ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY

Metal Contacts on ZnSe and GaN

Kristin J. Duxstad
Materials Sciences Division

May 1997
Ph.D. Thesis

RECEIVED

JUN 23 1997

OSTI

MASTER

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory
is an equal opportunity employer.

Metal Contacts on ZnSe and GaN

Kristin Joy Duxstad

Materials Science and Mineral Engineering
University of California, Berkeley

and

Materials Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, California 94720

Ph.D. Thesis

May 1997

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED HH

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Metal Contacts on ZnSe and GaN

by

Kristin Joy Duxstad

B.A. (Macalester College) 1991

B.M.E. (University of Minnesota) 1991

M.S. (University of California, Berkeley) 1994

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy
in

Engineering-Materials Science
and Mineral Engineering

in the

GRADUATE DIVISION

of the

UNIVERSITY OF CALIFORNIA, BERKELEY

Committee in charge:

Professor Eugene E. Haller, Chair

Professor Timothy D. Sands

Professor Roya Maboudian

Spring 1997

Abstract

Metal Contacts on ZnSe and GaN

by

Kristin Joy Duxstad

Doctor of Philosophy in Engineering-
Materials Science and Mineral Engineering

University of California, Berkeley

Professor Eugene E. Haller, Chair

Recently, considerable interest has been focused on the development of blue light emitting materials and devices. The focus has been on GaN and ZnSe, direct band gap semiconductors with bands gaps of 3.4 and 2.6 eV, respectively. To have efficient, reliable devices it is necessary to have thermally and electrically stable Ohmic contacts. This requires knowledge of the metal-semiconductor reaction behavior. To date few studies have investigated this behavior. Much information has accumulated over the years on the behavior of metals on Si and GaAs. This thesis provides new knowledge for the more ionic wide band gap semiconductors. The initial reaction temperatures, first phases formed, and phase stability of Pt, Pd, and Ni on both semiconductors were investigated.

Pd reacts on ZnSe at 200°C to form an epitaxial, ternary phase, $\text{Pd}_{5+x}\text{ZnSe}$. This phase is stable up to 450°C. Pt reacts at 575°C to form a layer of Pt_5Se_4 at the Pt/ZnSe interface. After annealing at 675°, the Pt_5Se_4 phase is no longer observed. Annealing of

Ni on ZnSe at 425°C results in the formation of laterally separated grains of a metastable Ni_xSe phase. After annealing at 450°C, grains of NiSe are observed.

The near noble metals do not react with GaN during annealing up to 800°C. Instead, the low surface energy and strong bonding of GaN cause the metal films to island and delaminate. This is analogous to the behavior of metal thin films on ceramics. Metals which form metal-nitride phases will react with GaN to form new phases at the interface. The formation of TiN at the Ti/GaN interface was observed.

The reactions of these metals on ZnSe and GaN are discussed in detail and correlated with predicted behavior. In addition, comparisons are made between these highly ionic semiconductors and Si and GaAs. The trends observed here should also be applicable to other II-VI and III-Nitride semiconductor systems, while the information on phase formation and stability should be useful in the development of contacts for ZnSe and GaN devices.

Table of Contents

1. Introduction	1
1.1 Significance of ZnSe and GaN	2
1.1.1 ZnSe Devices	4
1.1.2 GaN Devices	7
1.2 Interest in structural and electrical behavior of metal/semiconductor contacts	10
1.3 Interest in Pt, Pd, and Ni for contacts	11
2. Metal/Semiconductor Interfaces	13
2.1 Structural Behavior	13
2.1.1 Thermodynamics	14
2.1.2 Kinetics	16
2.1.3 Observed structural behavior of Pt, Pd, and Ni on Si and GaAs	19
2.1.4 Predicted structural behavior for metals on ZnSe and GaN	26
2.1.5 Observed structural behavior for metals on ZnSe and GaN	29
2.2 Electrical Behavior	36
2.2.1 Schottky-Mott Theory	36
2.2.2 Deviations from the Schottky-Mott model	39
2.2.3 Predicted behavior for ZnSe and GaN	40
2.2.4 Observed electrical behavior of contacts on ZnSe and GaN	43
3. Metal/Ceramic interfaces	56
3.1 Surface energy mismatch	56
3.2 Thermal expansion mismatch	60

3.3 Typical approaches to bonding metals and ceramics	64
4. Experimental Procedures	69
4.1 Surface preparation.....	69
4.2 Metal deposition	70
4.3 Annealing	70
4.4 Characterization.....	71
4.4.1 RBS.....	72
4.4.2 XRD	72
4.4.3 AES.....	73
4.4.4 XPS	73
4.4.5 TEM.....	74
5. Results and discussion	75
5.1 Surface Characteristics.....	75
5.2 Structural behavior of Pt, Pd, and Ni on ZnSe.....	84
5.2.1 Results.....	84
5.2.2 Discussion.....	103
5.3 Structural behavior of Pt, Pd, Ni, and Au on GaN	108
5.3.1 Results.....	108
5.3.2 Discussion.....	125
5.4 Structural behavior of Ti on GaN.....	128
5.4.1 Results.....	128
5.4.2 Discussion.....	134

6. Conclusions.....	135
7. Appendices.....	140
Appendix A: Properties of some semiconductors and metals	140
Appendix B: Schottky barrier height measurement methods.....	143
Appendix C: Characterization methods	147
C.1 Rutherford backscattering spectrometry (RBS).....	147
C.2 X-ray diffraction (XRD).....	153
C.3 Auger Electron Spectroscopy (AES)	156
C.4 X-ray photoelectron spectroscopy (XPS)	159
C.5 Scanning electron microscopy (SEM).....	161
C.6 Transmission electron microscopy (TEM)	163
Appendix D: Sputtering parameters	164
8. References.....	165

Acknowledgments

The path to a Ph.D. can be arduous and is often filled with digressions. Professor Eugene Haller provided the direction, encouragement, and resources to make this journey enjoyable. In addition, many people provided assistance along the way. A few will be mentioned specifically here, but many more played a role in this endeavor. Kin Man Yu provided invaluable expertise and insight into metal contact behavior on semiconductors and many hours of patient direction on the principles and operation of the RBS and x-ray equipment. Many of my results were confirmed through the use of TEM, and I must acknowledge Xi Wei Lin, Sergei Ruvimov, Zuzanna Liliental-Weber, and Linda Romano for their expertise in this technique. I am grateful for the support of all of my fellow graduate students, post-doctoral researchers, and staff who have joined our research group over the years. In particular, I am indebted to Jeff Beeman for his help with equipment and general lab protocol. Also, Hilary Baumann-Cherry and Chris Olsen must be thanked for their encouragement and assistance in all areas of the graduate school experience. I am especially indebted to Michèle Hirsch for all of her help with understanding the electrical behavior of metal/semiconductor contacts. Our collaboration and conversations were both enjoyable and scientifically fruitful. I would like to thank Professor Tim Sands and Professor Roya Maboudian for reviewing this dissertation.

This research was made possible by fellow researchers who were willing to provide samples to study metal/semiconductor reactions. I am obliged to Edith Bourret-Courchesne and Jim Walker for providing the ZnSe samples and to Dan Steigerwald, Bill

Imler, and others at the Hewlett-Packard Optoelectronics Division for the growth of GaN. The assistance of financial support in the form of fellowships from the University of California-Berkeley, AT&T Bell Laboratories, and the Intel Robert Noyce Foundation allowed me to pursue these studies.

On a more personal level, I would like to thank my parents for their unconditional support and love through the years. The values and ethics which they instilled are what has brought me to this point. I am most grateful for the love and support of my husband, Dave. Without his encouragement and understanding this work would not have been accomplished. As I embark on a new adventure, I pray that God will continue to bless me and those around me.

“Trust in the Lord with all your heart, and do not rely on your own understanding. In all your ways acknowledge Him, and He will direct your paths.” ~ Proverbs 3:5-6

1. Introduction

Recently, the scientific and technical communities have focused much effort on the development of materials for blue light emitting devices. Wide band gap semiconductors are of interest for blue light emitting diodes (LEDs), lasers, and photodetectors. These optoelectronic devices have several desirable applications in consumer electronics. For example, the development of a blue laser for use in optical compact disk technology would increase the storage density and playing time of the disks. A blue light emitting diode, in conjunction with already developed green and red LEDs, has been used to make large full-color flat panel displays. To make these applications commercially viable these optoelectronic devices must be efficient and highly reliable. One of the important components of any optoelectronic device is the contact between the semiconductor and the exterior circuit. This is generally made by a wire bonded to a thin metal film contacting the semiconductor.

In order to develop structurally and electrically stable devices it is crucial to gain an understanding of the behavior of the metal thin film/semiconductor contact. This entails studying the thermal and electrical stability of the interface after annealing. The aim of this work was to investigate the thermal stability of the near noble elemental metals (Pt, Pd, and Ni) on ZnSe and GaN. The focus was to determine which systems would remain stable under operating and processing conditions as well as which would react at the interface. For the systems which were not stable, we wished to characterize the reactions

occurring to determine whether they may be suitable for engineered contacts. All of these topics will be discussed in more depth in the following chapters.

1.1 Significance of ZnSe and GaN

Current research interest focuses on GaN and ZnSe, direct band gap semiconductors with band gap energies of 3.4 and 2.6 eV, respectively. Blue light emission from these materials was observed as early as the 1960s. (Lagerstedt et al., 1978; Ludwig and Aven, 1967) The band gap of these two materials can be tuned by alloying with other III-V or II-VI materials. Figure 1.1 shows the relationship between composition, band gap, and lattice parameter.

Figure 1.1: Relationship between band gap energy and lattice constant. (Matsuoka et al., 1994)

These materials have undergone a scientific and technical renaissance, due to the application of growth techniques such as molecular beam epitaxy (MBE) and organo-

metallic vapor phase epitaxy (OMVPE) and the first announcement of blue light emitting devices.(Haase et al., 1991; Nakamura et al., 1991) Haase, *et al.*(Haase et al., 1991) announced the development of a blue-green laser based on ZnSe at approximately the same time that Nakamura, *et al.*(Nakamura et al., 1991) announced the first blue LED developed from GaN. The introduction of both of these devices hinged on breakthroughs in epitaxial growth and processing of the materials.

Both GaN and ZnSe suffered from an inability to grow high quality bulk material, but the refinement of epitaxial growth techniques allowed growth of epitaxial layers with the necessary properties for optoelectronic devices. Stoichiometric material could be obtained through the non-equilibrium growth techniques, MBE and OMVPE.

	ZnSe	GaN
band gap (eV) (@ 300K)	2.6	3.4
crystal structure	zincblende (cubic)	wurtzite (hexagonal)
lattice parameter (Å)	a=5.668	a=3.189
		c=5.185
melting point (°C)	1520	1700 (sublimes)
thermal conductivity (W/K*cm)	0.19	1.3
substrate	(001) GaAs	(0001) sapphire/ 6H- SiC
lattice mismatch ($a_{\text{epi}}-a_{\text{sub}}$)/ a_{sub} (%)	3	13.8/ 4

Table 1.1: Selected materials properties of ZnSe and GaN

Table 1.1 shows a comparison of the basic properties of GaN and ZnSe. The lattice mismatch between substrate and epitaxial layer is much greater for GaN than for ZnSe, however with the use of a GaN or AlN buffer layer a layer of GaN with good emission properties can be grown.

The inability to obtain p-type doped layers in both materials also had to be overcome. Both could be easily doped n-type, but p-type doping was very difficult due to compensation by native defect donors and passivation. H passivation in materials grown by OMVPE was determined to be a major problem, due to the observation of the H-acceptor local vibrational mode by infrared spectroscopy. (Götz et al., 1996; Wolk et al., 1993) This problem was solved by using MBE growth (ZnSe) or rapid thermal annealing to remove the H (GaN). Thermal annealing cannot be used for ZnSe because it cannot be annealed at temperatures above 300°C without the introduction of a compensating n-type defect. (Chen et al., 1996)

The use of epitaxial growth methods and the removal of hydrogen passivation allowed the development of optoelectronic devices. The ability to obtain high quality crystalline films also makes it possible to study the basic properties of these exciting materials. Current progress in optoelectronic device development will be discussed in the following sections.

1.1.1 ZnSe Devices

Light emission from ZnSe was observed as early as 1967 under current injection. (Ludwig and Aven, 1967) The development of optoelectronic devices proved

difficult until consistent p-type doping was obtained through the use of nitrogen radicals in MBE growth.(Ohkawa et al., 1991; Park et al., 1990) It is easy to dope ZnSe n-type, but p-type doping requires growth by MBE to eliminate all compensating impurities and passivating H_2 and to allow the use of RF or plasma nitrogen sources for the p-type dopant. The p-type doping level is still limited to a maximum net hole concentration of approximately $1 \times 10^{18} \text{ cm}^{-3}$. This limitation is attributed to the solid solubility limit for N in ZnSe.(Gunshor et al., 1995)

Figure 1.2: Schematic cross section of a ZnSe based laser diode. (Neumark et al., 1994)

The ability to dope ZnSe p-type allowed the development of heterojunction structures for LEDs and laser diodes (LDs). (Haase et al., 1991; Yasuda et al., 1988) Figure 1.2 shows a diagram of the structure of the LD developed by Haase *et al.* The emitted light is from a CdZnSe quantum well. The amount of Cd incorporated adjusts the band gap energy and thus the wavelength of the light emitted from the quantum well. This first LD was operated only in pulsed mode at 77K. Higher operating temperature or duty cycle resulted in degradation of the light output.

Further study determined that the degradation was caused by the generation of 'dark line defects' in the quantum well region. (Tomiya et al., 1995) These defects are dislocations. They are nucleated at stacking faults and dislocations which are generated during growth due to the lattice mismatch between the substrate and epitaxial layer. The dislocations multiply in the quantum well region during operation and act as non-radiative recombination centers thus degrading the device. Many approaches have been tried to minimize the strain between the layers, and thus the as-grown dislocation density. Several groups have attempted growth with varying compositions of $\text{ZnS}_x\text{Se}_{1-x}$ or $\text{Zn}_x\text{Mg}_{1-x}\text{S}_y\text{Se}_{1-y}$ to find a compound which is lattice matched to the GaAs. (Okuyama et al., 1994; Qiu et al., 1993; Xie et al., 1992b) Other groups attempted to use $\text{In}_x\text{Ga}_{1-x}\text{As}$ as a buffer layer (Xie et al., 1992a) or used a newly developed bulk grown ZnSe substrate for homoepitaxy. (Boney et al., 1996) These techniques have reduced the initial dislocation density and have improved the lifetime of ZnSe based devices. The most recent report indicates that Ishibashi and coworkers have obtained room temperature, continuous operation of an LD for up to 100 hours. (Nakano, 1996)

The lack of a good Ohmic contact for p-type ZnSe also contributes to the degradation. The problem is that the energy level of the valence band (p-type semiconductor work function) is larger than the work functions of elemental metals. According to the Schottky model, which will be discussed in the next chapter, to obtain an Ohmic contact on a p-type semiconductor the work function of the metal must be larger than the work function of the semiconductor. This is not possible for p-type ZnSe, resulting in a Schottky contact for any metal on p-type ZnSe. The presence of the Schottky contact results in a large voltage drop across the contact at LED operating currents. The power dissipated adds to the heating of the device and aids in the generation of the dark line defects. Up to this point, no metal based Ohmic contacts have been developed. The contact scheme which appears most promising is a ZnSe/ZnTe graded contact. An Ohmic contact to p-type ZnTe is easily formed, so by gradually changing the composition from p-type ZnSe to p-type ZnTe a contact without a large Schottky barrier can be formed.(Gunshor et al., 1995) This scheme allows operation of the devices with a lower threshold voltage and less heating. This contact structure is used in the long lifetime LD devices.

1.1.2 GaN Devices

The first GaN light emitting diode was fabricated in 1978 using a metal-insulator structure. This was done because of an inability to obtain p-type GaN. (Lagerstedt et al., 1978) The first p-n junction GaN LED was announced in 1991 by Dr. Nakamura of the Nichia Corporation.(Nakamura et al., 1991) This development came soon after the discovery that p-type GaN could be obtained by Mg doping during growth followed by

Figure 1.3: Cross sections of LED structures. a) Initial structure announced in 1991. b) Optimized structure currently used in commercial LEDs. (Nakamura et al., 1991; Nakamura et al., 1994)

low energy electron beam irradiation (LEEBI). (Amano et al., 1989) Later it was reported that thermal annealing alone after growth was sufficient to activate the Mg. (Nakamura et al., 1992) Figure 1.3 shows schematics of the first LED structure developed by Nakamura and the optimized structure which is currently used. In the newer double heterojunction structure, the AlGaIn layers, because of their wider band gap, act to confine the carriers in the active Zn-doped InGaIn region, thus increasing efficiency.

The GaN layer directly on the sapphire substrate is grown at low temperature and acts as a buffer layer to accommodate the 13% lattice mismatch between the sapphire and GaN active region. The addition of the buffer layer decreases the density of misfit dislocations in the layers, however the dislocation density is still typically around 10^{10} cm^{-2} . (Heying et

al., 1996; Lester et al., 1995) The high efficiencies of these devices in the presence of large dislocation densities is an anomaly which is not yet well understood. Generally, dislocations act as non-radiative recombination centers, thus decreasing efficiency. In other III-V based LEDs dislocation densities on the order of 10^6 cm^{-2} are well known to practically eliminate light generation. (Lester et al., 1995) Obviously, the dislocations in GaN devices are less efficient as non-radiative recombination centers. The reasons for this are not yet known. The presence of dislocations also does not result in degradation of performance over time, as it does in ZnSe based devices. Extensive lifetime tests under high current and high temperature conditions have shown the GaN LEDs to be very robust. (Egawa et al., 1996; Osinski et al., 1996) Osinski *et al.* have observed that the main mode of failure is metal migration along defect tubes which eventually causes a short through the device.

The most recent development is the announcement of the GaN based laser diode (LD). (Nakamura et al., 1996a; Nakamura et al., 1996b) The LD has light output at a wavelength of 411 nm with a full width half maximum of 0.1 nm. Nakamura recently announced up to 35 hours of continuous operation at room temperature. (Nakamura, 1996) Nakamura speculates that the degradation is due to the large heat generation caused by high operating currents and voltages. Here the degradation problem mirrors that of ZnSe devices; the lack of a good Ohmic contact to p-type GaN results in a large voltage drop across the contact and significant device heating. P-type GaN also has a work function which is larger than any elemental metal and in addition, can not be doped

heavily p-type in order to form a tunneling contact. This again draws attention to the need for better Ohmic contacts.

1.2 Interest in structural and electrical behavior of metal/semiconductor contacts

The inability to form Ohmic contacts with elemental metals to p-type ZnSe and GaN means that more elaborate contacting schemes must be investigated. The ability to engineer useful contacts requires an understanding of the thin film reactions that occur at the interface between the metal and semiconductor. Also, the characteristics of the contact must not change during processing or device operation. This is particularly important for GaN devices which may be operated at high temperatures because of its wide band gap.

Knowledge of the reaction behavior of metals on semiconductors has proven to be essential in the development of devices. Silicide contacts on silicon and the more recent development of the Ge/Pd based contacts on GaAs formed by solid state regrowth are prominent examples. (Wang et al., 1995) Many studies have focused on the behavior of metals on Si, GaAs, and other III-V compound semiconductors (see chapter 2). These studies were fundamental for the development of stable Ohmic and Schottky contacts, improved theories for Schottky barrier heights, and increased understanding of thin film behavior. The focus of this work was to extend this knowledge to the more ionic wide band gap semiconductors, ZnSe and GaN. A better understanding of metal contacts on ZnSe and GaN may lead to novel insights which may also apply to other semiconductors. These two semiconductors are highly ionic and an understanding of the effects of this kind

of bonding may lead to new perspectives on semiconductor properties. Studying the reactions of thin metal films will also enhance the understanding of kinetics and phase formation in thin films, issues of great technological and scientific importance. As ZnSe and GaN based devices continue to be optimized, the properties of the contacts will become more important. With the understanding gained from basic studies of metal interactions and the corresponding electrical behavior, it should be possible to develop contacts which are thermally and electrically stable and provide the desired electrical behavior.

