. Pribble, S. T. Allen, J. W. Palmour, L. T. Kehias, T. J. Jenkins, IEEE Electron Device Letters, 20, 161 –163 (1999).
20. D. Qiao, Z. F. Guan, J. Carlton, S. S. Lau, and G. J. Sullivan, Appl. Phys. Lett. 74, 2652 (1999)
21. V. Tilak, R. Dimitov, M. Murphy, B. Green, J. Smart, W. J. Schaft, J. R. Shealy and L. F. Eastman, Mat. Res. Soc. Symp. Proc., 622, T7.4.1(2000).
22. S. -H. Lim, J. Washburn, Z. Liliental-Weber, and D. Qiao, Appl. Phys. Lett. 78, 3797 (2001).
23. M. Asif Khan, M. S. Shur and Q. Chen, Appl. Phys. Lett., 68, 3022(1996).
24. S. Murai, H. Masuda, Y. Koide, and M. Murakami, Appl. Phys. Lett. 80, 2934 (2002)
25. C. Lu, H. Chen, X. Lv, X. Xie, and S. N. Mohammad, J. Appl. Phys. 91, 9218 (2002)
26. J. S. Foresi and T. D. Moustakus, Appl. Phys. Lett., 62, 2859(1993).
27. M. W. Fay, G. Moldovan, P. D. Brown, I. Harrison, J. C. Birbeck, B. T. Hughes, M. J. Uren, and T. Martin, J. Appl. Phys. 92, 94 (2002).
28. K. O. Schweitz, P. K. Wang, S. E. Mohny, and D. Gotthold, Appl. Phys. Lett. 80, 1954 (2002).
29. M. W. Cole, D. W. Eckart, W. Y. Han, R. L. Pfeffer, T. Monahan, F. Ren, C. Yuan, R. A. Stall, S. J. Pearton, Y. Li and Y. Lu, J. Appl. Phys. 80, 278 (1996).
30. A. Zeitouny, M. Eizenberg, S. J. Pearton, and F. Ren, J. Appl. Phys. 88, 2048 (2000).
31. D. Selvanathan, F. M. Mohammed, A. Tesfayesus and I. Adesida, J.Vac.Sci.Technol. B22 2409(2004).
32. B. Luo, F. Ren, R. C. Fitch, J. K. Gillespie, T. Jenkins, J. Sewell, D. Via, A. Crespo, A.G. Baca , R. D. Briggs, D. Gotthold, R. Birkhahn, B. Peres and S. J. Pearton, Appl. Phys. Lett. 82, 3910 (2003).
33. H. W. Jang and J. -L. Lee, J.Appl.Phys.93,5416(2003).
34. R. C. Fitch, J. K. Gillespie, N. Moser, T. Jenkins, J. Sewell, D. Via, A. Crespo, A.M. Dabiran, P. P. Chow, A. Osinsky, J. R. LaRoche, F. Ren and S. J. Pearton, Appl.Phys.Lett. 84, 1495 (2004).
35. R. C. Fitch, J. K. Gillespie, N. Moser, T. Jenkins, J. Sewell, D. Via, A. Crespo, A.M. Dabiran, P. P. Chow, A. Osinsky, J. R. LaRoche, F. Ren and S. J. Pearton , J.Vac.Sci.Technol. B22, 619(2004).