1.3 Interest in Pt, Pd, and Ni for contacts

The near noble metals are desirable for contacts because of their large work functions, relatively high reactivity with semiconductors, and resistance to oxidation and corrosion. Pt, Pd, and Ni contacts have been studied extensively on Si and GaAs. (Canali et al., 1978; Ho et al., 1979; Sands et al., 1987a) Their behavior on these two semiconductors has been well characterized and will be discussed in detail in chapter 2. In general all three metals react at fairly low temperatures compared to other metals. Pt reacts at the highest temperature of the three, requiring annealing at 200°C to react on Si and 250°C to react on GaAs. Since the reaction temperatures of the near noble metals are lower than other metals we expect them to also have the lowest reaction temperatures on ZnSe and GaN. In addition, because they have the largest work functions of the elemental metals, they also should have the lowest Schottky barriers on p-type ZnSe and GaN, thus being the

best candidates for low resistance contacts to these p-type materials. The relation between work function and Schottky barrier will be further elucidated in chapter 2.

Our studies showed that while Pt, Pd, and Ni react on ZnSe, they do not on GaN. The surface of GaN behaves more like a very stable ceramic surface. This finding indicated that the best candidates for metals which will react on GaN are likely to be those which form metal-nitride phases and which are known to react on other nitride ceramics, such as AlN. In order to find a metal which will react on GaN, we chose to investigate Ti which is a strong nitride former. Chapter 3 will further discuss the behavior of metals on ceramic surfaces.

2. Metal/Semiconductor Interfaces

Metal contacts to semiconductors are one of the basic components of every semiconductor device and have been studied for many decades, but are still not completely understood. One of the important criteria for a contact in a device is that it must be reliable. The contact must be stable and maintain the desired properties during processing steps and operation. The properties of a contact can be broken into two main categories: structural and electrical. The behavior of the interface in both of these areas must be considered when choosing a contact metal. This chapter will discuss the theories behind expected structural and electrical behavior, the behavior observed at typical metal/semiconductor interfaces, and predictions for the ZnSe and GaN systems.

2.1 Structural Behavior

Certain structural characteristics are important for any contact to be used in a device. It is vital for the contact to provide good adhesion, high corrosion resistance, and to be compatible with any subsequent processing steps. Quality contacts are important for high yield and device reliability. To provide high yield and reliability, the thermal stability of the contact must be known. Any interdiffusion or reaction at the interface during processing or use may result in a degradation of electrical or mechanical behavior, therefore it is important to study these systems. Alternatively, a reaction at the interface may form a new phase which may be more stable and/or give more desirable electrical properties.

The ability of two materials in contact to form a new stable phase at an interface depends on a competition between kinetic phenomena and thermodynamic driving forces. To form, new phases must overcome the thermodynamic barrier to nucleation. To grow, the kinetics of the system must allow enough of each reactant to diffuse to the interface. It can be shown that if the nucleation step is the limiting factor, the system is reaction controlled and follows the relationship $X=Dt$, where X is the thickness of the reacted layer, D the diffusivity and t the time. If the diffusion of material to the interface is the limiting reaction, the system is diffusion controlled. In this case the layer growth follows the relationship $X^2=Dt$ and the layer grows with the square root of time. We will first consider in depth the thermodynamic factors governing new phase formation.

2.1.1 Thermodynamics

The thermodynamics of the system is concerned with the energy changes caused by the reaction at the interface. A good introduction to the science of thermodynamics can be found in (Swalin, 1962). The system always attempts to minimize its free energy. The free energy of an element or compound in a closed system at constant pressure is characterized by the Gibbs free energy, G . G is composed of two parts, the heat of formation, H , and the product of the temperature and the entropy of formation, $-TS$. H is a measure of the internal energy of the compound, while the entropy can be considered a measure of the disorder. A comprehensive reference for the Gibbs free energies of elements and compounds is (Kubaschewski et al., 1993). An additional term in the free

energy of an interfacial system is the surface energy at the interface due to broken bonds and strain at the interface.

To determine whether a reaction may take place at an interface, the free energy change of the system can be estimated. This requires a knowledge of the Gibbs free energies of the products and reactants as well as the additional interfacial energy created by the addition of a third phase. If two elements are in contact at an interface, the formation of the product phase must create an additional interface. The energy involved in the formation of this interface is very difficult to determine and is generally neglected in thermodynamic calculations. Instead, only the Gibbs free energies of the reactant and product phases are considered. By subtracting the Gibbs free energies of the reactants from the Gibbs free energies of the products, the overall energy change in the reaction can be determined. Further discussion of the method for calculating the free energy change is given in chapter 3. If this free energy change is negative then the reaction is likely to proceed. The more negative the free energy change, the greater the driving force for reaction. In many cases the Gibbs free energies are unknown, however a method to estimate the enthalpies of formation of metal compounds has been developed. (deBoer et al., 1958) This method has recently been used to predict phase diagrams and thin film reactions in several Si and GaAs systems. (Beyers, 1984; Beyers et al., 1987; Beyers et al., 1984; Bhansali et al., 1990; Schmid-Fetzer, 1988) This method has also been used to calculate ternary phase diagrams for several metal-GaN systems. (Mohny and Lin, 1996) These phase diagrams show which phases should be stable at particular temperatures and compositions in a closed system at constant pressure.

These calculated phase diagrams can provide an initial framework for determining which metals may react on semiconductor surfaces. The calculations however, assume the system is in thermodynamic equilibrium, which is unlikely. They also often assume that the system is closed, i.e., no constituents can be lost out of the system. This is not true for reactions on semiconductors such as GaAs or GaN, where the As or N can escape in a gaseous form. In addition, the accuracy of the thermodynamic data used in the calculations is not always known. Finally, in thin film systems it is often the case that kinetics plays a larger role in the reaction than thermodynamics.

2.1.2 Kinetics

The interdiffusion of elements at the thin film semiconductor interface plays a large role in the initial phase formation and the sequence of phases formed. Two good references for information on diffusion in thin films are (Gösele and Tu, 1982) and (Tu, 1985). The kinetics of thin film reactions tend to be much faster than in the bulk because of the cleanliness of the interfaces, small grains, and fast diffusion along grain boundaries and interfaces. (Tu, 1985) Interdiffusion must precede nucleation in order to obtain the proper composition of the nucleated phases. Often the first phase formed is not the most stable phase, due to diffusion considerations. (Pretorius, 1981) The rate limiting step in these reactions is often outdiffusion of one of the semiconductor elements. (Brillson, 1994) This is due to the difficulty in dissociation of the semiconductor which scales with its heat of formation.

One of the major differences between thin film and bulk diffusion couples is the sequence of phases formed. In a bulk diffusion couple all of the intermediate stable phases in the phase diagram will be present, but in a thin film couple generally only one phase will be present at a time. The various phases may then form in succession if the amount of reactants permits it. Gösele and Tu (Gösele and Tu, 1982) have determined that this is due to kinetic instabilities. They determined that the first phase to form would be the one with the lowest nucleation barrier. Their evaluation then showed that while the first phase was growing in a diffusion controlled manner, no other phase would form until it reached a critical thickness. In thin film systems this critical thickness usually can not be attained because of a limited supply of one reactant.

Figure 2.1: The three possibilities for second phase formation under different supply conditions of the component A and B in a planar A/B diffusion couple. The compound A_kB may coincide with either A_iB or A_nB. (Gösele and Tu, 1982)

Figure 2.2: Schematic diagrams showing the phase formation in a Si-Ni thin film and Si(crystal)/Ni film system. Initially the Ni_2Si phase is formed and then after one of the elements is consumed the system is driven toward equilibrium by the formation of compounds richer in the remaining element. The indicated temperatures are rough guides for the formation of phases for films a few thousand Å thick and an annealing time of 1 hour. (Ottaviani, 1979)

Figure 2.1 indicates the sequence of phases through which the reaction will proceed. If the supply of a reactant is exhausted before the critical thickness is reached, the relative amounts of the semiconductor and metal determine the phase sequence and final phase. Figure 2.2 shows an example of this phase formation behavior in the Ni-Si system. In this case it has been found that variations in the amount of reactants alters the phase sequence and final phases. (Ottaviani, 1979) While these studies can explain why, and in what situations, we can expect to see single or multiple phase formation, they can not predict

which phases will be formed. No method has been determined to clearly identify which phase will form first and what the following sequence of phases will be. This sequence depends on a combination of thermodynamics and kinetics.

2.1.3 Observed structural behavior of Pt, Pd, and Ni on Si and GaAs

The reactions of Pt, Pd, and Ni on Si and GaAs have been studied extensively and are well understood. Their behavior will be reviewed here and will later be compared to the predicted and observed reaction behavior of these metals on ZnSe and GaN. An extensive review of the reaction behavior of Pt and Pd on Si and GaAs can be found in (Duxstad, 1994) and will only be summarized here. The behavior of Ni will be discussed in more detail.

Of the three metals, Pt requires the highest annealing temperature to initiate reactions. On Si, annealing at 200°C and above results in the formation of Pt₂Si. (Muta and Shinoda, 1972) This phase grows in a diffusion controlled manner, i.e., the thickness increases with the square root of time, until all of the Pt is consumed. The Pt₂Si then begins to transform to PtSi. Figure 2.3 shows Rutherford backscattering spectra (RBS) of the reaction sequence. Some studies showed the formation of PtSi before all of the elemental Pt was consumed. (Bindell et al., 1976; Muta and Shinoda, 1972; Poate and Tisone, 1974) This was shown to be due to the presence of impurities at the interface or in the Pt film. (Canali et al., 1977; Crider and Poate, 1980) If the interface and Pt film are free of contamination, the PtSi phase does not nucleate until the Pt₂Si phase has consumed all of the elemental Pt.

The reaction of Pt on GaAs begins at 250°C with the diffusion of Ga into the Pt layer. This reaction is not inhibited by contamination at the interface. (Fontaine et al., 1983; Kumar, 1975; Murarka, 1974) The reaction forms a layered structure with PtAs₂ at the interface and Pt₃Ga in the film. As the reaction proceeds, more Ga diffused out into the Pt film and the phase changes to PtGa. If the Pt layer is thicker than 0.2 μm, the reaction may not go to completion because it becomes increasingly difficult for the Ga to diffuse through the growing PtAs₂ layer. Figure 2.4 shows x-ray diffraction (XRD) spectra showing the phase change from Pt₃Ga to PtGa. Note that the Pt₃Ga phase is present up to 4 hours of annealing. The layered structure has been attributed to a lower interfacial energy between the GaAs and PtAs₂ (Fontaine et al., 1983) or the higher diffusivity of Ga in Pt than As in Pt. (Sands et al., 1987b)

Figure 2.3: Backscattering spectra of samples annealed at 350°C for different times. The as deposited Pt layer is 2700 Å thick. For clarity in the silicon spectra, only a few cases are shown. (Canali et al., 1977)

Figure 2.4: Glancing angle x-ray diffraction spectra of a 1000 Å Pt/ GaAs sample before and after annealing. (Fontaine et al., 1983)

Pd has been observed to react on Si even during room temperature deposition. (Buckley and Moss, 1972; Fertig and Robinson, 1976; Ho et al., 1979) The reaction begins with the formation of a Pd_2Si layer. This layer grows in a diffusion controlled manner and will grow epitaxially on $\langle 111 \rangle$ Si. (Bower et al., 1973; Hutchins and Shepela, 1973; Sigurd et al., 1974) Figure 2.5 shows the reaction of Pd to form Pd_2Si at different

temperatures. Pd_2Si is stable up to 700°C , when PdSi precipitates form. (Hutchins and Shepela, 1973)

Figure 2.5: RBS spectra for Pd on Si annealed at various temperatures for 30 minutes. (Clement et al., 1988)

Pd on GaAs reacts at temperatures below 250°C to form a ternary, hexagonal phase. This phase grows epitaxially on the GaAs, in the same manner as the Pd_2Si phase. The approximate composition of the phase is Pd_4GaAs , but it exists over a range of compositions. (Sands et al., 1987a) Figure 2.6 shows RBS spectra of the formation of the ternary phase. Note that the very slanted profile makes it difficult to estimate compositions or determine if binary phases are present without the use of complementary characterization techniques. Above 250°C a second ternary phase nucleates at the grain boundaries of the first ternary phase. (Lin et al., 1988a; Sands et al., 1987a) This second phase exists with compositions between $\text{Pd}_2\text{Ga}_{1.3}\text{As}_{0.7}$ and $\text{Pd}_4\text{Ga}_{1.3}\text{As}_{0.7}$ and is not

Figure 2.6: RBS spectra for a Pd/GaAs sample before and after annealing at 500°C for 5 minutes. (Olowolafe et al., 1979)

epitaxial. Annealing above 400°C results in the formation of two binary phases, PdGa and PdAs₂. The relative amounts of these phases depends on how much As is allowed to sublime from the film. If the sample is annealed with a SiO₂ cap, i.e., no As is lost, the final phases are both present. (Yu et al., 1986) Films annealed in vacuum without a cap are dominated by the PdGa phase. (Kuan et al., 1985)

Ni begins to react on Si to form Ni₂Si at temperatures between 200 and 300°C. (Canali et al., 1978; Tu, 1975; Zheng et al., 1986) The formation of Ni₂Si is followed by the growth of the NiSi phase once all of the elemental Ni has been consumed. Interdiffusion of Ni and Si has been observed at 150°C. (Nemanich et al., 1984) In both phases Ni has been determined to be the dominant diffusing species. (Chu et al., 1974; Zheng et al.,

1986) This was determined by observing the motion of a Ag or Xe marker after annealing. The marker movement was detected through the use of RBS. The growth of the Ni_2Si and NiSi phases is diffusion controlled, i.e., the layer grows proportionally to the square root of time.

NiSi is stable up to 700°C , where it begins to transform to NiSi_2 . This silicon rich silicide grows in a interface controlled manner, i.e., the layer thickness increases linearly with time. (Tu, 1975) Contamination at the Ni/Si interface does not hinder the reaction behavior, however the annealing ambient does play a role. Canali *et al.* (Canali et al., 1978) observed that when the system was annealed in vacuum, the phases grew in sequence. If the annealing ambient was N_2 gas, they observed the coexistence of phases. Figure 2.7 shows RBS spectra for the two cases. They attributed this to the indiffusion of impurities. None of the nickel silicides form with an oriented relationship to the substrate, however NiSi_2 has been grown epitaxially on $\langle 111 \rangle$ Si by molecular beam epitaxy. (Hunt et al., 1986)

Ni on GaAs has been observed by transmission electron microscopy (TEM) to have formed either during deposition or during TEM sample preparation. (Lin et al., 1988b; Sands et al., 1987a) This indicates that formation takes place at temperatures below 150°C . A ternary phase, Ni_3GaAs is initially formed at the interface. The reaction is inhibited by oxides and this can result in a laterally inhomogeneous layer thickness. (Sands et al., 1987a) Figure 2.8 shows the experimental RBS spectrum of the reacted film and the corresponding theoretical simulation. The simulation shows good agreement between

the composition determined by TEM and by RBS. The composition was estimated by TEM by determining how much of the GaAs was consumed in the reaction.

Figure 2.7: Backscattering spectra of samples of Ni deposited on Si showing (a) the sequential formation of Ni₂Si and NiSi in vacuum-annealed samples and (b) the coexistence of Ni₂Si, NiSi, and unreacted Ni in samples annealed in N₂. (Canali et al., 1978)

Figure 2.8: RBS spectrum and simulation for Ni/GaAs sample annealed at 220°C for 10 min. Simulation is based on input from a TEM study. (Sands et al., 1987a)

The Ni₃GaAs phase is oriented with respect to the substrate. (Lin et al., 1988b; Ogawa, 1980; Sands et al., 1987a) This phase is stable up to 300°C. Above 300°C binary NiAs and NiGa phases begin to form. These are also oriented with the substrate and form in laterally separated grains. It is speculated that the lateral separation reduces the interfacial area between the NiAs and NiGa phases, thus reducing the interfacial energy of the system. (Sands et al., 1987a)

2.1.4 Predicted structural behavior for metals on ZnSe and GaN

Unlike the Si and GaAs systems, there is a dearth of information on metal-ZnSe and metal-GaN systems, but the studies which have been done will be reported in section 2.1.5. The increased ionic character of the bonding in ZnSe and GaN provides a new

variable with regard to reaction and Schottky barrier formation. Brillson (Brillson, 1982) has predicted that this greater ionicity will lead to the formation of more metal-anion phases rather than metal-cation phases. Elements with more dissimilar electronic structures will be more reactive. (Sands and Keramidas, 1994) As the semiconductor becomes more ionic, the anion (Se or N) becomes more electronegative and more likely to react with the transition metal. The cation (Zn or Ga), however, becomes more electropositive and less likely to react. A greater segregation between anion and cation phases in the reacted layer is also predicted. (Brillson, 1982) The strength of the chemical bonding between the metal and semiconductor anion will likely determine the extent of reactive anion outdiffusion and the concentration of dissociated cations near the interface.

The temperature for reaction is predicted to depend on the heat of formation of the semiconductor (Brillson, 1982) and the strength of metal-metal bonding. (Sands, 1989) Brillson believes that the rate limiting step is the dissociation of the semiconductor, which scales with the semiconductor heat of formation. (Brillson, 1994) Sands argues that, in addition, metals with stronger metal-metal bonds will require higher temperatures for reaction because more energy is required to break the bonds. (Sands, 1989) Both of these trends have been observed in the reactions of metals on Si and GaAs. If these trends continue, Pt should have the highest reaction temperature and Pd the lowest on ZnSe and GaN. In addition, because the heat of formation of both ZnSe and GaN is higher than that of Si or GaAs, these reactions should take place at higher temperatures. Reactions will also take place at higher temperatures if the metal film is epitaxial to the substrate. (Palmstrom and Sands, 1993) This is because the interfacial energy of the system is low.

This may result in higher reaction temperatures for metals on GaN, because most metals have been found to be epitaxial or highly oriented in the as-deposited state. (Liu et al., 1996)

Better reaction predictions can be made if the ternary phase diagram of the metal/compound semiconductor system is known. In the ZnSe system these diagrams have not been experimentally determined or theoretically calculated. Metal/GaN phase diagrams have been predicted for a wide range of metals based on thermodynamic calculations. (Mohney and Lin, 1996) In the cases of Pt, Pd, and Ni a metal-Ga phase is predicted to form with the release of N₂ gas. At 600°C, these three metals should react on GaN according to the thermodynamic data. Figure 2.9 shows calculated Ni/GaN phase diagrams for various N₂ pressures. Because the product of the reaction is a gas phase, the pressure of N₂ in the annealing chamber will vary the extent of the reaction. A lower N₂ pressure will allow the reaction to proceed further to form the more Ga rich binary phase, as shown in figure 2.9c. Pt and Pd are not known to form metal-N phases and the known Ni-N phases are relatively unstable.

These predictions are based solely on thermodynamics. The actual reactions which occur may be very different depending on the kinetics of the reaction. Newman *et al.* (Newman et al., 1993) have determined that GaN has a very large kinetic barrier to dissociation and therefore reactions may not proceed as predicted. In addition, the thermodynamic data which were used to calculate the phase diagrams may not be accurate. The heat of formation of GaN was determined by studies in the 1970s and early

Figure 2.9: Calculated Ni-Ga-N phase diagram at 600°C. The nitrogen corner of the diagram represents a) N_2 at 1 atmosphere pressure, b) N_2 at 10^{-2} atmosphere pressure, and c) N_2 at 2×10^{-4} atmosphere pressure. (Mohney and Lin, 1996)

1980s (Karpinski et al., 1984; Madar et al., 1975; Thurmond and Logan, 1972) and the quality of the GaN and accuracy of the data is unknown.

2.1.5 Observed structural behavior for metals on ZnSe and GaN

The thermal stability of metals on GaN and ZnSe has not been studied as extensively as metals on Si and GaAs. As interest in these materials continues to grow, interest in and knowledge of metal reactions will continue to increase. Currently a significant amount of the information available is based on x-ray photoemission studies of monolayer coverages

of metal. Because of the ease of gas diffusion through such thin layers (Sands, 1989) and the influence of non-linear diffusion in layers less than 10 Å thick (Tu, 1985), these studies may not be applicable to thicker layers.

Observations of Al, Co, Cu, and Pd on ZnSe with photoemission spectroscopy indicated that these elements are disruptive to the surface when evaporated, even when the substrates are held at room temperature. (Vos et al., 1989) This means that deposition of the metal changes the bonding of ZnSe as measured by photoemission. Co, Cu, and Pd grow in a layer by layer mode, while Al exhibits island growth. All four materials show evidence of Zn atoms dissolving into the growing overlayer, but no new phases were observed by Vos *et al.*.

Figure 2.10: Zn 3d emission as a function of deposition for Al, Co, Cu, and Pd. Surface disruption is reflected by the appearance of a low-binding-energy component which is related to Zn atoms dissolved in the surface and near-surface region of the metal overlayer. (Vos et al., 1989)

Figure 2.10 shows the photoemission spectra for these four metals as a function of deposition thickness. The growing peak on the right side of the substrate peak is attributed to Zn dissolved in the overlayer. Further study of Co showed that there is segregation of Se to the surface of the Co layer. (Anderson et al., 1989) Anderson *et al.* observed that in layered Au/Co structures with Au as the bottom layer, Co still diffused through to interact with the ZnSe. With Co as the bottom layer, Zn was extracted from the Co layer into the Au layer. Chen *et al.* (Chen et al., 1994) observed the formation of an Al_2Se_3 phase when depositing monolayers of Al on ZnSe. The photoelectron peak of the Al 2p level shifted and the Se peak broadened, in addition they saw the peak attributed to Zn in the overlayer. This was interpreted as phase formation and agrees with the prediction of metal-anion phase formation.

Ti and Ce were also studied with photoemission and were found to react with ZnSe. The photoemission spectra showed a peak indicating Zn dissolved in the overlayer, and a peak attributed to a reaction of Zn with the metal. (Vos et al., 1989) Au and Ag overlayers, however, do not react with ZnSe. (Chen et al., 1994; Vos et al., 1989) Deposition of a few monolayers does not disrupt the surface and instead leaves an abrupt interface. All of these photoemission measurements were done with a maximum coverage of 15 Å.

With thicker layers of 1000 Å to 2000 Å, Ag was observed to maintain an abrupt junction with ZnSe after annealing up to 300°C for 30 minutes. (Fijol et al., 1995) Secondary ion mass spectroscopy (SIMS) and auger electron spectroscopy (AES) both gave no indication of Ag diffusion into the ZnSe. Thick Au layers, however, showed

diffusion of Au into the ZnSe and outdiffusion of Zn and Se after annealing at 350°C for 90 minutes. (Fijol et al., 1995) Figure 2.11 shows the AES depth profiles of Au/ZnSe interfaces both before and after annealing. Both SIMS and AES detected the presence of a ZnO layer at the surface. Indium also diffused into ZnSe after annealing at 250°C. (Wang and Holloway, 1992) The formation of a good Ohmic contact by In on n-ZnSe was attributed to an increased surface carrier density caused by the indiffusion of In.

(a)

(b)

Figure 2.11: Auger depth profiles for Au/ZnSe contacts a) as-deposited, and b) heated to 350°C for 90 minutes. (Fijol et al., 1995)

More of the information on metal/GaN contact reactions is based on thick film ($>500\text{\AA}$) studies. Most of the studies show little or no reaction between the metal and GaN unless anneals are done at very high temperatures. This is very reasonable considering the thermal stability of GaN. An interesting feature of most metals on GaN is that they tend to be highly oriented after deposition. Metals deposited by evaporation tend to be epitaxial on the GaN surface (Liu et al., 1996), and this may partially explain their thermal stability.

Two studies have been performed using monolayer coverages of Al and Ni on GaN. (Bermudez et al., 1996; Bermudez et al., 1993) These two metals show very different behaviors. Ni is unreactive on the surface until it is annealed at temperatures above 600°C in ultra-high vacuum. Above this temperature the GaN begins to decompose and the N diffuses through the Ni. At the interface there is some intermixing between the Ni and Ga, but no phase formation is observed by x-ray photoemission spectroscopy.

Al, however, reacts to form AlN even at room temperature. This, again, is a metal-anion phase as predicted. This reaction was observed by peak shifts in the Auger electron spectrum and it occurs only for the first monolayer of Al. Further deposited Al remains metallic, however metallic Ga is mixed into the overlayer. When the system is annealed at 800°C in ultra-high vacuum, the GaN decomposes and more AlN is formed. Smith *et al.* (Smith et al., 1996a) also observed the formation of a new phase at the Al/GaN interface after annealing at 650°C for 30 minutes. The Al layer was $2500\text{\AA}$ thick. The new phase was observed by TEM, but was not identified.

1000 Å thick layers of Ni were investigated by Guo *et al.* (Guo et al., 1996b). They found that a Ni_3Ga_4 phase was formed at the interface during deposition and that Ni_xN phases were formed after annealing at 200°C. They determined the presence of these phases by x-ray diffraction (XRD), however their interpretation of the XRD peaks was flawed. Figure 2.12a shows an XRD spectrum from their paper of the Ni/GaN system after annealing at 400°C. Figure 2.12b shows an XRD spectrum of an GaN/ Al_2O_3 sample with no Ni deposited. A comparison of the peaks indicates that the peaks indexed as the reacted phases are present in the substrate sample. The peak which they identify as the (400) Ni_3Ga_4 is simply the K_β peak for GaN. The peaks indexed as Ni_xN phases are in the same location as the Al_2O_3 substrate peaks. Clearly the occurrence of this reaction can not be determined solely through the use of XRD.

Figure 2.12: X-ray diffraction spectra of (a) Ni/GaN/ Al_2O_3 annealed at 400°C for 30 minutes (Guo et al., 1996b) and (b) unannealed GaN/ Al_2O_3 .

Phase formation for metals on GaN has been observed in other systems. Cole *et al.* observed that annealing W at 900°C for 1 minute resulted in the formation of W₂N at the interface. Sc reacts at the interface to form ScN during an initial deposition of 10 Å or less. (Kaplan et al., 1996) The thickness of the ScN layer increases with the substrate temperature, however no excess Ga build-up was observed by AES. The location of the released Ga has not been determined.

Cordes *et al.* observed the formation of TiN after annealing Ti on GaN at 850°C. They also identified the presence of Ti₂GaN by XRD. The formation of TiN was also identified by TEM in Ti/Al/Ni/Au multilayer contacts. (Ruvimov et al., 1996b) 5 Å of TiN was identified at the Ti/GaN interface before annealing. After annealing at 900°C for 30 seconds the TiN layer increased in thickness to 100-150 Å. This phase is oriented to the GaN substrate. Luther *et al.* (Luther et al., 1997) also investigated the stability of Ti and Ti/Al contacts to GaN. They found no clear indication of phase formation after annealing at 400°C for 5 minutes. At this temperature a significant amount of interdiffusion occurred between the Ti and Al layers in the Ti/Al contact, but there was no indication of dissociation of the GaN.

Trexler *et al.* (Trexler et al., 1995) observed the behavior of Au and Au/Ni contacts after annealing up to 600°C. They found no apparent decomposition of GaN for either system. In the Au/Ni system, there was some indication of Ni indiffusion through the Au into the GaN. This was measured by AES depth profiling. In this system there are no known Au-N phases, and this may help explain the lack of reaction up to this temperature.

The behavior which has currently been observed for metal reactions on ZnSe and GaN agrees reasonably well with the predicted behavior. The phases formed are exclusively metal-anion phases and the reactions are taking place at higher temperatures. Further studies of the reaction behavior of other metals on these semiconductors are necessary to verify these trends.

2.2 Electrical Behavior

There are two types of electrical behavior of metal/semiconductor contacts; rectifying, or Schottky, and nonrectifying, or Ohmic. A Schottky contact is one in which a barrier exists for the majority carrier to move from the metal into the semiconductor. An Ohmic contact is one in which carrier flow in both directions is easy because the barrier height is negligible. The basics of barrier formation will be discussed in the following sections. In these sections the descriptions will assume that the metal is contacting an **n-type** semiconductor with **electrons** as the majority carriers. The details of metal/semiconductor contacts are covered in many semiconductor device textbooks, for example see Sze (Sze, 1981). A very complete review of the subject has been written by Rhoderick and Williams (1988).

2.2.1 Schottky-Mott Theory

The behavior of the Fermi energy equilibrium in a metal/semiconductor contact is similar to that of an abrupt p-n junction. When the metal and semiconductor come into contact, the Fermi levels must equilibrate. If we consider a metal whose Fermi level lies

below that of an n-type semiconductor, we encounter the situation appearing in figure 2.13.

Figure 2.13: Formation of Schottky barrier. (Schroeder, 1990)

ϕ_M is the work function of the metal and is defined as the difference between the Fermi level in the metal and the vacuum level. When the metal and semiconductor are brought into contact, electrons will flow from the semiconductor into the metal to find lower energy states. This creates a region on the semiconductor side that is depleted of free carriers. The fixed positive space charge from the depleted donors results in band bending. Electrons will flow until the Fermi levels align. This situation has now created a potential barrier for electrons wishing to pass in either direction. The difference between the metal work function, ϕ_M , and the semiconductor work function, ϕ_s , is the barrier height, ϕ_B .

These barriers are called Schottky barriers, after Walter Schottky who developed the theory of the potential barrier between 1923 and 1938. (Schottky, 1923; Schottky, 1938;

Schottky and Deutschmann, 1929) Mott proposed the mathematical relation that the barrier height was due to the difference in the work functions in 1938. (Mott, 1938) The underlying theory has come to be known as the Schottky-Mott theory. The barrier height can be measured by several methods, two of these are described in appendix B.

Schottky barriers are used to form diodes. The height of the barrier for carriers moving from the semiconductor to the metal can be adjusted by applying a bias. Depending on the polarity, the bias can make it easier or harder for electrons to flow out of the semiconductor. With the polarity in the reverse direction, the barrier is high and few electrons can pass into the metal; with the polarity in the forward direction, electron flow into the metal becomes easy. To first order, applying a bias does not affect the height of the potential barrier for electrons traveling from the metal to the semiconductor. This means the system can never provide a good Ohmic contact in both directions if the barrier is larger than a few kT . The current flow is asymmetric for positive and negative bias. Contrary to p-n junctions where electrons and holes flow in the forward bias state, in Schottky diodes only majority carriers flow.

Ohmic contacts can also result from metal/semiconductor contacts with the proper relationship between metal and semiconductor work functions. Ohmic contacts are important for many semiconductor devices. When building a laser, for example, it is important that current be able to flow through the device without a significant voltage drop or power loss due to contact resistances. If the metal work function is smaller than the semiconductor work function (for an n-type semiconductor), the equilibration of the Fermi levels may not result in a barrier, as shown in figure 2.14. In this case, electrons can

flow easily in either direction and there is no potential barrier, the contact is Ohmic. Another method to create Ohmic contacts is to form a highly doped surface layer. A very highly doped layer results in a very narrow depletion region because of the high concentration of space charge. Electrons can tunnel through this narrow barrier, in either direction, with ease. This highly doped layer can sometimes be created by the reaction between a metal and the semiconductor. (Sands and Keramidas, 1994)

Figure 2.14: Ohmic contact on an n-type semiconductor.

2.2.2 Deviations from the Schottky-Mott model

The previous section gives an idealized view of the electrical behavior of metal/semiconductor contacts. Barrier heights at metal/semiconductor contacts can not usually be predicted by the difference in the work functions. In reality, energy levels at the surfaces and interfacial layers must be considered. There are several competing theories which attempt to describe and predict the barrier height formed at an interface. The basic premise of all these theories is that electron states exist within the semiconductor band gap

near the metal/semiconductor interface. When the semiconductor and metal come into contact the transfer of electrons to equilibrate the Fermi levels can occur between the metal and the surface, or interface, states of the semiconductor. If the density of these states is high enough the semiconductor bulk is not involved in the electron transfer and the Fermi level may be pinned. In this case the Fermi level energy is determined only by the energy of the interface states and is not dependent on the difference between the metal and semiconductor work functions. Barrier heights of many metals on Si and GaAs are pinned by this mechanism.

There is no consensus on the source of these interface states. Bardeen (Bardeen, 1947) suggested that the states evolved from surface states generated from the interruption of the bulk periodic potential. Heine (Heine, 1965) proposed that the states were due to metal electron wave functions. Some of the states in the metal lie within the band gap of the semiconductor and the wave functions for these states will decay exponentially into the semiconductor. These have been termed metal induced gap states, or MIGS. More recently, Spicer *et al.* (Spicer et al., 1979) proposed that the states are generated by defects formed by the interaction of the semiconductor surface atoms and the adsorbed metal atoms on the surface. To date there has been no concrete evidence to unequivocally prove that one of these theories is correct for all cases.

2.2.3 Predicted behavior for ZnSe and GaN

The ideal barrier height of a metal/semiconductor contact can be predicted by the Schottky-Mott model if the work functions of the metal and semiconductor are known.

The work function of a semiconductor is equivalent to the electron affinity plus the difference between the bottom of the conduction band and the Fermi level. For both ZnSe and GaN the electron affinity is approximately 4.1 eV. This results in a work function for ZnSe which varies between 4.1 and 6.7 eV. For GaN the work function varies between 4.1 and 7.5 eV. The work functions for various metals are given in appendix A. For an Ohmic contact on n-type ZnSe or GaN the metal work function must be less than 4.1 eV. According to the Schottky model, Al is the only common metal which should form an Ohmic contact on n-type ZnSe or GaN. In order to form an Ohmic contact on p-type material the metal work function must be greater than 6.7 or 7.5 eV for ZnSe and GaN respectively. No elemental metals have work functions this large, therefore all metals should form Schottky contacts on p-type ZnSe and GaN.

The discussion above assumes that the ideal Schottky-Mott model will be obeyed. This assumption is predicted to be valid because of the large ionicity of GaN and ZnSe (see appendix A). It has been observed (Kurtin et al., 1969; Mead, 1969) that for very covalent semiconductors, such as Si and GaAs, the barrier height does not depend on the metal work function, while for very ionic semiconductors, such as CdS and ZnO, the barrier height varies linearly with the metal work function. Figure 2.15 shows the variation in Fermi level stabilization with the electronegativity difference of the semiconductor. S is the measure of the change in barrier height over the change in metal work function. In the ideal Schottky-Mott model, S should be equal to one.

Figure 2.15: Dependence of $S = d\phi_B/d\phi_M$ on the electronegativity difference between the components of the compound. (Foresi and Moustakas, 1993)

Kurtin *et al.* speculate that the Schottky-Mott model is followed for ionic semiconductors because no surface states are generated within the band gap. Calculations show that there is little energy differential between an atom at the surface and an atom in the bulk, therefore if there are no energy states at a particular energy in the bulk, they will also be nonexistent at the surface. Calculations based on the MIGS theory (Louie et al., 1977) also show that as the semiconductor becomes more ionic the penetration depth of the metal electron wave functions as well as the density of states decrease. Thus, as indicated in figure 2.15, barrier heights on GaN should closely follow the Schottky-Mott model, while the relation between barrier heights and metal work function on ZnSe will not have a slope of 1.

From these calculations we can predict that the barrier height formation should approximately follow the Schottky-Mott model. If this is indeed the case, then it should be difficult to form Ohmic contacts on both n- and p-type ZnSe and GaN. The Schottky-Mott model predicts that no elemental metals should form Ohmic contacts on p-type ZnSe and GaN and only Al should form a good Ohmic contact to n-type material. Ohmic contacts to n-type material could be formed by doping the surface layer heavily to form a tunneling contact. This is not possible on p-type material because in both systems it is difficult to dope heavily p-type due to the formation of compensating defects.

2.2.4 Observed electrical behavior of contacts on ZnSe and GaN

ZnSe

Table 2.1 lists measured Schottky barrier heights on ZnSe. Most experiments have been performed on n-type ZnSe because p-type material is difficult to obtain. A complete review of the electrical behavior of metals on ZnSe can be found in (Duxstad, 1994) or (Fijol and Holloway, 1996). Recently a few studies have investigated the effect of surface preparation on the barrier height. Chen *et al.* (Chen et al., 1994) report that a 2-3 monolayer thick interfacial Se layer in a Au/p-ZnSe contact decreases the barrier height from 1.15 eV to 0.89 eV. They do not speculate as to the role of the Se in the contact. Ishikawa *et al.* (Ishikawa et al., 1996) found that after etching the surface to remove the native oxide the turn-on voltage of a Ni/p-ZnSe diode is reduced.

Metal	ϕ_{SB} n-type (eV)	ϕ_{SB} p-type (eV)	Metal	ϕ_{SB} n-type (eV)	ϕ_{SB} p-type (eV)
Al	0.58(Vos et al., 1989) 0.55(Chen et al., 1994)	2.15(Chen et al., 1994)	Fe	1.09 (calc) (Continenza et al., 1990)	
Ag	1.06(Vos et al., 1989)		Hg	1.4- 1.5(Marshall et al., 1989)	
Au	1.45(Vos et al., 1989) 1.41(Anderson et al., 1989) 1.35- 1.4(Marshall et al., 1989) 1.5(Akimoto et al., 1991) 1.55(Chen et al., 1994)	1.15(Chen et al., 1994)	HgSe	Ohmic	Ohmic (Hiei et al., 1993) 0.6-1.0 (calc) (Lansari et al., 1992)
Ce	0.50(Vos et al., 1989)		In	Ohmic(Dreilus et al., 1990)	
Co	1.0(Vos et al., 1989) 0.98(Anderson et al., 1989)		Pd	1.48(Vos et al., 1989)	
Cu	1.1(Vos et al., 1989) 1.1 (bulk) (Mead, 1965)		Pt	1.4 (bulk) (Mead, 1965)	
			Ti	0.85(Vos et al., 1989) 0.7 (bulk) (Mead, 1965)	

Table 2.1: Measured barrier heights for various metals on ZnSe.

Figure 2.16 shows the correlation between metal work function and measured barrier height on n-type ZnSe. The work function for each metal is an average of the reported values shown in table 2.1. The data shows that in general the barrier height increases with metal work function, as predicted by Kurtin. (Kurtin et al., 1969) Figure 2.15 shows that the slope predicted by Kurtin is approximately 0.5 for ZnSe with an electronegativity difference of 0.8. Using a linear fit to the data in figure 2.16, an experimental slope of 0.72 can be determined. This indicates that the barrier heights do not vary linearly with the metal work function as predicted for an ideal Schottky-Mott diode, but that the greater ionicity of ZnSe decreases the effect of pinning at the interface. This correlation was also observed by Vos *et al.* (Vos et al., 1989) in photoemission studies of monolayer coverages of metals on ZnSe.

Clearly, this behavior makes Ohmic contact formation by elemental metals on p-type ZnSe difficult if not impossible. No elemental metal has a large enough work function to form an Ohmic contact on p-type ZnSe. The lowest resistance Ohmic contacts on p-type ZnSe are graded ZnSe/ZnTe structures. (Fan et al., 1993; Han et al., 1995) These are complicated MBE grown structures which either use a multiple-quantum well structure or a ternary compound layer which gradually alters the composition from p-type ZnSe to p-type ZnTe. It is then possible to make an Ohmic contact to p-type ZnTe using Au. While the contact resistance of these structures is quite low ($\sim 10^{-3}$ - $10^{-4} \Omega\text{cm}^2$), they are thermally unstable and the contact resistance degrades during operation due to resistive heating. (Fijol and Holloway, 1996) The problem of reliable low resistance contacts to p-type ZnSe has not yet been solved.

Figure 2.16: Barrier height versus metal work function for metal contacts on n-type ZnSe.
 $S = d\phi_B/d\phi_M = 0.7175$.

There have only been a few reports which correlate the barrier heights observed to the microstructure or thermal stability of the metal/semiconductor interface. Fijol *et al.* (Fijol *et al.*, 1995) found that the breakdown voltage of Au and Ag contacts on p-type ZnSe could be minimized by annealing. In the Au case, the minimum breakdown voltage occurred after annealing at 350°C for 30 minutes and was attributed to tunneling through deep acceptor levels formed by indiffusion of Au. In the case of Ag, the minimum breakdown voltage was obtained after annealing at only 150°C for 45 minutes. No diffusion was observed at this temperature. The lower breakdown voltage was attributed to the incorporation of interfacial O in the ZnSe, thus increasing the surface carrier

density. Good Ohmic contacts have been formed on n-type ZnSe with In after annealing at 250°C for a few minutes. (Wang and Holloway, 1992) There was some indiffusion of indium in this contact and the low resistance of the contact was attributed to near-surface doping by In.