36. D. Selvanathan , L. Zhou, V. Kumar, I. Adesida and N. Finnegan, J.Electron.Mater.32 335(2003).
37. X. A. Cao, S. J. Pearton, G. Dang, A. P. Zhang, F. Ren, and J. M. Van Hove, Appl. Phys. Lett. 75, 4130 (1999).
38. H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Svedlov, and M. Burns, J. Appl. Phys. 76 (2), 1363 (1994).
39. S. Nakamura and G. Fasol, The Blue Laser Diode ~Springer, Heidelberg,1997.
40. S. M. Sze, Physics of Semiconductor Devices, John Wiley & Sons, New York (1981).
41. http://www.onr.navy.mil/sci_tech/information/312_electronics/ncsr/properties.asp.
42. D. W. Palmer, www.semiconductors.co.uk, 2004a.
43. O. Ambacher, J. Phys. D: Appl. Phys. 31, 2653 (1998).
44. H. Omiya, F. A. Ponce, H. Marui, S. Tanaka, and T. Mukai ,Appl. Phys. Lett. 85, 6143 (2004).
45. M. -R. Park and W. A. Anderson, Mat. Res. Soc. Symp. Proc. 680E, E6.5.1 (2001).
46. C. H Lin, D. L. Hibbard, A. Au, H. P. Lee, Z. J. Dong, F. J. Szalkowski, J. Chen, and C. Chen, Mat. Res. Soc. Symp. 639, G4.8.1 (2001).
47. T. Gessmann, Y.-L. Li, E.L. Waldron, J.W. Graff, E.F. Schubert, J.K. Sheu, Appl. Phys. Lett. 80, 986 (2002).
48. J. K. Kim, J.-L. Lee, J. W. Lee, H. E. Shin, Y. J. Park, and T. Kim, Appl. Phys. Lett. 73, 2953 (1998).
49. V. R. Reddy, Mater. Chem.Phys. 93 286 (2005).
50. D. Selvanathan, L. Zhou, V. Kumar, I. Adesida and N. Finnegan, J.Electron. Mater. 32, 335 (2003).
51. G. -T. Chen, C. -C. Pan, C. -S.Fang, T. -C. Huang, J. -I.Chyi, M. -N. Chang, S. -B. Huang and J. -T.Hsu, Appl. Phys. Lett. 85, 2797 (2004).
52. K. A. Rickert, A. B. Ellis, J. K. Kim, J. L. Lee, F. J. Himpsel, F. Dwikusuma, and T. F. Kuech, J. Appl. Phys. 92, 6671 (2002).
53. Q. Z. Liu and S. S. Lau, Solid-State Electron. 42, 667 (1998).
54. M. W. Wang, J. O. McCaldin, J. F. Swenberg, T. C. McGill, and R. J. Hauenstein, Appl. Phys. Lett. 66, 1974 (1995)

55. T. Mori, T. Kozawa, T. Ohwaki, Y. Taga, S. Naagai, S. Yamasaki, S. Asami, N. Shibata, and M. Koike, *Appl. Phys. Lett.* 69, 3537 (1996).
56. L. S. Yu, D. Qiao, L. Jia, S. S. Lau, Y. Qi, and K. M. Lau, *Appl. Phys. Lett.* 79, 4536 (2001).
57. L. S. Yu, L. Jia, D. Qiao, S.S. Lau, J. Li, J.Y. Lin, and H.X. Jiang, *IEEE Trans. Electron. Devices* 50, 292 (2003).
58. X. A. Cao, S. J. Pearton, G. Dang, A. P. Zhang, F. Ren, and J. M. Van Hove, *Appl. Phys. Lett.* 75, 4130 (1999).
59. P. J. Hartlieb, A. Roskowski, R. F. Davis, W. Platow, and R. J. Nemanich, *J. Appl. Phys.* 91, 732 (2002).
60. D. L. Hibbard, R. W. Chuang, Y. S. Zhao, C. L. Jensen, H. P. Lee, Z. J. Dong, R. Shih, and M. Bremser, *J. Electron. Mater.* 29, 291 (2000).
61. K. Shiojima, T. Sugahara, and S. Sakai, *Appl. Phys. Lett.* 74, 1936 (1999).
62. Y. J. Lin, *Appl. Phys. Lett.* 86, 122109 (2005).
63. K. Shiojima, T. Sugahara, and S. Sakai, *Appl. Phys. Lett.* 77, 4353 (2000).
64. T. Sawada, Y. Ito, N. Kimura, K. Imai, K. Suzuki, and S. Sakai, *Appl. Surf. Sci.* 190, 326 (2002).
65. C. K. Tan, A. Abdul Aziz, and F. K. Yam, *Appl. Surf. Sci.* 252, 5930 (2006).
66. Y. J. Lin and C. W. Lin, *J. Electron. Mat.* 33, 1036 (2004).
67. T. B. Massalski (Ed.), *Binary alloy phase diagrams* (ASM International, Materials Park, Ohio, 1990).
68. X. A. Cao, S. J. Pearton, F. Ren, and J. R. Lothian, *Appl. Phys. Lett.* 73, 942 (1998).
69. X. A. Cao, F. Ren, J. R. Lothian, S. J. Pearton, C. R. Abernathy, J. C. Zolper, M. W. Cole, A. Zeitouny, M. Eizenberg, and R. J. Shul, *MRS Internet Journal of Nitride Semiconductor Research*. 4 (1999).
70. *Handbook of the Physiochemical Properties of the Elements*, edited by G.V. Samsonov, IFI-Plenum, New York, (1968).
71. M. W. Cole, F. Ren, and S. J. Pearton, *J. Electrochem. Soc.* 144, L275 (1997).
72. A. Zeitouny, M. Eizenberg, S. J. Pearton, and F. Ren, *J. Appl. Phys.* 88, 2048 (2000).
73. J. Kim, F. Ren, A. G. Baca, and S. J. Pearton, *Appl. Phys. Lett.* 82, 3263 (2003).