Recently two studies have reported on the spatial variation of Au/ZnSe barrier heights. (Coratger et al., 1995; Morgan et al., 1996) These measurements were performed using a specialized scanning tunneling microscope setup which allows the current voltage characteristics to be measured on a very small area. Coratger *et al.* found barrier height variations between 1.48 and 2.15 eV on chemically etched ZnSe surfaces. Using the I-V technique, they macroscopically measured the barrier height to be 1.6 eV. The maximum of the distribution of barrier heights is 1.65 eV, which agrees very well with the macroscopic measurement. Studies by Morgan *et al.* (Morgan et al., 1996) gave barrier height variations between 1.33 and 1.43 eV. These measurements were performed on ZnSe samples which were capped by Se before being removed from the growth chamber. This difference in surface preparation may explain the difference in measured barrier height.

GaN

The reported values for as-deposited Schottky barriers on GaN are given in table 2.2. These values are found for contacts which have been deposited by evaporation, have not had the surface ion-beam etched prior to metal deposition, and have doping levels below 10^{18} cm^{-3} . The effects of deposition, surface preparation, and doping will be discussed

further. Most of the measurements are again on n-type material because of the difficulty in p-type doping.

Metal	ϕ_B (eV), n-type	ϕ_B (eV), p-type
Al	Ohmic (Foresi and Moustakas, 1993; Smith et al., 1996a)	
Ag	0.82 (Kampen and Monch, 1996)	
Au	0.91 (Khan et al., 1995) 0.87 (Schmitz et al., 1995) 1.03 (Kalinina et al., 1996) 0.95 (Götz et al., 1995) 0.84 (Hacke et al., 1993)	2.48 (Kuzntsov et al., 1995)
Cr	0.55 (Kalinina et al., 1996)	
Ni	0.95 (Schmitz et al., 1995) 1.12 (Kalinina et al., 1996)	
Pb	0.73 (Kampen and Monch, 1996)	
Pd	0.94 (Schmitz et al., 1995) 1.11 (Wang et al., 1996) 0.92 (Guo et al., 1995)	
Pt	1.1 (Mohammad et al., 1996; Schmitz et al., 1996b; Wang et al., 1996) 1.0 (Duboz et al., 1996; Guo et al., 1995)	
ScN	1.0 (Kaplan et al., 1996)	
Ti	0.58 (Binari et al., 1994)	

Table 2.2: Measured barrier heights for various metals on GaN.

According to the model of Kurtin (Kurtin et al., 1969), the barrier heights of metals on GaN should vary linearly with the metal work function with a slope of 1. Figure 2.17

graphs the relation between barrier height and metal work function. Using a linear fit the slope can be determined to be 0.44. The slope for GaN is lower than that for ZnSe, while the prediction is for the slope to be higher.

Figure 2.17: Barrier height versus metal work function for metal contacts on n-type GaN.
 $S = d\phi_B/d\phi_M = 0.44$.

This difference can be accounted for by using a different definition of ionicity. Kurtin bases his explanation of the difference in behavior on differing levels of ionicity of the compounds. The definition used for ionicity is simply the difference in electronegativities of the two elements in the compound. This definition was originally established by Pauling in the 1930s. (Pauling, 1960) Pauling later adjusted his definition to account for

compounds which were not tetrahedrally coordinated, but had resonating bonds. As our understanding of solid state physics expanded, new definitions of ionicity were developed based on ionic and covalent potential energy contributions to the average energy of the band gap. Phillips (Phillips, 1973) developed a definition in which the fractional ionic character of the bond depends on the magnitude of the ionic (antisymmetric) potential compared to the covalent (symmetric) potential. This new definition correlates well with certain semiconductor behavior, such as the crystal structure of the solid (i.e., wurtzite or zincblende) and the cohesive energy. Using this definition, the ionicity of ZnSe is 63%, while that of GaN is 50%. This revised ionicity scale also agrees with the observed behavior of Schottky barrier heights on ZnSe and GaN. Future revisions of some barrier height measurements may, however, alter the slope.

Some of the tabulated values of barrier heights may change as our understanding of GaN continues to evolve. Recent studies have begun to indicate that the preparation techniques used prior to metal deposition or the metal deposition technique itself may affect the measured barrier height. Surface preparation has been documented to affect the Schottky barrier height in other semiconductor systems. (Brillson, 1994) Ishikawa *et al.* (Ishikawa et al., 1997) investigated the change in electrical behavior for metal contacts on p-type GaN with or without buffered HF etching prior to metal deposition. They observed a slight improvement in the I-V characteristics. There was a slight decrease in the turn-on voltage for the diode after the etching. They did not determine barrier heights. They speculate that this improvement was due to the removal of a thin contamination layer at the interface.

Hirsch *et al.* (Hirsch et al., 1996) also observed a similar behavior for Ti contacts on GaN. These contacts had an approximate as-deposited barrier height of 0.2 eV. The barrier height increased with annealing up to 230° C to a stable barrier of 0.45 eV. This increase could be due to the consumption of an interfacial contamination layer by the Ti. No macroscopic interfacial reaction was observed by Rutherford backscattering spectrometry or x-ray diffraction. Annealing also caused changes in the electrical behavior of Pd Schottky contacts on n-type GaN. (Schmitz et al., 1996a) The barrier height increased after annealing at temperatures above 300°C, however the interactions at the interface were not characterized

Ion bombardment also appears to have an affect on the electrical properties of the contact. Ping *et al.* (Ping et al., 1995) have found that reactive ion etching (RIE) prior to metal deposition creates damage which is detrimental to Schottky barrier formation. When the plasma bias exceeded 150 V or 0.3 W/cm², the ideality factor of a Pd/n-GaN barrier began to increase and the barrier height began to decrease. Even higher plasma voltages caused larger ideality factors and smaller barriers. Fan *et al.* (Fan et al., 1996) have observed that by reactive ion etching the substrate prior to deposition of Ti multilayer contacts, the contact resistance is 2-5 times lower. Indeed, all of the reported very low resistance Ti-based contacts were fabricated using a RIE etch step. (Guo et al., 1996a; Lin et al., 1994; Wu et al., 1995) It is speculated that the RIE process preferentially etches the N, leaving a highly N deficient layer at the surface of the GaN. These N vacancies act as donors and provide a highly doped layer at the interface which allows for the formation of an electron tunneling contact.

This effect has been observed for Schottky contacts on GaAs. The sputtering depletes the surface of As and generates a damaged n-type surface layer. (Wang and Holloway, 1984) This is further supported by the formation of Ohmic contacts on annealed GaN. (Lester et al., 1996) Lester *et al.* have determined that low resistance contacts can be formed simply by pre-annealing the GaN at 1120°C. It is believed that at this temperature the GaN begins to decompose and N vacancies are generated in the surface layer. (Vartuli et al., 1996) A Ti/Al contact deposited on unannealed GaN had rectifying characteristics, while the same contact deposited on annealed GaN had a contact resistance of only $1.3 \times 10^{-3} \Omega \text{cm}^2$.

Further evidence for the effect of surface damage comes from the typically poor behavior of Schottky diodes deposited by sputtering. Most reports of sputtered contacts indicate that the sputtered contact is either Ohmic or a leaky diode in the as-deposited state. (Cordes and Chang, 1997; Ingerly et al., 1997; Luther et al., 1997; Miller and Holloway, 1996) Studies by Hirsch (Hirsch, 1997) showed that deposition by sputtering resulted in a Ohmic contact. Figure 2.18 shows I-V curves for two Pd diodes on n-GaN. Both diodes were chemically cleaned in the same manner then the Pd was deposited either by sputtering or by evaporation. The sputtered Pd contact was also backspattered prior to metal deposition using the parameters given in chapter 4. The linear dotted line was obtained by measuring between two Pd contacts, while the solid line was measured with one Pd contact and one Al contact. The evaporated Pd contact (solid line) clearly shows diode behavior with very low leakage current in the reverse direction.

Figure 2.18: I-V curves for sputtered and evaporated Pd contacts on GaN. The dotted line in the inset graph represents the sputtered contacts.

Very low contact resistances are obtained for Ti based contacts on RIE etched GaN in the as-deposited state. However, the lowest contact resistance is obtained after annealing at 900°C for 30 seconds. (Fan et al., 1996) It has been observed that annealing at this temperature results in the formation of a TiN layer at the interface of the Ti and GaN. (Cordes and Chang, 1997; Ruvimov et al., 1996b) It is believed that the formation of the TiN layer removes N from the GaN, thus increasing the level of doping near the interface and improving the tunneling behavior. Contact resistances as low as $10^{-7} \Omega\text{cm}^2$ have been

reported. (Fan et al., 1996) This is the lowest contact resistance currently reported. Thus the combination of RIE etch and TiN formation gives very good Ohmic contacts on n-GaN.

Ohmic contacts have also been formed using highly doped ($>10^{18} \text{ cm}^{-3}$) n- and p-type GaN. (Mori et al., 1996; Smith et al., 1995) The low resistance of these contacts is most likely due to tunneling. Ohmic contacts on 10^{18} cm^{-3} n-type GaN were formed by Al, Ti, and TiN and had resistances between $650 \Omega\text{cm}^2$ for as-deposited Ti and $9.9 \times 10^{-3} \Omega\text{cm}^2$ for annealed Ti contacts. The contacts on 10^{18} cm^{-3} p-type GaN were formed by Au or a Au/Mg/Au multilayer and had contact resistances between 53 and $214 \Omega\text{cm}^2$. Cole *et al.* (Cole et al., 1996) found contact resistances as low as $8 \times 10^{-5} \Omega\text{cm}^2$ for sputtered W on 10^{18} cm^{-3} n-type GaN. The contacts were always Ohmic, however this low value of contact resistance was obtained after annealing at 600°C for 1 minute. This annealing resulted in the formation of W_2N at the interface. They attribute the low contact resistance to the new phase formation, however the high doping and sputter damage at the interface make an exact determination difficult.

Mori *et al.* (Mori et al., 1996) measured the contact resistances of Pt, Ni, Au and Ti on p-type GaN doped with Mg to a concentration of 10^{20} cm^{-3} . The resulting carrier concentration was not specified. They found all four metals to have contact resistances in the range of $0.025 \pm 0.01 \Omega\text{cm}^2$. These contact resistances are much too high to act as good Ohmic contacts for devices. Lin *et al.* have obtained contact resistances as low as $6 \times 10^{-5} \Omega\text{cm}^2$ using an InN/GaN superlattice to contact to n-GaN. The thermal stability of this contact has not been explored. The use of Ni, Pd, and Cr as contacts to p-type GaN

has also been investigated. (Trexler et al., 1996) All three metals were deposited on $9.8 \times 10^{16} \text{ cm}^{-3}$ p-type GaN and were capped with Au. Trexler *et al.* found that the contacts were rectifying in the as-deposited state but became increasingly Ohmic with annealing. The lowest contact resistance obtained was for the Cr/Au contact and was $4.3 \times 10^{-1} \Omega \text{cm}^2$. They have observed the formation of a Cr:N phase and a Au:Ga phase at the interface. The reaction may result in the formation of the good Ohmic contact, while the formation of both N and Ga phases may prevent the formation of N vacancies near the GaN surface.

The studies of Schottky barriers of various metals on GaN have shown that the Fermi level is not pinned at the interface, however the variation in barrier height is not as great as that predicted by Kurtin. This may be explained by our greater understanding of the definition of ionicity. There are, however, a number of questions which remain to be answered. The effects of surface damage on contact electrical properties has not been clearly identified nor have good Ohmic contacts been developed for p-type GaN. It appears that the Ti/Al contacts can provide good Ohmic behavior on n-type GaN. A greater understanding of the thermal stability of elemental metals on GaN may lead to an ability to engineer a good Ohmic contact to p-type GaN.

3. Metal/Ceramic interfaces

The behavior of metal/ceramic interfaces subject to annealing tends to be much different from the behavior observed at metal/semiconductor interfaces. As described in the previous chapter, metal thin films tend to react with semiconductor materials to form new phases, however most metals do not react with, and usually have poor adhesion to, ceramic materials. Ceramics are generally considered to be stronger, more refractory, and have a greater ionic character to their bonding than either metals or semiconductors. (Nicholas and Mortimer, 1985) They also tend to be less reactive and less thermally and electrically conductive. There have been many studies of the properties and optimization of metal/ceramic interfaces because of the wide variety of applications for ceramics from integrated circuit packaging to rotors and spark plugs. Several excellent reviews of metal/ceramic joining have been published, for example see (Kumar and Greenhut, 1991; Nicholas, 1990; Nicholas and Mortimer, 1985). This chapter will focus on the behavior observed at metal/ceramic interfaces which is typically not seen in metal/semiconductor systems. This includes surface energy and thermal expansion mismatch, which are observed in the metal/GaN system. The chapter will conclude with a discussion of the typical approach used for bonding metals to ceramics and how this can be applied to the GaN system.

3.1 Surface energy mismatch

Every solid and liquid is characterized by a surface energy due to the discontinuity of the bonding at the surface. This is really an interfacial energy as the surface is an interface

between solid and vapor, solid and liquid, or liquid and vapor. The surface energy can be defined as the energy required to form a new unit area of surface and a simple estimation of this energy can be made by calculating the energy required to break the bonds and rearrange the atoms at the surface. (Adamson, 1990) Because it depends on the number of bonds broken, the surface energy will be different for different crystallographic planes of a crystalline solid. In addition, the surface energy varies with the type of bonding. In general, the more ionic the bonding the lower the surface energy. (Naidich, 1981; Nicholas and Mortimer, 1985) Table 3.1 gives values of the surface energy at a specific temperature for a number of different materials. It has a slight dependence on temperature due to entropy effects. Surface energy is also often described by the term surface tension. The two terms are often used interchangeably and have the same units, although surface energy

	Surface Energy (ergs/cm ²)	Temperature (°C)
Al ₂ O ₃	905	1850
TiC	1190	1100
Ni	1778	1454
Pt	1800	1769

Table 3.1: Surface energies of various materials at specific temperatures.

is usually expressed in the dimensions of energy/area and surface tension in the dimensions of force/length.

The most common method to measure the surface energy of a solid is to put a sessile drop of a liquid with a known surface energy on it, as shown in figure 3.1 By measuring

the contact angle, θ , between the liquid and solid, and utilizing the Young equation (equation 3.1), the difference between the solid-vapor and solid-liquid surface tensions can be determined. The Young equation is simply a balance of the forces at the liquid, vapor, and solid contact point.

Figure 3.1: Definition of the contact angle.

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (3.1)$$

In this equation γ is the surface tension, while the subscripts refer to the interface: l, liquid; s, solid; and v, vapor. Three regimes of behavior are defined based on the value of θ .

$\theta > 90$	nonwetting
$\theta < 90$	wetting
$\theta = 0$	spreading

Nonwetting behavior indicates that the liquid will agglomerate on the surface. This is because the surface energy of the drop plus the interfacial energy between the drop and

solid is larger than the surface energy of the solid/vapor interface. The system wants to minimize its total energy so the high surface energy material (liquid) agglomerates into a drop exposing more of the low energy solid/vapor interface. If the surface energy of the drop plus the solid/liquid interfacial energy is less than the energy of the solid/vapor interface the liquid will want to spread out and maximize its surface area while minimizing the area of the solid/vapor interface. Spreading is a special case of wetting and is undesirable because it results in excessive flow on the surface.

Nonwetting behavior is very typical for liquid metals on ceramics, because liquid metals tend to have much higher surface energies than ceramics. This type of behavior is also observed after annealing metal thin films on ceramics. If the annealing temperature is high enough the metal atoms have sufficient mobility to agglomerate and decrease the interfacial energy. (Maskell et al., 1987) Surface diffusion can occur at temperatures as low as $0.3T_{\text{melt}}$. (Ohring, 1992) Figure 3.2 shows an example of Pt island formation on a ceramic substrate. The observation of this behavior gives a clear indication that the film has a higher surface energy than the substrate. This dewetting behavior is clearly undesirable for metal/ceramic joining applications where agglomeration may cause voids in the bond and decrease adhesion. This is also detrimental for metal/semiconductor contacts because of deleterious effects on electrical properties. Agglomeration can easily result in metal films which are no longer continuous and thus do not electrically conduct.

Figure 3.2: Scanning electron micrograph of a sputtered 100 nm Pt film on a zirconia substrate after annealing for 4 days at 700°C. (Maskell et al., 1987)

3.2 Thermal expansion mismatch

Another common problem at metal/ceramic interfaces results from the difference in thermal expansion coefficients (α) between the metal and the ceramic. Table 3.2 shows a comparison of the coefficient of linear thermal expansion for metals and ceramics. The linear thermal expansion coefficient is given in units of strain per degree Celsius, and is a measure of how much a material will expand upon heating. Note that most metals, with the exception of the refractory metals, have much larger thermal expansion coefficients than the ceramics. Since α is much larger for metals, a metal thin film on a ceramic substrate will want to expand more than the ceramic substrate, however the metal film will be constrained by the substrate and a compressive stress will be generated in the metal.

If the compressive stress generated is large enough, the metal may fail and delaminate from the substrate. This behavior is called spalling and an example is shown in figure 3.3. If the metal film was in tension, film cracking would be expected.

	α ($\times 10^6$ cm/cm $^{\circ}\text{C}$)	E (GPa)
Ni	13.3	206.9
Pd	11.7	112.4
Pt	8.9	146.9
Ti	8.4	115.8
Al ₂ O ₃	8	-
ZnSe	7.7	-
Ta	6.5	186.2
GaAs	6.9	-
GaN	6	-
AlN	5	-
Si	5	-

Table 3.2: Linear thermal expansion coefficients for various materials and elastic modulus, E, for metals. (Brandes and Brook, 1992)

Figure 3.3: SEM image of a Ti film grown at 973K in the c-axis orientation on sapphire.
(Peddada et al., 1990)

The differential thermal strain generated can be calculated simply by multiplying the difference in thermal expansion coefficients, $\Delta\alpha$, by the difference in temperature, ΔT , as shown in equation 3.2.

$$\Delta\varepsilon = \Delta\alpha * \Delta T \quad (3.2)$$

Thus the strain generated is a function both of the thermal expansion coefficient mismatch and the temperature change. Note that this is a differential strain, since the initial strain state of the metal film is unknown. Some sources claim sputtered films tend to be under compressive stress (Westwood, 1988), while others claim an initial tensile stress state. (Thorton and Hoffman, 1989) It is clear from table 3.2 that while the thermal mismatch

between the near noble metals and GaN is rather large, it is even larger between these metals and other semiconductors, such as Si. Although the thermal mismatch between Si and the near noble metals is larger, thermally generated compressive stress is a much smaller problem because the systems are not heated to high temperatures. Because of the thermal stability of GaN and other ceramics, processing and operating temperatures can be very high. The large temperature difference between the metal deposition temperature and the annealing temperature then generates a large compressive strain in the metal film.

When determining whether the generated strain will result in compressive failure, the stress generated and the strength of the metal and the metal/GaN interface must be considered. The change in stress can be calculated by multiplying the change in strain by the elastic modulus, E , of the metal, and dividing by Poisson's ratio, ν , as shown in equation 3.3.

$$\Delta\sigma = \frac{E}{1-\nu} \times \Delta\varepsilon \quad (3.3)$$

Table 3.2 gives values of the elastic modulus for various metals. Poisson's ratio is usually around 0.3 for metals. The exact values are given in appendix A. Obviously, the largest amount of stress will be generated in a Ni thin film, since it has the largest elastic modulus. To determine whether the stress generated is likely to cause failure, the stress must be compared to the failure limit of the metal. Unfortunately, there is little data available on strengths of metals under compression, the values available are for the ultimate tensile strength. These values can still be used for comparison and are given in table 3.3. A range of values is given for each metal, because the measured tensile strength depends on

how the metal was prepared and tensile strengths for sputter deposited metal films are not available. It is clear from this table that while Ni will have a large stress generated because of its large elastic modulus, failure may not occur because of the strength of the material. Pt and Pd, however, while having low elastic moduli also have low ultimate tensile strengths, thus being more prone to failure.

	Ni	Pd	Pt	Ti	Ta
Ultimate Tensile Strength (MPa)	310-600	140-195	125-145	240-700	205-485

Table 3.3: Ultimate tensile strength of various metals. (Brandes and Brook, 1992)

This behavior is detrimental to metal/semiconductor contacts because of the possible catastrophic mechanical failure of the contact as well as degradation of electrical conductivity. To minimize this, metals and substrates with similar coefficients of thermal expansion or high strength must be used. GaN has a thermal expansion coefficient of 6×10^{-6} cm/cm°C, metals with similar expansion coefficients include Ta (6.5×10^{-6} cm/cm°C) and Mo (5.1×10^{-6} cm/cm°C).

3.3 Typical approaches to bonding metals and ceramics

One of the most common bonding methods is brazing. This involves putting a thin metal film on the ceramic and heating. The bonding can be caused by interdiffusion or by actual reaction at the interface. Bonding of metals to sapphire has been extensively

studied and recently there have been a number of studies on bonding metals to AlN. (Brow et al., 1991; Carter and Papageorge, 1992; He et al., 1996; Westwood and Notis, 19) Several issues must be considered when determining which metals will form good bonds, including the two discussed in the prior sections. A metal with a similar coefficient of expansion is desired in order to avoid compressive stress failure in the metal film, or cracks in the ceramic caused by tensile stresses. In addition, the metal should wet the ceramic surface, so that continuous coverage is obtained. It has been observed that if the metal has a strong affinity for bonding with one of the two elements of the ceramic, it is more likely to wet. (Nicholas and Mortimer, 1985) This is attributed to bonding occurring at the interface of the metal and ceramic. Interfacial reactions and new phase formation at the interface can also lead to better wetting.

The formation of an interfacial reaction product could lead to a lower interfacial energy than between the ceramic and the elemental metal. The driving force for reaction in an interfacial system is the decrease of the total energy, therefore the decrease of interfacial energy due to new phase formation can be an additional driving force for reaction in the system. If the interfacial reaction has a large enough negative free energy, the formation of the new phase may be more advantageous than agglomeration of the metal on the ceramic. Most brazing is done with a metal alloy which includes an active metal. An active metal is one which is capable of changing the ceramic surface chemistry and enhances the ability of the alloy to wet and bond to the ceramic. (Nicholas and Mortimer, 1985) The metal may just form a bond with one of the ceramic elements or it may react to form a new phase. Ti is a very commonly used metal, both on Al_2O_3 and AlN. Several

authors have reported that Ti forms TiN at the AlN/Ti interface at temperatures as low as 300°C. (Carter and Papageorge, 1992; He et al., 1996; Westwood and Notis, 19) When Ti is one of the elements in a metal alloy, wetting of the ceramic is enhanced and segregation of Ti to the interface is observed. (Brow et al., 1991) Other examples of metals which are termed active and have been observed to enhance wettability of Al₂O₃ are niobium, tantalum, chromium, and zirconium. (Nicholas and Mortimer, 1985)

Since chemical reaction is an effective means to improve wettability and adhesion, it is desirable to predict which metals will react on the substrate. Some guidance can be obtained from equilibrium thermodynamic data. The Gibbs free energy of the reaction can be calculated using equation 3.4 and tabulated thermodynamic data. (Kubaschewski et al., 1993)

$$\Delta G = \Delta H_{298} - T\Delta S_{298} \quad (3.4)$$

This calculation is an estimate because it ignores the temperature dependence of the enthalpy and entropy. The tabulated thermodynamic data gives ΔH_{298} , the standard enthalpy, or heat, of formation, and the standard entropy, S_{298} , of each substance. ΔS_{298} , the change in entropy for the reaction, can be calculated from the standard entropies with a knowledge of the chemical reaction. For example, if

the change in entropy equals the standard entropy of the product minus the standard entropies of the reactants.

$$\Delta S_{298} = 2S_{MN} - (2S_M + S_{N_2})$$

Figure 3.4: Gibbs free energy of formation for various nitrides.

Figure 3.4 gives a graphical comparison of the heats of formation for several nitrides. This type of diagram is called an Ellingham diagram. It provides a quick visual method for determining the relative stability of nitrides. Any nitride can be reduced by any metal whose nitride is lower in the diagram. For example, the free energy of ZrN is much lower than that of TaN, this indicates that at a Zr/TaN interface the Zr would react to form ZrN and Ta. From this diagram we observe that any of these metals should react with GaN over this range of temperatures. Not included in this diagram are several other metal

nitrides whose free energies of formation are higher than GaN. These include Fe_8N , Fe_4N , Mg_3N_2 , Ni_3N and Ca_3N_2 . This type of diagram has proven useful for predicting which metals will react on AlN and Si_3N_4 . Indeed, Ta and Zr have been observed to react with Si_3N_4 . (Suganuma, 1990)

The equilibrium thermodynamic data can only provide a guideline for which metals may react because the actual reaction will not be in thermodynamic equilibrium and the kinetics of the reaction are unknown. The reaction will not take place if the annealing temperature does not provide enough energy for diffusion of the constituents. In addition, the accuracy of the thermodynamic data is not always known. The thermodynamic data for the formation of GaN was determined in the 1960s and 1970s (Madar et al., 1975; Munir and Searcy, 1965; Thurmond and Logan, 1972), and the quality of the GaN used in these studies may not have been equivalent to that of the material in use today. Also, GaN has been reported to have a large kinetic barrier to dissociation (Newman et al., 1993), indicating that interfacial reactions may be inhibited by kinetics. However, the thermodynamic data can provide an initial estimate of which metals are more likely to react.

4. Experimental Procedures

4.1 Surface preparation

The intention of the surface preparation procedure was to minimize contamination at the interface between the semiconductor and metal. All samples were first degreased in a sequence of solvents. They were first boiled in xylenes for three minutes, then boiled in acetone for three minutes, and finally boiled in methanol for three minutes. Samples were blown dry with N_2 . Various wet etching solutions were investigated for removing the remaining oxide on the surface. The results for the various solutions will be discussed in chapter 6. The etching mixture which left the cleanest surface was one which included HF. Some samples were cleaned in 49% HF for 30 seconds and others were subjected to a buffered oxide etch solution (BOE) for 5 minutes. BOE is composed of 6 parts (by volume) NH_4F and 1 part 49% HF. This is then diluted for etching by a ratio of 10 parts (by volume) water to 1 part BOE. Samples were then placed immediately in the metal deposition system.

Some samples were sputter etched prior to metal deposition. The experimental results section will clarify which samples were sputter etched and how that affected the reaction. Samples were sputter etched in a model 2400 Perkin-Elmer sputtering system for 6 minutes. Ar^+ ions were used with a forward power of 100 W. The 'tune' was set to 1238, the 'load' at 860, and the 'target bias' was 650 V. The 'tune' and 'load' are used to match the impedance of the substrate table system with that of the coaxial cable bringing the RF power from the generator. The 'tune' controls the capacitance in the circuit, while

the 'load' controls the coupling between the primary and secondary circuits of the network. Profilometer measurements indicated that approximately 1000Å were removed during 6 minutes of backspattering.

4.2 Metal deposition

Approximately 800Å of metal were deposited using one of two systems. Metals were either sputtered using the model 2400 Perkin-Elmer sputterer or they were evaporated using a Veeco electron beam evaporator. The parameters used for sputtering the various metals are shown in appendix C. The base pressure in the sputterer was generally 4×10^{-6} Torr after a minimum of 7 hours of pumping. The base pressure in the evaporator was generally 5×10^{-7} Torr after a minimum of 4 hours of pumping. The evaporator has a lower base pressure because the system is kept under vacuum between depositions.

4.3 Annealing

Two methods of annealing were used. For long annealing times (longer than 3 minutes) a Type 54241 Lindberg Hevi-Duty tube furnace was used. During annealing either N₂ or a mixture of 96% N₂ and 4% H₂ flowed through the furnace. The N₂-H₂ mixture is also called forming gas. It is used to minimize the formation of oxides during annealing. When annealing, the furnace was allowed to reach the specified temperature and then the sample, in a quartz holder, was inserted. The temperature would oscillate for a few minutes and then restabilize. At the end of the annealing period, the samples were placed at the end of the annealing tube, which was at room temperature. They were cooled in the flowing gas for approximately ten minutes.

For short annealing times a Heatpulse 210 rapid thermal annealer by AG Associates was used. This system allows a sample to be heated to high temperatures ($<1000^{\circ}\text{C}$) for short times (<3 minutes). The temperature is measured by a thermocouple embedded in a Si wafer. The sample is placed on this wafer in the quartz chamber. N_2 gas flows through the chamber to minimize oxidation. High-intensity tungsten-halogen lamps are computer controlled to heat to the desired temperature. When heating to temperatures above 800°C the system first heats the chamber to 400°C for 10 seconds. This step is intended to improve repeatability.

4.4 Characterization

Several complementary materials characterization tools were utilized to determine whether changes were occurring at the metal/semiconductor interface and what those changes were. Appendix C gives an overview of each of the techniques. This overview includes a brief description of the theory behind the method, an explanation of what information can be obtained from the technique, and a discussion of the advantages and disadvantages. An excellent resource for information on materials characterization methods is "Encyclopedia of Materials Characterization", edited by C. Brundle, C. Evans, Jr., and S. Wilson.

The two primary characterization techniques used were Rutherford backscattering spectrometry (RBS) and x-ray diffraction (XRD). These two techniques were used to first determine at what temperature the reaction began taking place. RBS provided the information on when interdiffusion began to take place in the system, while XRD gave

information on new phase and solid solution formation. Auger electron spectroscopy (AES) and scanning electron microscopy (SEM) were also used. AES can provide information on surface composition or give a depth profile of composition. SEM provides an image of the surface of the sample. While the SEM can not image the interface, it was useful in cases where delamination or agglomeration occurred. X-ray photoelectron spectroscopy (XPS) was used to determine surface composition and, in one case, to give composition information with depth. Transmission electron microscopy (TEM) was a vital part of the characterization as it was the only method to visually observe the interface. In addition, it can provide composition and phase information.

4.4.1 RBS

RBS measurements were performed with a 1.95 MeV $^4\text{He}^+$ beam with a scattering angle of 165° . The beam spot was 1 mm in diameter on the sample. A Si surface barrier detector was used with an acceptance angle of approximately 2 msr and an energy resolution of approximately 20 keV. 4 μC of charge was collected at a current of 6-10 nA. A circular shield biased to -900V surrounded the sample to suppress any secondary electrons.

4.4.2 XRD

XRD was performed with a Siemens D5000 diffractometer in both the glancing angle and θ - 2θ geometries. Cu K_α x-rays of energy 8 keV were used. Spectra were generally taken over a 2θ angular range of 30 - 80° . This range was chosen because it included the majority of the peaks of interest.

For glancing angle measurements a 3° incident angle was used. 1° and 0.3° slits were used in slots 1 and 2 at the exit of the x-ray source. This combination was found to be most sensitive to the presence of new compounds in these systems. For θ - 2θ diffraction, slits of 1° and 1° were used in slots 1 and 2 on the x-ray source and 1° and 0.1° in slots 3 and 4 on the x-ray detector. The x-ray scans were performed with a 0.1° step size and 2 seconds of data collection per step. Each scan took approximately 20 minutes to perform. This step size was small enough to resolve all peaks in the spectra.

4.4.3 AES

AES was performed with a Phi 660 scanning auger microscope with an electron beam voltage of 3 kV and an analyzer resolution of 0.6% of the peak energy. The beam current was typically near 90 nA. The sample stage was set at an angle of 50° for sputtering and data collection. A Ga^+ beam was used for sputtering with an energy of 20 keV, spot size of $1\text{ }\mu\text{m}$, and beam current of 3 nA. The sputter rate was controlled by the magnification chosen for the ion gun beam. In most cases the sputter rate chosen was approximately 100 Å per minute.

4.4.4 XPS

XPS was performed with a Phi 5300 system. A 1.1 mm diameter circular aperture and the K_α -line of a Mg x-ray source were used. A pass energy of 179 eV was used which gave an analyzer resolution of 4.5 eV. Data was acquired for 3 minutes with the detector at an angle of 15° . A 3kV Ar^+ ion gun was used to sputter the samples with a sputter rate of approximately 100 Å per minute over a 2 mm diameter area.

4.4.5 TEM

TEM was performed using a JEOL 200CX high-resolution microscope operated at 200 kV. Cross-sectional samples were prepared by gluing two one mm thick pieces face to face, followed by mechanical grinding, and finally ion milling on a liquid nitrogen cooled stage to obtain electron transparency. Energy dispersive spectroscopy (EDS) and selected area diffraction (SAD) were done in the TEM to identify composition and lattice structure, respectively. This work was done by several microscopists at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory.

5. Results and discussion

5.1 Surface Characteristics

In order to obtain accurate data on metal/semiconductor interactions and to obtain consistent reactions it is imperative that the interface be free of oxides or contaminants. Since metals could not be deposited in-situ after crystal growth in this study, chemical methods or sputtering had to be used to clean the surface prior to metal deposition. At the time that this study commenced there was little information in the literature regarding the effects of cleaning or etching on the morphology and composition of the surfaces. For this reason the surface characteristics of ZnSe and GaN were investigated as a function of cleaning method. Recently, reports have been published discussing the surface composition and morphology after cleaning. (Edwards et al., 1996; Lee et al., 1996; Liu et al., 1995; Pearton et al., 1994; Shul et al., 1996; Smith et al., 1996b) These results will be discussed and compared to the results obtained in this study. XPS measurements were performed on ZnSe and GaN surfaces prepared by a variety of methods. These measurements were intended to determine the amount of contaminants on the surface of as-grown layers and the changes after various surface treatments.

The details of the cleaning study on ZnSe can be found in (Duxstad, 1994). The results will be summarized here. Measurements were taken on as-grown, Ar⁺ sputter etched, HF etched, and K₂Cr₂O₇ etched samples. Table 5.1 shows the relative atomic concentrations of C, O, Se, and Zn on the surfaces before and after cleaning. The sample which was sputter etched for two minutes. This was followed by an in situ XPS measurement.

	As grown	Sputter Etched	5 minute air exposure	K ₂ Cr ₂ O ₇ etch	HF etch
C 1s	51.00	18.56	46.85	58.67	50.27
O 1s	17.99	2.12	6.67	7.31	13.50
Se 3d	24.09	52.04	36.44	31.58	29.41
Zn 2p3	6.92	27.28	10.05	2.44	6.82
Se:Zn	3.48	1.91	3.63	12.94	4.31

Table 5.1: Atomic concentration percentages for C, O, Se, and Zn on samples prepared with various surface treatments.

The sample was then removed to the loadlock and exposed to air for 5 minutes and remeasured. These results clearly show that sputter etching is the most effective method for removing C and O contamination. The sputtering does, however, affect the ratio of Se to Zn on the surface. It appears that Se is preferentially sputtered from the surface. Sputtering also causes some damage at the surface. The amount of damage was investigated by using channeling RBS and found to be not very significant.

A recent study by Liu *et al.* (Liu et al., 1995) also showed that HF cleaning of the ZnSe surface can reduce the O concentration. HF does not etch the ZnSe. They found that some etching mixtures, such as 1% Br in methanol or boiling NaOH left the surface with a rough morphology. Their suggestion for the best cleaning is to etch with NH₄OH/H₂O₂ followed by etching with CS₂ to remove excess Se left on the surface by the first treatment. This sequence leaves a smooth and stoichiometric surface.

Several cleaning methods for GaN were also characterized. None of the chemical cleaning steps etched the GaN, only Ar⁺ sputtering actually etched away the surface layer. Figure 5.1 shows an XPS spectra for an as-grown GaN wafer. This wafer was not etched or cleaned prior to taking this spectrum. Note that there is an obvious presence of O and

C on the surface. Both XPS and AES peaks are visible. XPS peaks are labeled with the orbital from which the electron came, while the Auger peaks are labeled with the transition type (KLL, LMM, etc.). No appreciable amount of other contaminants is observed. Note that only the C KLL Auger peak is labeled. The C 1s peak (285 eV) overlaps the Ga LMM peak (281 eV). Unfortunately, this means that a quantitative determination of the amount of C on the surface is not possible because the sensitivity factor for the C Auger peak is not known.

Figure 5.1: XPS spectrum of an as-grown GaN surface.

Figure 5.2 shows XPS spectra for GaN samples which were treated with two different etching solutions. Both wafers were first cleaned in a sequence of solvents, as described in chapter 4. One was etched for 30 seconds in 49% HF, the other was etched for 30 seconds in HCl. Both samples were rinsed in distilled water and blown dry with N₂. The spectra were taken after the samples had been in air for approximately 30 minutes.

The O and C peak heights on the HCl etched sample are approximately the same as that observed on the as-grown sample. Atomic concentration percentages are given in table 5.2. The O concentration is decreased only slightly by the HCl etch. A comparison of the C KLL peaks also shows that there is little decrease in C contamination on the surface. The HCl etch does cause the surface to become less Ga rich. After the HCl etch a small amount of Cl can be detected on the surface as indicated by the presence of the Cl LMM Auger peak in figure 5.2a. The C concentration is not calculated because the Cls XPS peaks are overlapped by Ga Auger peaks.

	As grown	In-situ		HCl etch	Ex-situ HF etch	BOE etch
		1 min. Ar ⁺ sputter	2 min. Ar ⁺ sputter			
N	22.69	44.8	46.17	33.8	29.26	21.8
O	19.80	10.19	3.99	19.6	11.78	19.7
Ga	57.51	45.01	49.83	46.7	58.96	58.5
Ga:N	2.53	1.00	1.08	1.38	2.02	2.69

Table 5.2: Atomic concentration percentages for N, O, and Ga on samples prepared with various surface treatments.

The HF etching solution (figure 5.2b) and the buffered oxide etching mixture (BOE) (table 5.2) significantly decrease the percentage of O on the surface. BOE is a mixture of 1 part (by volume) HF and 6 parts NH₃F. This is then diluted for etching by a ratio of 10 parts (by volume) water to 1 part BOE. The HF and BOE etching solutions remove almost as much O from the surface as sputtering. They do not, however, remove a significant amount of C. The C KLL peak is still clearly visible in the spectrum. In addition, etching leaves some F bonded on the surface. In the spectrum for the HF etched

sample (figure 5.2b) the F KLL Auger peak is visible at 600 eV. On the BOE etched sample the F 1s XPS peak is also visible. This indicates that some bonds on the surface may be passivated by F. This wet etching removes more O than etching with HCl, but still does not remove much C. Smith *et al.* (Smith et al., 1996b) also found that HCl and HF etching solutions were able to remove some O and C from the surface, but could not leave the surface free of O and C contamination.

Figure 5.3: XPS spectrum of a GaN surface after two minutes of Ar^+ sputtering.

Figure 5.3 shows a spectrum of a sample which was Ar^+ sputtered for two minutes. The sample was sputtered using the parameters given in chapter 5. This sputtering cycle should have removed approximately 200 Å of GaN. Sputter etching significantly reduced the amount of O and C contamination on the surface. The O AES peak is no longer visible, and the O XPS peak is almost unidentifiable. In addition the C Auger peak has also disappeared. Ar^+ sputtering appears to be the preferred method for removing

contaminants from the surface. Note that there is very little change in the atomic concentrations between the sample sputtered for one minute and the sample sputtered for two minutes. Most of the contamination is removed within one minute of sputtering.

A detrimental aspect of sputtering is that it can cause damage to the surface. The amount of damage after sputtering can be investigated using channeling RBS. When the incident ion is aligned with a channel in a perfect crystal very few ions will be backscattered. A comparison of the number of ions backscattered from a channel gives an indication of the degree of perfection of the crystal. Figure 5.4 shows 1.8 MeV RBS channeling results in a random direction and along the $\langle 0001 \rangle$ direction. The figure shows the random spectrum as well as channeled spectra for as-grown and sputtered samples. The sample was sputtered at room temperature using the Perkin-Elmer sputtering system with the parameters given in chapter 4. The signal for the backspattered sample increases only slightly, indicating very little damage at the surface. The small peak at 1.55 MeV is due to Pd contamination on the surface. This contamination came from backspattering off the sample holder in the chamber. This can be reduced by careful mounting of the sample and use of clean sample holders.

Figure 5.4: 1.8 MeV RBS channeling experiments on as-grown and Ar^+ sputtered GaN.