74. B. Luo, F. Ren, R. C. Fitch, J. K. Gillespie, T. Jenkins, J. Sewell, D. Via, A. Crespo, A. G. Baca, R. D. Briggs, D. Gotthold, R. Birkhahn, B. Peres, and S. J. Pearton, *Appl. Phys. Lett.* 82, 3910 (2003).
75. R. Khanna, S. J. Pearton, F. Ren, and I. Kravchenko, *J. Electrochem. Soc.* 11, G804 (2005).
76. R. Khanna, S. J. Pearton, F. Ren, I. Kravchenko, C.J. Kao and G.C. Chi, *Appl. Phys. Lett.* 87, 052110 (2005).
77. R. Khanna, S. J. Pearton, F. Ren, and I. Kravchenko, *Appl. Surf. Sci.* 252, 5814 (2006).
78. T. N. Oder, P. Martin, J. Y. Lin, H. X. Jiang, J. R. Williams, and T. Isaacs-Smith, *Appl. Phys. Lett.* 88, 183505 (2006).
79. R. T. Tung, *Mater. Sci. Rep.* R35, 1 (2001).
80. L. Stafford, L. F. Voss, S. J. Pearton, J. -J. Chen, and F. Ren, submitted.
81. Michael Shur, *Physics of Semiconductor Devices* (Prentice-Hall, Engelwood Cliffs, NJ, 1990).
82. C. Merz, M. Kunzer, U. Kaufmann, I. Akasaki, and H. Amano, *Semicond. Sci. Technol.* 11, 712 (1996).
83. H. Nakayama, P. Hacke, M.R.H. Khan, T. Dtechprohm, K. Hiramatsu, and N. Sawaki, *Jpn. J. Appl. Phys.* 35, L282 (1996).
84. J. R. Waldrop and R. W. Grant, *Appl. Phys. Lett.* 68, 2879 (1996).
85. J. S. Kwak, O. H. Nam, and Y. Park, *Appl. Phys. Lett.* 80, 3554 (2002).
86. J. S. Kwak, O. H. Nam, and Y. Park, *J. Appl. Phys.* 95, 5917 (2004).
87. M.W. Cole, F. Ren, and S. J. Pearton, *J. Electrochem. Soc.* 144, 275 (1997).
88. K. Shiojima, S. Sugitani, and S. Sakai, *Appl. Surf. Sci.* 190, 318 (2002).
89. T. Okumura, *Jpn. J. Appl. Phys.* 24, L437 (1985).
90. M. Passlack, N. E. J. Hunt, E. F. Schubert, G. J. Zydzik, M. Hong, J. P. Mannaerts, R. L. Opila, and R. J. Fischer, *Appl. Phys. Lett.* 64, 2715 (1994).
91. M. Lenzlinger and E. H. Snow, *J. Appl. Phys.* 40, 278 (1969).
92. Z. Weinberg, *J. Appl. Phys.* 53, 5052 (1982).
93. H. Zhang, E. J. Miller, and E. T. Yu, *J. Appl. Phys.* 99, 023703 (2006).