The use of Ar^+ sputtering provides a good method for removing contamination from the GaN surface without creating significant structural damage. This cleaning method does affect the ratio of Ga to N on the surface of the sample. Table 5.2 gives the Ga to N ratios. The Ga:N ratio decreases significantly after sputtering, with the surface becoming less Ga rich and approaching a 1 to 1 ratio of Ga to N. This is surprising since it has been speculated that N should be preferentially sputtered from the surface. (Lin et al., 1994) Preferential sputtering is common for compound materials and in most III-V semiconductors the group V element (As, P, etc.) is preferentially sputtered. (Pearton et

al., 1990; Wang and Holloway, 1984) It appears, however, that GaN behaves differently. Pearton *et al.* (Pearton et al., 1994) have also observed that N is not preferentially sputtered by Ar⁺. Their measurements were done using AES. Pearton and Lee (Lee et al., 1996) also report that sputtering does not increase the average surface roughness of the GaN.

The affect of annealing on the bare GaN surface was also investigated. Vartuli *et al.* showed that after annealing for 10 seconds at 1000°C in N₂, N was lost from the surface of the GaN. If the GaN begins to decompose at the temperatures used for annealing, this will affect the reactions at the interface. Possible surface decomposition was investigated after annealing at 800°C for 2 hours. 800°C was chosen because it was the highest temperature used in the study. The annealing was not done in-situ.

	as-deposited	annealed
C 1s	13.34	17.80
N 1s	67.51	41.07
O 1s	7.05	24.98
Ga 2p3	12.11	16.15
Ga:N	0.18	0.39

Table 5.3: Atomic concentration percentages for various elements on the surface of as-deposited GaN and GaN annealed at 800°C for 2 hours in flowing N₂.

As-deposited and annealed samples were then analyzed using XPS. Table 5.3 shows the change in atomic concentration percentages after annealing. A significant increase in the O and C concentrations on the annealed surface indicates increased contamination and possibly increased oxide growth on the surface. Note that the C 1s peak is overlapped by a Ga LMM, thus some of the calculated increase in C concentration may be due to the

increase in Ga concentration after annealing. The ratio of Ga to N on the surface also doubled. This may indicate some loss of N from the surface. Ga particles on the surface, however, were not observed using SEM. This indicates that the surface stoichiometry change was not too radical. Surface decomposition should be even less when the surface is covered with an approximately 800 Å thick layer of metal.

Of the wet etches studied, the HF and BOE etches removed the most contamination from the GaN surface. The most complete cleaning was obtained by Ar⁺ sputtering. Since the cleanliness of the interface is crucial for consistent reactions, almost all GaN samples in the study were backspattered prior to metal deposition. The ZnSe samples were backspattered prior to deposition of Pt and Ni. The Pd reaction occurs only if the sample is treated with just an HF etch. This may be because there is a difference in the ratio of Se to Zn on the surface. An HF etch leaves a higher percentage of Se on the surface than the sputtering and the Pd may react more strongly on a Se terminated surface.

5.2 Structural behavior of Pt, Pd, and Ni on ZnSe

5.2.1 Results

Pd/ZnSe

As-deposited Pd was first seen to react after annealing for 10 minutes at 200°C, which is higher than the reaction temperature of Pd on GaAs, Si, or Ge. The reaction on ZnSe progresses quickly and after 30 minutes of annealing a 940 Å thick Pd layer has completely reacted. Figure 5.5 shows RBS spectra from samples annealed at 200°C for 10 and 30 minutes compared to the as-deposited spectrum with an initial Pd thickness of

1040Å. A second sample with an initial Pd thickness of 940Å and annealed for 30 minutes is also shown. From these spectra it is clear that interdiffusion takes place between the Pd and ZnSe. After annealing for 10 minutes a small peak at the surface in the Pd signal indicates that not all of the Pd has fully reacted.

Figure 5.5: RBS spectra of Pd/ZnSe annealed for various times at 200°C with different as-deposited Pd thicknesses.

After 30 minutes of annealing, a uniform Pd signal is observed indicating that all of the Pd film may be reacted with the ZnSe and the concentration of Pd throughout the reacted layer is uniform. Two different peak heights are observed after 30 minutes of annealing depending on the initial Pd thickness. This indicates that some of the Pd remains unreacted

in the thicker layer or there is a variation in composition in the reacted layer. If we assume that a ternary phase is forming, as in the Pd/GaAs system, a Pd-ZnSe ternary phase would have a nominal composition range of $\text{Pd}_{5+x}\text{ZnSe}$, with $x \approx \pm 1$. The formation of a ternary phase with variable composition is comparable to the formation of variable composition, ternary phases in the Pd/GaAs (Kuan et al., 1985; Sands et al., 1987a) and Pd/InP (Caron-Popowich et al., 1988) systems. It is not possible, based on the RBS data alone, to rule out the presence of binary phases.

Figure 5.6: X-ray spectra of Pd/ZnSe for as-deposited samples and samples annealed for various times at 200°C.

The θ -2 θ x-ray spectra in figure 5.6 provide crystallographic information on the Pd/ZnSe reaction. After annealing for 10 minutes at 200°C, three new peaks have appeared and the intensity of the Pd diffraction peaks has decreased substantially. This is in agreement with the RBS spectrum in figure 5.5 which shows a partially reacted Pd film. After 30 minutes annealing, the new peaks have more than doubled in intensity while the Pd peaks are no longer observable. The diffraction peaks from the reacted phase were not observed in XRD taken in the fixed glancing angle geometry, indicating that the reacted phase is epitaxial or well-textured with the substrate. Figure 5.7 shows a wide angle scan of the observed sequence of peaks. The presence of the sequence of high intensity (00l) peaks also indicates that this phase is highly textured. Peaks for most other planes are not observable in the θ -2 θ geometry, because the ternary phase is oriented. The observed intense diffraction peaks correspond to calculated (00l) peaks of the ternary $\text{Pd}_{5+x}\text{ZnSe}$ phase. Table 5.3 gives the measured and calculated lattice spacings for the observed peaks. This tetragonal phase was previously observed with $a = 0.3952$ nm and $c = 0.6914$ nm and a composition of $\text{Pd}_{5.14}\text{ZnSe}$. (El-Boragy and Schubert, 1970) This identification is corroborated by selected area diffraction from TEM analysis. Pd also reacts to form a ternary, oriented phase on GaAs at temperatures below 250°C. (Kuan et al., 1985; Sands et al., 1987a; Yu et al., 1986) Pd_2Si also forms with an epitaxial relationship after the reaction of Pd on Si. (Buckley and Moss, 1972)

Figure 5.7: Wide range θ - 2θ scan of Pd/ZnSe sample annealed at 200°C for 4 hours and 40 minutes. Labels give (hkl) values for $\text{Pd}_{5+x}\text{ZnSe}$.

<i>hkl</i>	<i>d</i> (Å)		Relative intensity (measured)
	Calculated	Measured	
(001)	6.914	6.896	16
(002)	3.457	3.450	89
(003)	2.305	2.304	79
(004)	1.729	1.727	100
(040)	0.988	0.988	4
(141)	0.949	0.947	11

Table 5.3: Summary of measured and calculated lattice spacings (*d*) for $\text{Pd}_{5+x}\text{ZnSe}$.

The existence of the epitaxial ternary phase is substantiated by selected area diffraction in transmission electron microscopy (TEM), presented in figure 5.8d. Diffraction spots due to reflections from the ZnSe [110] zone axis are marked by black dots, while the principal reflections from the $\text{Pd}_{5+x}\text{ZnSe}$ [100] zone axis are indicated by lines. The

orientational relationship between the two crystals is determined to be: $\text{ZnSe}[110] // \text{Pd}_{5+x}\text{ZnSe}[100]$ and $\text{ZnSe}(002) // \text{Pd}_{5+x}\text{ZnSe}(001)$. This diffraction pattern reveals that the $\text{Pd}_{5+x}\text{ZnSe}(010)$ plane (indexed with outlined number) is parallel to $\text{ZnSe}(2\bar{2}0)$ (indexed with white number). Since the interplanar spacing of $\text{Pd}_{5+x}\text{ZnSe}(010)$ ($d_1 = 0.395$ nm) is nearly twice that of $\text{ZnSe}(2\bar{2}0)$ ($d_2 = 0.200$ nm), the lattice mismatch at the interface between $\text{Pd}_{5+x}\text{ZnSe}$ and ZnSe is quite small ($\approx 1.3\%$), which explains why $\text{Pd}_{5+x}\text{ZnSe}$ tends to grow epitaxially on the $\text{ZnSe}(001)$ substrate. TEM micrographs (figures 5.8a-c) reveal the morphology of the as-grown and reacted films. The micrographs show that the ternary phase forms in a complete layer and as the reaction proceeds the layer thickness increases and the grains become more oriented. The as-grown ZnSe surface is slightly faceted and the interface becomes smoother after the reaction occurs. The reacted layer above the ZnSe also becomes less uniform in thickness after annealing for thirty minutes.

This ternary phase remained thermally stable during annealing up to 4.5 hours at 200°C and 30 minutes at 400°C . After annealing for 30 minutes at 300 and 400°C the x-ray peaks shift to slightly smaller d values with higher temperature annealing, indicating a slight variation in composition. The thickness of the reacted layer also increases slightly compared to the annealing at 200°C . This is different from the behavior of Pd on GaAs, where a second ternary phase nucleates at grain boundaries of the first ternary phase at temperatures just above 250°C . (Sands et al., 1987a)

Figure 5.8: TEM micrographs showing the progression of phase formation at the thin film Pd/ZnSe interface, (a) Morphology of the as-deposited sample, (b) Pd_{5+x}ZnSe layer formed after annealing for 10 minutes at 200°C, (c) increase in thickness of the Pd_{5+x}ZnSe layer after annealing for 30 minutes at 200°C, (d) selected area diffraction showing orientational relationship of the reacted Pd_{5+x}ZnSe phase with the substrate, ZnSe [110]||Pd_{5+x}ZnSe[100].

RBS and XRD results show that the ternary $\text{Pd}_{5+x}\text{ZnSe}$ phase is stable up to 450°C. Above 450°C the Pd film begins to island on the surface and Pd diffuses completely through the ZnSe layer to react with the GaAs layer below. Figure 5.9 shows TEM micrographs of the microstructure after annealing at 500°C for 30 minutes. The Pd remaining at the surface of the sample has formed a Pd_7Se_4 phase, as identified by SAD and XRD. At the GaAs/ZnSe interface large precipitates have formed which are a Pd-Ga phase. In some locations large reacted areas, such as shown in figure 5.9b, are observed. These areas contain Pd, Zn, Se, Ga, and As, and are not a single phase, but a mixture of several phases comprised of these elements. The exact phases present have not yet been identified.

Figure 5.9: TEM micrographs showing interface deterioration after annealing at 500°C for 30 minutes. (a) Pd-Ga precipitates at ZnSe/GaAs interface, (b) large reacted area at ZnSe/GaAs interface.

Pt/ZnSe

In the Pt/ZnSe system no significant reaction or interdiffusion is seen by RBS or XRD, until it is annealed at temperatures of 550°C or above. Pt agglomerates on the ZnSe surface after annealing at 450°C for 72 hours, but again there is no new phase formation detectable by RBS or XRD. Cross-sectional TEM analysis indicates that there is a small amount of interdiffusion and very small precipitates of a new phase after annealing at

450°C. The first evidence of phase formation by RBS and XRD occurs after annealing at 575°C. Figure 5.10 shows RBS spectra for Pt films annealed at 575°C for 10 and 30 minutes compared to the as-deposited spectrum. After 10 minutes some Zn has diffused through the Pt layer and after annealing for 30 minutes the Zn concentration has increased further. Using RUMP, an RBS simulation program, (Doolittle, 1986) the concentration of Zn in the Pt is estimated to be 20% after annealing for 30 minutes at 575°C. Although there is a significant amount of Zn in the layer, no Zn-Pt compound can be identified by XRD. There may be little driving force for phase formation because Zn is soluble in Pt up to 20%.

Figure 5.10: RBS spectra of Pt on ZnSe annealed at 575°C and 650°C for various times.

There is no in-diffusion of Pt to the ZnSe/GaAs interface, as in the case of Pd. The Pt diffraction peaks do shift to lower d values after annealing indicating a decrease in the lattice parameter of 0.017 Å. The formation of a solid solution of Pt:Zn with the smaller Zn atoms substituting for the Pt can contribute to such a decrease in lattice parameter. The Pt diffraction peaks also become narrower indicating grain growth in the film or a reduction of inhomogeneous strain in the layer. Most of the narrowing occurs in the first 10 minutes of annealing. SAD verifies that no Zn-Pt compounds form.

After annealing for 30 minutes at 575°C, RBS shows that the onset of the Pt peak has moved to a slightly lower energy. RUMP simulation shows that this is due to an approximately 50 Å layer of Zn which accumulates on the surface, thus showing that Zn is the main diffusing species during the reaction. The RBS spectrum of the sample annealed at 650°C gives further evidence that Zn is diffusing to the surface. In this spectrum we clearly see that the onset of the Pt peak occurs at a lower energy and there is large peak indicating the presence of Zn at the surface of the sample.

While no Pt-Zn phases are detected, a binary Pt-Se phase does form. XRD identifies the presence of the Pt_5Se_4 phase as shown in figure 5.11. Pt_5Se_4 is a monoclinic phase with $a=6.577$ Å, $b=4.610$ Å, $c=11.122$ Å, and $\beta=101.59^\circ$. After annealing for 10 minutes, the (302) peak appears at $2\theta = 48.5^\circ$. After 30 minutes, the (123) peak at $2\theta= 50.5^\circ$ appears and the intensity of the (302) peak increases. There is also a decrease in the Pt peak heights, indicating that Pt has been consumed in the reaction. The small intensity and different orientations of the Pt_5Se_4 peaks indicate that the phase is not epitaxially oriented with the substrate.

Figure 5.11: X-ray spectra of Pt on ZnSe for the as-deposited sample and samples annealed for various times at 575°C.

The presence of this phase is verified by SAD as shown in figure 5.12c. The particular grain chosen for SAD gives an orientational relationship with the substrate of $\text{Pt}_5\text{Se}_4[\bar{1}\bar{2}0]||\text{ZnSe}[110]$. The grains are randomly oriented with respect to the substrate. The micrograph in figure 5.12b shows that after annealing for 30 minutes the Pt_5Se_4 has formed a continuous layer, although the thickness varies between 33 nm and 73 nm. The reaction of the ZnSe with the Pt seems to affect the ZnSe layer differently than the Pd reaction. It is observed that the ion milling, which is required to form the TEM samples,

results in some voids in the ZnSe near the interface, which is the light area directly below the Pt_5Se_4 layer in figure 5.12b. This would suggest a compositional variation in the region which is related to the outdiffusion of Zn or that the reaction between Pt and Se has weakened the ZnSe layer in this region.

Figure 5.12: TEM micrographs showing progression of phase formation in Pt/ZnSe system during annealing at 575°C. (a) morphology of as-deposited Pt on ZnSe substrate, (b) Pt_5Se_4 layer formed after annealing at 575°C for 30 minutes, (c) selected area diffraction showing orientational relationship of Pt_5Se_4 grain with substrate. $\text{Pt}_5\text{Se}_4 [\bar{1}\bar{1}\bar{1}] \parallel \text{ZnSe} [110]$

Increased Zn outdiffusion and the formation of Pt-Zn phases occurs after annealing at higher temperatures. Figure 5.13 shows an XRD spectrum from a Pt film annealed at 675 °C for 30 minutes. The exact Pt-Zn phases present have not been identified as there are a number of Pt-Zn phases to which these peaks may belong. The peaks for the Pt_5Se_4 layer are no longer evident indicating that this phase no longer exists at the interface after this annealing cycle. It was not possible to perform TEM for the phase identification because the metal layer repeatedly peeled off during sample preparation. After annealing at 575°C the interface was weakened by the formation of voids. During annealing at the higher temperature the interface further deteriorates and TEM sample preparation is no longer possible.

Figure 5.13: X-ray spectra showing peaks of various Pt-Zn phases appearing in the Pt/ZnSe system after annealing at 675°C for 30 minutes.

The reaction of Pt on ZnSe is very sensitive to contaminants. Consistent reactions could not be obtained without a comprehensive cleaning. Samples which were annealed for a longer time would be less reacted than those annealed for shorter times at the same temperature. More details can be found in (Duxstad, 1994). To get consistent behavior the samples must be solvent cleaned, etched in 49% HF for 30 seconds, and backspattered with Ar^+ ions for 6 minutes. The backspattering process removes approximately 350Å of ZnSe. In addition, the Pt target was pre-sputtered for 2 minutes before deposition. This treatment cleans contaminants off the surface and reduces any contamination in the Pt film deposited from the target. The observed non-uniformity in the thickness of the Pt_5Se_4 layer may be due to the presence of residual local contaminants on the ZnSe surface which slow down or inhibit the reaction.

Ni/ZnSe

The outdiffusion of Zn and Se is the first indication of changes at the Ni/ZnSe interface observed by RBS. This occurs after annealing at 350°C for 72 hours. No changes could be detected by RBS or XRD after annealing for only 30 min. at this temperature. TEM, however, provides an indication that there is formation of up to 50Å diameter precipitates at the interface after 30 min. of annealing at 300°C. (Ruvimov et al., 1996a) Figure 5.14 shows RBS spectra of Ni thin films annealed for 30 minutes at 400° and 425°C compared to 1 hour at 450°C and an as-deposited Ni film. The initial Ni thickness was 700Å. Zn has diffused out to the surface and Se has diffused partially through the layer after annealing at 400 and 425°C. Note that after the 400°C annealing the onset of the Ni signal has been pushed back to lower energy, indicating that Zn has accumulated on the

surface of the film. There is an increase in the amount of Se in the layer after annealing at 425°C, although it has still not diffused completely through the Ni layer. This indicates that the reacted morphology is a layered structure.

Figure 5.14: RBS spectra of Ni on ZnSe annealed between 400°C and 450°C for various times.

After annealing at 425°C, new peaks are observed in XRD which correspond to a Ni-Se phase. Figure 5.15 shows XRD spectra from before and after annealing. The new peak at $2\theta=35.6^\circ$ corresponds to $d=2.52 \text{ \AA}$. The advent of this peak is coincident with that of a second peak at $2\theta=75.4^\circ$ ($d=1.26 \text{ \AA}$). This peak is not shown in the spectrum.

Figure 5.15: X-ray spectra of Ni/ZnSe for as-deposited sample and samples annealed at 425°C and 450°C.

SAD indicates that these peaks are caused by Ni-Se precipitates formed at the Ni/ZnSe interface. EDS in the TEM shows that the ratio of Ni to Se in this phase ranges from between 1 to 1.5. The XRD and SAD patterns are consistent but can not be correlated with any Ni-Se phase in the literature. This phase forms as separated grains, as shown in the TEM micrograph in figure 5.16. The grains are approximately 100 nm wide and

protrude approximately 50 nm into the ZnSe. In plan view, the diameter of the grains varies between 50 and 100 nm. This phase does not extend to the surface, which agrees with the RBS observation that Se has not diffused out to the surface. Between these grains and above them is a Ni-Zn solid solution.

Annealing at 450°C results in the observation of two new XRD peaks at $d=2.11\text{\AA}$ and $d=1.923\text{\AA}$ as seen in figure 5.15. This corresponds to the formation of NiSe. The observed peaks are the (002) and (012) peaks, respectively. The intensity of these peaks increases after annealing at 450°C for 1 hour, while the peak for the Ni_xSe ($1 < x < 1.5$) phase decreases. EDS of the TEM sample shows that the ratio of Ni to Se in this new phase ranges between 0.6 and 1. This second NiSe phase has been observed previously in a Ni-Se thin film, (Singh et al., 1978) and is cubic with $a=4.3\text{ \AA}$. Peaks for both phases are observed in samples annealed at 350°C for 72 hours with approximately equal intensities. The phase which forms initially is Ni_xSe . With longer annealing or higher temperatures the phase transforms to NiSe as more Se is incorporated into the grains. This indicates that the Ni_xSe phase may be metastable in the presence of excess Se.

Figure 5.16c shows that the NiSe phase also forms as separated grains. These grains are larger than those formed at 425°C, and have diameters in plan view between 100 and 200 nm. Above this layer of separated grains and between them there is still a solid solution of Zn in Ni and within this region are small inclusions of NiSe. The thin layer of Zn at the surface observed by RBS could not be found by TEM due to the high vapor pressure of Zn and the ion milling required for sample preparation. Careful TEM observation of a plan view specimen annealed at 425°C for 30 minutes shows that the

NiSe phase is already present in small amounts at the lower temperature. A more detailed discussion of the microstructure can be found in (Ruvimov et al., 1996a).

Figure 5.16: TEM micrographs showing the progression of phase formation in the Ni/ZnSe system during anneals at 425°C and 450°C. (a) as-deposited Ni on ZnSe, (b) grains of Ni-Se phase formed at interface after annealing at 425°C for 30 minutes, (c) grains of NiSe formed at interface after annealing at 450°C for 1 hour.

5.2.2 Discussion

The lowest initial reaction temperature of the near noble metals on ZnSe occurs for Pd which reacts at 200°C. The highest is found for Pt, which reacts at 575°C. This trend is also observed for Si and GaAs, as shown in Fig. 5.17. This figure compares the heat of vaporization of the metal to the initial reaction temperature for Si, GaAs, and ZnSe. The reaction temperature increases with the heat of vaporization of the metal, which is a measure of the binding energy between the metal atoms. This implies that more thermal energy is needed to begin the reaction when the metal is more strongly bonded. The reaction temperature also increases with the heat of formation of the semiconductor. Si has the lowest reaction temperatures and the lowest heat of formation. There are also trends regarding orientation, sensitivity to contaminants, and morphology, in the reactions of the near noble metals on Si, GaAs, and ZnSe. These will be discussed further.

Figure 5.17: Initial reaction temperature versus metal heat of vaporization for reactions of the near noble metals on Si, GaAs, and ZnSe.

Palladium

The layer of $\text{Pd}_{5+x}\text{ZnSe}$ grows very quickly in the first 10 minutes of reaction and then the growth rate slows. This is typical of a diffusion controlled reaction, which is characterized by a growth rate of the reacted layer that is proportional to the square root of time. The proportionality factor is the interdiffusion coefficient which is exponentially dependent on the activation enthalpy of the reaction. This activation enthalpy can be determined from the change in reacted layer thickness during a series of isothermal anneals. It is difficult to determine the exact layer thickness from RBS because of the compositional variation in the reacted layer, but the activation enthalpy for the reaction could be determined from a more detailed TEM study.

The reactions of Pd are characterized by oriented films which often form in a granular structure. Pd_2Si forms with an epitaxial relationship to a $\langle 111 \rangle$ Si substrate while the ternary compound on GaAs tends to form in slightly misoriented grains. (Kuan et al., 1985; Sigurd et al., 1974) $\text{Pd}_{5-x}\text{ZnSe}$ also forms in oriented grains which become more epitaxial as the reaction proceeds. Also, as on GaAs, Pd on ZnSe forms an oriented ternary compound. In the GaAs system, a second ternary phase forms when annealed at higher temperatures. This is then followed by the appearance of M_xGa_y and M_xAs_y binary phases. In the Pd/ZnSe system no second ternary phase is observed. Above 450°C the reaction is no longer controllable and Pd diffuses to the ZnSe/GaAs interface to form Pd-Ga precipitates in a non-planar reaction. Reactions of Pd metal on Si, GaAs and ZnSe, are not affected by impurities or surface cleanliness.

The initial Pd reaction, which occurs at 200°C , may be useful for electrical contacts. The reaction takes place at a low enough temperature that the electrical characteristics of the ZnSe film should not be affected. The reaction provides a planar, epitaxial interface which is desired for electrical contacts. In addition, the reaction is not very sensitive to contaminants or oxides and therefore the surface does not require special preparation, such as backspattering or in situ metal deposition. This is because the Pd is able to absorb the contaminants into the metal layer. Detailed electrical measurements are needed to determine the Schottky barrier height or contact resistivity of the ternary phase on n- and p-type ZnSe in order to develop Pd-based contacts on ZnSe. The formation of this phase is very similar to the initial formation of the ternary phase on GaAs. This ternary phase formation on GaAs has been utilized to form Ohmic contacts using solid phase epitaxial

regrowth. This process may also be useful for Ohmic contacts to p-type ZnSe using Li, for example, as a dopant.

Platinum

The reaction of Pt on both ZnSe and GaAs is characterized by the formation of a metal-anion phase at the metal/semiconductor interface and outdiffusion of the cation. (Fontaine et al., 1983) In the GaAs case the outdiffusion of Ga also results in the formation of Pt-Ga phases, but no metal-cation phases form in the ZnSe case. This may be due to the fact that the solubility of Zn in Pt is 20%. In both cases the main moving species appear to be the cation and the Pt. The cation diffuses out, while the Pt diffuses in and reacts with the anion which remains at the interface. This vertical phase stratification is expected in films which have thicknesses greater than the grain size. (Sands et al., 1987b) It is likely that the reaction will result in lateral phase separation if the thickness of the Pt layer is less than the grain size of the reacted phase.

The Pt reaction is very sensitive to contamination or oxides at the interface between the ZnSe and Pt, because Pt does not react with the contaminants. Consistent reaction behavior is obtained only if the samples are HF etched and Ar⁺ backspattered prior to deposition of the metal. An HF dip etch alone does not remove enough of the C and O from the surface of the ZnSe. X-ray photoelectron spectroscopy measurements have shown that sputtering removes more of the C and O from the surface. The variation in thickness of the Pt₅Se₄ layer is an indication that even after sputtering the surface, the reaction does not proceed at a uniform rate across the sample. This may be due to areas of contamination which remain on the surface. The reaction of Pt on ZnSe appears to be

more sensitive to contamination than the reactions on Si or GaAs. The reaction of Pt on Si is sensitive to impurities in the Pt film. (Crider and Poate, 1980) While the presence of oxygen in the Pt film was observed to change the temporal formation sequence of observed silicide phases, the reaction on GaAs is not sensitive to native oxides, (Sands et al., 1987a) but is slowed by the presence of thick oxides. (Kumar, 1975)

The reaction of Pt on ZnSe is not amenable to contact formation by alloying. The temperature for reaction is too high and will adversely affect the electrical properties of the ZnSe. In addition, although the reacted Pt_5Se_4 layer is complete, the thickness is not uniform which will lead to inconsistencies in the electrical properties.

Nickel

In the reaction on ZnSe, no ternary phase is observed, rather separated grains of a Ni-Se binary phase begin to form initially. This is in contrast to Ni on GaAs which begins with the formation of a ternary phase Ni_3GaAs , followed by the formation of laterally separated grains of binary Ni-Ga and Ni-As phases at higher temperatures. The formation of NiAs grains is observed at a slightly higher temperature in the Ni/GaAs reaction and these are also separated, but by a Ni-Ga binary phase. The reaction of Ni on ZnSe is not extremely sensitive to the surface preparation, as Ar^+ backspattering is not necessary for the new phases to form. The reactions of Ni on Si and GaAs are also not sensitive to oxides unless they are thicker than the native oxides.

This reaction is also not desired for electrical contact formation. Again the reaction temperature is too high to maintain the electrical characteristics of the ZnSe. Also, the reaction does not provide a laterally homogeneous film for a contact. The laterally

separated grains that are formed will provide contacts in parallel with areas where no phase has formed, most likely leading to inconsistent and unpredictable results.

5.3 Structural behavior of Pt, Pd, Ni, and Au on GaN

5.3.1 Results

Pt/GaN

Figure 5.18 shows RBS spectra of as-deposited and annealed Pt films on GaN. No change in the structure is observed after annealing of 30 minutes below 700°C. Between 700°C and 800°C a significant change is observed. There is an increase in signal between the Pt signal tail and the Ga edge (1.45-1.65 MeV) in the RBS spectrum. This could be interpreted by Pt indiffusion taking place. However in this case there is an alternate cause. If it were a reaction we would expect the Pt peak to widen and the onset of the Ga signal from the GaN substrate to be pushed back as GaN is consumed in the reaction. Neither of these indicators is observed. Moreover, the signal in this energy range is rather flat indicating a uniform distribution of Pt. A normal depth diffusion profile should follow an error function distribution. Therefore, these RBS spectra must be interpreted as Pt coalescing on the surface of the film through lateral surface diffusion. The formation of islands leads to much thicker metal coverage in some areas, resulting in the low signal extending beyond the main Pt peak as well as decreasing the height of the main Pt peak.

Figure 5.18: RBS spectra of Pt on GaN as-deposited and annealed for 30 minutes at various temperatures.

More of the film forms islands as the temperature increases as is indicated by the corresponding increase in the RBS signal in the 1.4-1.6 MeV range. The amount of the surface which is covered by particles can be estimated from the relative height of the main Pt signal and the signal between 1.4 and 1.6 MeV. Comparing these heights shows that approximately 4% of the surface is covered with particles after annealing at 700°C, 8.6% after 750°C, and 14% after 800°C. The agglomeration also exposes the GaN surface beneath after annealing at 800°C, which then leads to the Ga signal at 1.5 MeV indicating Ga exposed at the surface.

The lack of reaction is evident from x-ray diffraction. The x-ray spectra in Figure 5.19 show the as-deposited Pt on GaN and a sample annealed for 30 minutes at 800°C. The only new peaks observed correspond to different orientations of Pt. In the as-deposited case, the Pt is highly (111) oriented. During annealing, grain growth and reorientation occurs due to the agglomeration, which leads to the observation of x-ray peaks from many different planes.

Figure 5.19: XRD of Pt on GaN: a) annealed at 800°C for 30 minutes and b) as-deposited.

Changes in the surface morphology were observed by SEM in samples annealed at a temperature as low as 600°C. Figure 5.20 shows a sequence of SEM micrographs showing the evolution of the surface morphology. Figure 5.20a shows that the as-deposited surface is smooth and featureless. After annealing at 600°C for 30 minutes we begin to see small particles of Pt appearing on the surface of the Pt film. With further annealing (up to 90 min.) at this temperature, the surface morphology does not change significantly. The size of the Pt particles increases only slightly. Increasing the annealing temperature to 725°C brings more dramatic changes, as shown in Figure 5.20c. This surface morphology is seen after annealing for only 5 minutes at this temperature. Much larger Pt particles are observed on the surface and the remaining film between the particles coalesces and begins to reveal dark areas of GaN between the islands. This behavior becomes much more pronounced in the sample annealed at 800°C for 90 minutes (Figure 5.20d). This structure is evident after annealing for 30 minutes and remains the same for annealing times up to 150 min. This morphology coincides with the interpretation made from the RBS data. From these micrographs, we can calculate the percent of the area of surface covered by the Pt particles. The percentages determined by this method agree well with those determined by comparing the RBS signal heights.

Figure 5.20: SEM micrographs of the surface of Pt on GaN; a) as-deposited, b) annealed at 600°C for 30 minutes, c) annealed at 725°C for 30 minutes, d) annealed at 800°C for 90 minutes.

Energy dispersive spectroscopy shows clearly that the bright particles are Pt and the black areas are exposed GaN. The gray film between the Pt particles may be a thin layer of Pt over the GaN or a solid solution of Pt and Ga. Unfortunately, the atomic radii of Pt and Ga are very similar, making it difficult to determine by XRD whether a solid solution is formed. The Pt (111) peak does shift from an as-deposited value of $d=2.274\text{\AA}$ to $d=2.258\text{\AA}$ after annealing at 800°C . The bulk value for the (111) spacing is $d=2.265\text{\AA}$. This shift is significantly larger than the measurement error of the diffractometer. This indicates that the film is slightly under tension as-deposited and is either under compressive stress after annealing or it may have incorporated some Ga.

By measuring the average distance between the Pt particles we can determine the necessary surface diffusion coefficient required to obtain this morphology. The average distance between particles after annealing at 725°C for 5 min. is $2.3\text{ }\mu\text{m}$, therefore the average distance traveled by a Pt atom is half this value. Using the one dimensional, infinite source diffusion model, $x=2(Dt)^{1/2}$, D is found to be $1.1\times 10^{-11}\text{ cm}^2/\text{sec}$. The diffusion coefficient calculated from an empirical model for FCC metals, $D=0.014\exp(-6.54T_m/T)$, (Ohring, 1992) is $2.1\times 10^{-8}\text{ cm}^2/\text{sec}$. Thus the amount of observed diffusion is possible at this temperature.

The agglomeration behavior of the Pt is very different if the surface of the GaN is not backspattered prior to metal deposition. Figure 5.21 shows the change in the island structure. This structure looks very similar to the agglomeration of Pt on ZrO substrates after annealing at high temperature. An example of this behavior was shown in figure 3.2.

This change in behavior is therefore attributed to the presence of an oxide on the surface of the GaN. This oxide is removed by backsputtering.

Figure 5.21: Pt on GaN after annealing at 750°C for 30 minutes. The surface of the GaN was not backspattered prior to metal deposition.

Pd/GaN

No changes in the structure of the interface or the Pd film are observed below 700°C by RBS, as shown in Figure 5.22. Annealing at 700°C shows only a very slight thickening of the Pd film. After annealing at 725°C and above, a significant decrease in the height of the Pd peak and a large RBS signal, near 1.5 MeV, indicates the presence of Ga at the surface. This could be interpreted as phase formation, however x-ray diffraction shows no additional peaks corresponding to Pd-Ga phases below 800°C. SEM shows that instead

the GaN is exposed due to lateral inhomogeneity. Figure 5.23 shows micrographs of the as-deposited Pd surface and the surface after annealing at 725°C for 60 minutes. The morphology of the Pd film has become rougher and there are approximately 1 μm diameter areas where the Pd film has delaminated from the substrate. AES shows clearly that there is no Pd remaining on the GaN side of the fracture surface and no Ga or N exists on the exposed backside of the Pd film. Some agglomeration is also observed.

Figure 5.22: RBS spectra of Pd on GaN as-deposited and annealed for 30 minutes at various temperatures.

Figure 5.23: SEM micrographs of Pd on GaN; a) as-deposited and b) after annealing at 725°C for 60 minutes.

Delamination in thin metal films is usually attributed to compressive stress being generated due to thermal expansion. The Pd layer has a higher thermal expansion coefficient than the sapphire substrate, thus when the system is brought up to high temperatures the sapphire substrate constrains the expansion of the metal film. This generates a significant amount of compressive stress in the thin film. The stress can be calculated using the equations given in chapter 3 and causes the thin film to buckle and fail by delamination. For Pd on GaN annealed at 725°C, the differential compressive stress is approximately -791 MPa. This is significantly larger than the ultimate tensile strength for Pd which is 168 MPa and can explain the delamination failure observed.

Annealing at 800°C gives an indication of possible phase formation between Pd and Ga. Since there are no known Pd-N phases, the only reaction which can be expected is that between Pd and Ga. Also, since Pd has the lowest bond energy of the three metals, we would expect to see a reaction at a lower temperature for Pd than the other metals. Figure 5.24 shows x-ray diffraction data from a sample which was annealed at 800°C for 30 minutes. This sample also shows effects due to delamination in the RBS spectrum. There are several peaks in the XRD spectrum which can be attributed to the formation of Ga_2Pd_5 . This is an orthorhombic phase with $a=5.485 \text{ \AA}$, $b=18.396 \text{ \AA}$, and $c=4.083 \text{ \AA}$.

Figure 5.24: XRD spectrum of Pd on GaN annealed at 800°C for 30 minutes.

The peaks observed correspond to a variety of planes, indicating that the phase formed is not oriented relative to the substrate. In addition, the low intensity of these peaks indicates that the amount of the phase formed is not very large. A number of these peaks could also be attributed to substrate peaks, however a glancing angle XRD spectrum verified the presence of peaks from the Ga_2Pd_5 phase.

Ni/GaN

In the Ni system, no changes are observed by RBS after annealing up to 700°C as long as the sample is capped with a $1000 \text{ \AA}$ layer of SiO_2 . Figure 5.25 shows an example of an uncapped Ni sample which was annealed at 500°C .

Figure 5.25: RBS spectra of Ni on GaN as-deposited and annealed at 500°C for 1 hour. The spectra were obtained with a 45° sample tilt.

A significant amount of O is incorporated into the Ni layer. No changes are observed by RBS or XRD below this temperature. XRD at 500°C also shows peaks which correspond to NiO. Since no reaction with the GaN is observable up to this temperature, a capping layer must be used to investigate reactions at higher temperatures.

SiO₂ was chosen as a capping material because it is very stable and should not be reduced by Ni. (Kubaschewski et al., 1993) SiO₂ can easily be etched using HF without removing the Ni. After annealing, the SiO₂ layer was always removed prior to sample characterization. The highest annealing temperature used in the study was 750°C. Following the annealing cycle the SiO₂ capping layer was etched off and the surface of the Ni was analyzed using AES. No Si was observed verifying that no reaction took place between the Ni and SiO₂. The particle induced x-ray emissions (PIXE) were also monitored during RBS measurements to verify that no Si was detected. With the SiO₂ capping layer, no changes were detected in the RBS spectra until the annealing temperature reached 700°C. At 700°C and above an RBS signal appears indicating the presence of Ga at the surface. This can be seen in the spectra in figure 5.26. Note that there is no O incorporation observed in these samples.

Again, the RBS spectra alone are not sufficient to decide whether or not a reaction is occurring. The decrease in the height of the Ni peak and the onset of the Ga signal could be attributed to a reaction taking place, however SEM of the surface indicates that the Ga signal at the surface is due simply to islanding of the Ni. Figure 5.27 shows SEM micrographs of the Ni surface both before and after annealing. Annealing at 700°C for 30 minutes results in a roughening of the surface and the appearance of some areas where the

Ni has islanded to expose the GaN surface. After annealing at 750°C for 60 minutes the Ni film has agglomerated significantly and exposed the GaN surface in larger areas. Thus, the Ga signal observed at the surface in the RBS spectrum can be explained by this agglomeration.

Figure 5.26: RBS spectra of Ni/GaN samples annealed with an SiO₂ cap.

Figure 5.27: SEM micrographs of Ni on GaN; a) as-deposited, b) annealed at 700°C for 30 minutes, c) annealed at 750°C for 60 minutes.

XRD gives further evidence that no phases have formed. Figure 5.28 shows an x-ray spectrum of a sample annealed at 750°C for 1 hour. No new peaks are observed which would correspond to new phases. There is a slight possibility that Ni_xN phases may have formed which had their signals overlapped by the Al_2O_3 substrate signals. For these phases to form and not be detected, the phase must have formed epitaxially to the substrate and no Ni-Ga phase must have formed. Since reacted Ni phases do not show a strong tendency for epitaxy on Si and GaAs (see chapter 2), this is unlikely. In addition there would be very small driving forces for Ni_xN formation as the heat of formation is almost zero. (Kubaschewski et al., 1993)

Figure 5.28: X-ray spectrum of Ni on GaN annealed at 750°C for 60 minutes.

Ni has a thermal expansion coefficient which is over twice that of GaN. More compressive stress is generated in the Ni thin film during annealing than in the Pd thin film, because of the larger differential in thermal expansion and the larger value of Young's modulus. 1.5 GPa of compressive stress is generated in the thin film using the estimation shown in chapter 3, but no delamination failure is observed in this case however. This can be attributed to two differences. Ni has a much higher tensile strength than Pd, therefore it may also be stronger in compression. More importantly, the Ni film is capped with 1000 Å of SiO₂ during annealing and this probably maintained the planarity of the film.

Au/GaN

A cursory study of the behavior of Au on GaN was performed using one set of samples. This study sought to further verify the inert behavior of non-nitride forming metals on GaN. Au was expected to behave similarly to Pd and Ni because it has a fairly low surface energy (~ 1200 erg/cm²) and a high thermal expansion coefficient (14.1×10^{-6} K⁻¹). The Au was deposited by sputtering and annealed between 250° and 800°C. No phase formation was observed by RBS or XRD with annealing up to 800°C.

The behavior of Au after annealing did indicate that compressive stress was being generated in the metal film. Figure 5.29 shows SEM micrographs of the as-deposited Au film and films annealed at 450° and 500°C. The hillock features begin to form at a much lower temperature (450°C) because of the higher thermal expansion coefficient and the lower melting temperature. It is not clear whether these are actual hills of Au or whether the film is beginning to delaminate and buckle at these locations. After annealing at 500°C the hillocks appear slightly faceted and some have entirely delaminated from the surface.

Between the large hillocks is a linear pattern of much smaller hillocks. The reason for this pattern is unknown. It may possibly be due to microscopic defects on the surface of the GaN which also follow this pattern and provide nucleation sites. However, no defects were observed by SEM.