94. Introduction to Nitride Semiconductor Blue Lasers and Light-Emitting Diodes, edited by S. Nakamura and S.F. Chichibu (Taylor and Francis, London, 2000).
95. M. Meneghini, L. -R. Trevisanello, U. Zehnder, T. Zahner, U. Strauss, G. Meneghesso and E. Zanoni, IEEE Trans. Electron. Dev. 53, 2981 (2006).
96. S. Bychikhin, D. Pogany, L. K. J. Vandamme, G. Meneghesso, and E. Zanoni, J. Appl. Phys. 97, 123714 (2005).
97. M. Pavesi, F. Rossi, and E. Zanoni, Semicond. Sci. Technol. 21, 138 (2006).
98. F. Rossi, M. Pavesi, M. Meneghini, G. Salviati, M. Manfredi, G. Meneghesso, A. Castaldini, A. Cavallini, L. Rigutti, U. Strass, U. Zehnder, and E. Zanoni, J. Appl. Phys. 99, 053104 (2006).
99. X. A. Cao and S.D. Arthur, Appl. Phys. Lett. 85, 3971 (2004).
100. X. A. Cao, S. F. LeBoeuf, M. P. D'Evelyn, S. D. Arthur, J. Kretchmer, C. H. Yan, and Z. H. Yang, Appl. Phys. Lett. 84, 4313 (2004).
101. X. A. Cao, J. M. Teetsov, M. P. D'Evelyn, D. W. Merfeld, and C. H. Yan, Appl. Phys. Lett. 85, 7 (2004).
102. S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto and H. Kikyou, Jpn. J. Appl. Phys., Part 2 36, L1059 (1997).
103. C. Y. Hsu, W. H. Lan and Y. S. Wu, Appl. Phys. Lett. 83, 2447 (2003).
104. A. P. Zhang, B. Luo, J. W. Johnson, F. Ren, J. Han and S. J. Pearton, Appl. Phys. Lett. 79, 3636 (2001).
105. T. Maeda, Y. Koide and M. Murakami, Appl. Phys. Lett. 75, 4145 (1999).
106. L. -C. Chen, J. -K. Ho, C. -S. Jong, C. C. Chiu, K. -K. Shih, F. -R. Chen, J. -J. Kai and L. Chang, Appl. Phys. Lett. 76, 3703 (2000)
107. D. Qiao, L. S. Yu, S. S. Lau, J. Y. Lin, H. X. Jiang and T. E. Haynes, J. Appl. Phys. 88, 4196 (2000).
108. H. S. Venugopalan, S. E. Mohny, J. M. DeLucca, B. P. Luther and G. E. Bulman, J. Vac. Sci. Technol. A 16, 607 (1998).
109. C. -F. Chu, C. C. Yu, Y. K. Wang, J. Y. Tsai, F. I. Lai and S. C. Wang, Appl. Phys. Lett. 77, 3423 (2000).
110. L. F. Voss, R. Khanna, S. J. Pearton, F. Ren and I. I. Kravchenko, Appl. Phys. Lett. 88, 012104 (2006).

111. L. F. Voss, R. Khanna, S. J. Pearton, F. Ren, and I. I. Kravchenko, *Appl. Surf. Sci.* 253, 1255 (2006).
112. W. Zagozdzon-Wosik, D. Radhakrishnan, C. Darne, I. Rusakova, P. van der Heide, Z.-H. Zhang, J. Bennett, L. Trombetta and P. Majhi, *Rev. Adv. Mater. Sci.* 8, 185 (2004).
113. Y. D. Qi, H. Liang, D. Wang, Z. D. Lu, W. Tang and K. M. Lau, *Appl. Phys. Lett.* 86, 101903 (2005).
114. X. Guo and E. F. Schubert, *Appl. Phys. Lett.* 78, 3337 (2001).
115. A. Chitnis, J. Sun, V. Mandavilli, R. Pachipulusu, S. Wu, M. Gaevski, V. Adivarahan, J. P. Zhang, M. Asif Khan, A. Sarua and M. Kuball, *Appl. Phys. Lett.* 81, 3491 (2002).
116. P. G. Eliseev, P. Perlin, J. Furioli, P. Sartori, J. Mu, and M. Osinski, *J. Electron. Mater.* 26, 311 (1997).
117. G. Franssen, E. Litwin-Staszewska, R. Piotrkowski, T. Suski, and P. Perlin, *J. Appl. Phys.* 94, 6122 (2003).
118. J. M. Shah, Y. L. Li, T. Gessmann and E. F. Schubert, *J. Appl. Phys.* 94, 2623 (2003).
119. S. H. Wang, S. E. Mohny, and R. Birkhahn, *J. Appl. Phys.* 91, 3711 (2002).

BIOGRAPHICAL SKETCH

Lars Voss was born in Pittsburgh, Pennsylvania in 1982. He spent most of his life in Erie, Pennsylvania, until graduating from McDowell Senior High School in 2000. He then enrolled at The Pennsylvania State University where he earned a Bachelor of Science in Engineering Science, with a minor in electronic and photonic materials, in May 2004. While there, he had the opportunity to work for Prof. Paul Koch in plastics engineering technology at Penn State Erie during the summer and with Prof. P.M. Lenahan in his Semiconductor Spectroscopy Laboratory.

After his undergraduate education, Lars enrolled at the University of Florida in the Materials Science and Engineering Department and began his graduate study under Prof. Stephen J. Pearton. During the summers of 2006 and 2007, he worked as an intern at Sandia National Laboratories under the direction of Drs. Albert G. Baca and Randy J. Shul.