Figure 5.29: SEM micrographs of Au on GaN; a) as-deposited, b) annealed at 450°C for 30 minutes, c) annealed at 500°C for 30 minutes.

The diffusion coefficient necessary to allow the hillocks to form can be estimated using the simple one dimensional diffusion model we used in the case of Pt on GaN. The average distance between the hillocks after annealing at 450°C is 3.08 μm . This leads to a diffusion coefficient of $3.3 \times 10^{-12} \text{ cm}^2/\text{sec}$. Using the empirical model developed for FCC metals, $D = 0.014 \exp(-6.54T_m/T)$, the estimated diffusion coefficient at this temperature is $7.8 \times 10^{-8} \text{ cm}^2/\text{sec}$. This indicates that the amount of diffusion observed can be explained by surface diffusion of the Au.

At 450°C the thermal compressive stress generated in the film is approximately 267 MPa. This value is lower than that of Pd or Ni due to a lower annealing temperature and because the Young's modulus of Au is lower. However, failure is still likely because the ultimate tensile strength is lower as well. The compressive stress is twice the ultimate tensile strength (UTS) at 450°C and 2.75 times the UTS at 500°C.

5.3.2 Discussion

The lack of reactions for these metals on GaN shows that the systems are fulfilling the prediction for a higher reaction temperature with a higher semiconductor heat of formation. GaN is even more stable than ZnSe, therefore reaction temperatures are still higher. The only possible reaction observed was the formation of a Pd-Ga phase after annealing at 800°C. It is not surprising that Pd would react at the lowest temperature, since it has the lowest metal-metal bond strength.

The behavior observed for the near-noble and noble metals on GaN is very different from typical behavior of metals on semiconductors. No clear reactions have been

observed, rather the films have been seen to have poor adhesion, to agglomerate, and to delaminate from the surface. This type of behavior is more typically ascribed to metal films on ceramic surfaces. These are systems where the metal has a much higher surface energy than the ceramic substrate and the metal has a much higher thermal expansion coefficient than the substrate. Both of these cases appear to be applicable to these metal/GaN systems, although the surface energy of GaN is not known. Further comparisons are made below.

Platinum

In the case of Pt on GaN the metal film tends to agglomerate on the surface of the GaN. This phenomenon of island formation is often observed for interfaces between thin metal films and ceramics. (Cawley, 1991; Maskell et al., 1987) The dewetting occurs because the ceramic has a low surface energy while the metal has a high surface energy. In order to minimize the total surface energy of the system, the metal agglomerates to minimize its surface area and exposes more surface area of the low surface energy ceramic. This indicates that GaN must have a low surface energy and that any bonding between the Pt and GaN does not significantly decrease the interfacial energy of the system. Bonding between the Pt and GaN could result in a decrease of the interfacial energy which could compensate for the high surface energy of the metal. This does not happen in this extremely unreactive system.

This behavior is not amenable to contact formation if the system must be processed at high temperatures. This agglomeration degrades the electrical properties by decreasing the amount of continuous film available for conduction. Temperatures in excess of 600°C for

30 minutes will result in agglomeration of the contact. This agglomeration may also occur at lower temperatures if the system is annealed for a long time. This may cause contact degradation if the device is operated at high temperatures for long periods of time. Clearly, this system is also not a candidate for the formation of alloyed contacts.

Palladium, Nickel, and Gold

In the cases of Pd, Ni, and Au, behavior which is more commonly ascribed to metal/ceramic than metal/semiconductor systems is again observed. This type of behavior in thin metal film/ceramic systems is attributed to compressive stress generated in the metal film at high temperatures due to differences in the thermal expansion coefficients of the metal and substrate. (Peddada et al., 1990) In this case, GaN has a small linear thermal expansion coefficient compared to Pd, Ni, and Au. (See appendix A for specific values.) The amount of strain generated in the film can be estimated by the product of the difference in thermal expansion coefficients and the change in temperature from deposition temperature to annealing temperature. The linear thermal expansion coefficient for Pt is lower than that for the other three metals, therefore less compressive strain is generated during annealing and delamination is not observed.

The behavior of all of these metals on GaN indicates that the surface of GaN behaves more like a ceramic than a typical semiconductor. The surface energy and linear thermal expansion coefficient are low compared to most metals. The best candidates for reactions on GaN are likely to be metals which form M-N phases and which are known to react on other nitride ceramics, such as AlN. For this reason, the behavior of Ti was investigated. This metals forms a nitride with a large negative heat of formation (as indicated in figure

3.4) and there should be a large driving force for reaction on GaN. In addition, Ti has a low surface energy compared to other metals. It also has a low thermal expansion coefficient, so less compressive stress should be generated during annealing.

5.4 Structural behavior of Ti on GaN

5.4.1 Results

The behavior of Ti on GaN is very different from that of the more noble metals. No dewetting or delamination is observed by SEM up to 700°C, however reactions do not take place until very high temperatures are reached. One of the difficulties in working with Ti is its affinity for oxygen. Annealing at 500°C and above results in the incorporation of a significant amount of oxygen in the Ti layer. Figure 5.30 shows RBS spectra of Ti/GaN samples annealed in flowing N₂ in a tube furnace. The initial Ti layer thickness in these samples was 650 Å. Note that after annealing for 30 minutes at 500°C, O has been incorporated about halfway into the film. After annealing at 600°C for 30 minutes, O has diffused all the way through the Ti layer. The composition of the Ti-O layer can be estimated in both cases by using RBS simulation programs. The composition is approximately TiO. Because the O and N signals are very small in RBS and they are superimposed on the Ga signal it is very difficult to determine if there is any contribution from N diffusion. AES can not be used to do complementary depth profiling because the only N AES peak is overlapped by a Ti AES peak.

Figure 5.30: RBS spectra of Ti on GaN before and after annealing in flowing N_2 .

The only indication of possible phase formation from XRD is the shift of the Ti peak from $d=2.358 \text{ \AA}$ to $d=2.389 \text{ \AA}$ after annealing at 500°C for 30 minutes. This peak could be attributed either to TiO or TiN phases. A sign of possible TiN phase formation was the color change of the sample. After annealing at 500°C the sample became gold colored which is the characteristic color of TiN . Annealing at 600°C resulted in a transparent sample, which is characteristic of the insulator TiO . Depth profiling by XPS, however, showed that the color change was due to TiN formation at the surface of the sample, not at the Ti/GaN interface. Figure 5.31 shows XPS depth profiles of an as-deposited sample

and one annealed at 500°C. The Ti peak has been deconvoluted into its metallic, oxide, and nitride components based on the slight energy shifts of the peak due to differences in bonding. The energies for the three different components are shown in table 5.3. These shifts agree well with tabulated values. (Briggs and Seah, 1990) The three Ti components are graphed separately.

	Ti Binding Energy (eV)	
	2p _{1/2}	2p _{3/2}
metal	459.5	453.4
oxide	464.4	458.6
nitride	461.4	455.1

Table 5.3: Binding energy chemical shifts of various Ti components.

The Ti was deposited by sputtering and had an approximate thickness of 600 Å. This gives an approximate sputter rate 0.7 Å/second for elemental Ti. Note that the XPS sputtering rate decreases after annealing when the Ti film has become oxidized. In the as-deposited sample there is some oxygen incorporated at the surface and the indication of a small layer of TiO₂ at the surface. The O and N levels in the Ti film are approximately 10%. This contamination may be due to the presence of O and N in the Ar gas used for sputtering. At the interface in the as-deposited sample there is an approximately 80 Å thick layer which exhibits a photoelectron peak with the energy ascribed to Ti bonded to N. This indicates that some of the Ti in this region may be bonded to N rather than to other Ti atoms. The peak shift for Ti bonded to Ga is unknown, however the results from the annealed sample indicate that the peak observed at the interface can be assigned to Ti bonded to N.

(a)

(b)

Figure 5.31: XPS depth profiling of Ti/GaN interfaces a) as-deposited, b) after annealing at 500°C for 30 minutes. The chemical shifts of the Ti in the metallic, oxide, and nitrides states are graphed separately.

After annealing, figure 5.31b, the O level in the Ti film rises from approximately 10% to almost 30%. In addition the N signal shows a peak up to 17% near the surface of the sample. The peak width indicates that an approximately 135 Å thick layer of TiN has formed at the surface of the film. This is due to indiffusion and reaction with the N₂ annealing gas. The formation of this layer explains the gold-colored appearance of the film after annealing. The TiN peak near the interface has not widened as compared to the as-deposited sample indicating that reaction has not occurred at the interface.

Ti has been observed to react to form TiN in Ti/Al and Ti/Al/Ni/Au contacts on GaN. (Ruvimov et al., 1996b) TEM was used to characterize the Ti/GaN interface of these contacts both before and after annealing at 900°C for 30 seconds. In the as-deposited sample a thin layer of TiN was observed at the interface. TiN is a cubic phase which exists over a range of stoichiometry and lattice parameters. The lattice parameter for stoichiometric TiN is $a = 4.242 \text{ Å}$. The observed lattice parameter was $a = 4.235 \text{ Å}$. Annealing results in significant metal interdiffusion and reaction as well as a thickening of the TiN layer. In the Ti/Al contact the TiN layer grew to 50 Å in thickness, while in the Ti/Al/Ni/Au contact the TiN layer was 100-150 Å thick after annealing. The TiN layer was oriented relative to the substrate with the following relationship: $\{111\} \text{TiN} // \{0001\} \text{GaN}$, $[110] \text{TiN} // [1100] \text{GaN}$, and $[112] \text{TiN} // [10\bar{1}0] \text{GaN}$.

The presence of this phase was also detected by XRD as shown in figure 5.32. The XRD peak was only observed for the annealed Ti/Al/Ni/Au sample, as the layer thickness in the other samples was too thin to detect. Peaks for other binary metal alloys were also detected. The TiN layer may have been able to grow thicker in the 4 metal layer sample

because less Ti reacted with Al. In the Ti/Al sample the amount of Ti available for reaction was limited by the formation of Ti_3Al . In the 4 metal layer system the Al prefers to react with the Au and Ni, leaving more elemental Ti to form TiN. To form TiN, nitrogen must be removed from the substrate. This leaves N vacancies and should leave some elemental Ga as well. No elemental Ga layer or precipitates or phase formation between Ti-Ga was observed. Some Ga was detected by EDS in the other metal layers, indicating some possible outdiffusion of Ga.

Figure 5.32: XRD spectrum of Ti/Al/Ni/Au contact after annealing at 900°C for 30 seconds.

5.4.2 Discussion

This reaction follows the prediction of Brillson (Brillson, 1982) that the formation of metal-anion phases should be formed. This agrees with the trend established by the metal-ZnSe reactions. In the cases of Pt, Pd, Ni, and Au, no stable nitrides are known and no reactions were observed. The high temperature for reaction was also anticipated due to the large heat of formation of GaN. The initial temperature for reaction has not been determined. This requires careful annealing in truly oxygen and nitrogen free environments.

The reaction of Ti on GaN further supports the argument that GaN behaves very much like a ceramic in its interfacial reaction behavior. No dewetting or delamination is seen due to the lower thermal expansion coefficient and surface energy of Ti. In addition, the reaction at the interface to form TiN probably results in a lower interfacial energy, thus promoting the stability of the metal. Ti has been commonly observed to be a reactive metal on other nitride ceramics such as AlN. (Carter and Papageorge, 1992) This indicates that other nitride-forming metals may also react on GaN.

6. Conclusions

The thermal stability of the near noble metals on ZnSe and GaN has been determined. Solid-state reactions of Pt, Pd, and Ni on ZnSe are initiated by thermal annealing at 575°, 200°, and 300-350°C respectively. The initial reactions of Pd and Pt on ZnSe are very similar to their reactions on GaAs. Pd tends to first form a ternary oriented phase, $\text{Pd}_{5+x}\text{ZnSe}$, while Pt reacts to form a Pt_5Se_4 layer at the interface. The Pd reaction appears to be diffusion controlled, as the growth of the reacted layer slows with time. The reaction of Pt is very sensitive to contaminants and oxides at the interface (as are its reactions on Si and GaAs), while the Pd reaction is uninhibited by small amounts of contamination or oxide. The Ni reaction on ZnSe, however, is rather different from that on GaAs. Ni begins to react at 300-350°C to form separated grains of a Ni-Se phase at the interface between the Ni and ZnSe. This is in contrast to the reaction of Ni on GaAs which initially forms a ternary Ni_3GaAs phase.

In the GaN system, the only reactions observed were the formation of Pd-Ga phases after annealing at 800°C and the formation of TiN. No phase formation occurred in the Pt, Ni, or Au systems with annealing to 800°C, or in the Ti system with annealing to 500°C. Unlike other metal/semiconductor interfacial systems, dewetting and delamination of the metal was seen. Agglomeration of Pt began after annealing as low as 600°C. This behavior is often seen at the interface of high surface energy metals and low surface energy ceramics. The islanding tends to lower the interfacial energy of the system. Islanding was also noted in the Pd and Ni systems after annealing at 700°C. This behavior

strongly indicates that the surface of the GaN behaves more like a ceramic than a typical semiconductor.

In the Au and Pd systems delamination occurred due to compressive stress generated during annealing. The stress was generated because of the difference in linear thermal expansion coefficients of the metal and substrate. This is also typically observed in metal/ceramic systems. Significant compressive stress was also generated in the Ni thin films, however they did not exhibit failure because of the presence of a SiO₂ capping layer during annealing.

The increase in reaction temperature on ZnSe from Pd to Ni to Pt parallels the increase in binding energy of the metal. This continues the trend observed in the reactions of these metals on Si and GaAs. This trend may also be followed in the GaN system. The reaction of Pd on GaN occurs at a lower temperature than those of Pt or Ni. Perhaps with even higher temperature annealing the reactions of Ni or Pt may be observed. This fulfills the prediction that the metal reaction temperature should vary with the binding energy of the metal. Further studies of other metals should be performed to verify this.

In addition, the reactions on ZnSe and GaN take place at higher temperatures than the corresponding reactions on Si and GaAs. This trend follows an increase in the semiconductor heat of formation from Si to GaAs to ZnSe, as predicted. This indicates that dissociation of the semiconductor is an important step in the reaction. In most reactions, metal-anion phases were observed indicating that the driving force for formation of these phases is larger than for the metal-cation phases. This was predicted to occur

because of the greater ionicity of these compound semiconductors and therefore larger electronegativity differences between the metal and semiconductor anion.

The lack of reactions on GaN does not agree with the predictions of thermodynamic calculations. These calculations predict reactions to form metal-cation phases at temperatures as low as 600°C. This discrepancy may be due to assumptions made in the calculations. The calculations assume that the system is in thermodynamic equilibrium and that no element will escape from the system during annealing. In addition, the data used for the heat of formation of GaN may not be accurate. Finally, kinetics may play a larger role in the reaction than thermodynamics.

The information obtained from these studies should aid in the development of better quality and more highly reliable ZnSe and GaN devices. The stability and reaction data can be used to engineer contacts with better mechanical and electrical properties. The only reaction on ZnSe which provides an interesting possibility for the formation of electrical contacts by alloying is that of Pd. The Ni and Pt reactions take place at a temperature which is above the temperature at which a compensating defect forms and degrades the electrical characteristics of ZnSe. In addition these reactions do not result in a laterally homogeneous contact. The Pd reaction is particularly interesting because it is very planar and controllable and the ternary phase forms with an epitaxial relationship with the substrate. This type of behavior is similar to the Pd ternary phase formation on GaAs and may lead to the development of various Pd-based alloyed Ohmic or Schottky contact structures similar to those developed for GaAs. However, the electrical characteristics of the contact between $\text{Pd}_{5+x}\text{ZnSe}$ and ZnSe have not yet been determined. The stability of

Pt and Ni above temperatures at which ZnSe devices will be operated makes them suitable candidates for stable Schottky contacts.

The metal/ceramic type behavior observed for noble metals on GaN indicates that a different approach must be taken than has typically been used in engineering metal-semiconductor contacts. The low surface energy and linear thermal expansion coefficient of GaN must be considered when determining which metals may act as good contacts on GaN. This will be important both when looking for metals which may react on GaN and when considering which metals may be stable at high temperatures. To obtain stable, non-reactive contacts at high temperatures it may be necessary to use metals with fairly low surface energies which will remain wetted on the surface. In addition, they must also have fairly low thermal expansion coefficients or high yield strengths to avoid failure under thermally generated compressive stress. The best candidates for reactions on GaN are likely to be metals which form M-N phases and which are known to react on other nitride ceramics, such as AlN. A good example of this is the observed reaction of Ti to form TiN. The best candidates for non-reactive contacts which will remain stable at high temperatures are the noble and near-noble metals. Temperatures must remain low enough for agglomeration and delamination not to occur.

The trends observed here should also be applicable to other II-VI and III-Nitride semiconductor systems, while the information on phase formation and stability should be useful in the development of contacts for ZnSe and GaN devices. The desire for blue light emitting devices and their commercial applications continues to encourage further investigation of the ZnSe and GaN systems. As these devices continue to be optimized,

the properties of contacts will become more important. With the understanding gained from basic studies of metal interactions and the corresponding electrical behavior, it should be possible to develop contacts which are thermally and electrically stable and provide the desired electrical behavior.

7. Appendices

Appendix A: Properties of some semiconductors and metals

General Semiconductor Properties

Property	ZnSe	GaN	Si	GaAs
E_g @300K(eV)	2.58	3.39	1.12	1.42
E_g @low T(eV)	2.80 (OK)	3.50 (1.6K)	1.17 (OK)	1.52 (OK)
crystal structure	zincblende	wurtzite	diamond cubic	zincblende
lattice param.(Å)	a=5.668	a=3.189 c=5.185	a=5.431	a=5.653
Tmelt (K)	1793	2000	1688	1511
m^*_h	0.6	0.6	0.54	0.51
m^*_e	0.16	0.19	0.98/0.19	0.07
χ_s (eV)	4.09	4.1	4.05	4.07
n-type dopant	Cl- 26.9meV	Si- 33meV	P- 45 meV	Si- 58 meV
p-type dopant	N- Li- 66-114 meV	Mg- 160- 250meV	B- 45 meV	Zn- 31 meV
ther. exp. coeff.	7.7×10^{-6} /K	6×10^{-6} /K	2.6×10^{-6} /K	6.86×10^{-6} /K
$-\Delta H^\circ_{298}$ (KJ/mol)	163.2	109.6	0	74.1
S°_{298} (J/molK)	71.1	29.7	18.8	64.2
Ecohesive	1.29	2.24	2.32	1.63
$\Delta\chi$	0.8	1.4	0	0.4
ionicity (Pauling)	15	39	0	4
ionicity (Phillips)	63	50	0	31

Data from (Kubaschewski et al., 1993; Phillips, 1973) and Landolt and Börnstein,

Numerical Data and Functional Relationships in Science and Technology: New Series.

General Properties of Metals

Property	Pt	Pd	Ni	Au	Ta	Ti
Atomic No.	78	46	28	79	73	22
Crys. Struc.	fcc	fcc	fcc	fcc	bcc	hex
lattice param. (Å)	a= 3.923	a= 3.889	a= 3.523	a= 4.079	a= 3.298	a=2.950 c=4.686
T _{melt} (°C)	1769	1555	1455	1065	3014	1677
ther. exp. coeff. ($\times 10^{-6} \text{ K}^{-1}$)	9	11.7	13.3	14.1	6.5	8.9
resistivity ($\mu\Omega\text{cm}$)	10.5	10.8	6.9	2.2	13.5	47.8
heat of vaporization ^a (eV/molecule)	5.85	3.94	4.45	3.82	8.10	4.87
ϕ_M (eV) ^b	5.32	4.97	5.01	4.82	4.19	4.3
χ_s ^c	2.28	2.20	1.91	2.54	1.50	1.54
surface energy (mJ/m ²)	2356	1956	1920	1140	2150	1933
Poisson's ratio, ν	0.39	0.39	0.31	0.42	0.34	0.36
Young's modulus, E (GPa)	170	121	200	79	186	120
ultimate tensile strength average, (MPa)	135	168	310	130	345	470

All data from (Brandes and Brook, 1992) except:

a (Kubaschewski et al., 1993)

b (Sze, 1981)

c (Mönch, 1993)

Work functions of clean metal surfaces in vacuum data from (Sze, 1981)

Appendix B: Schottky barrier height measurement methods

There are several methods for measuring the Schottky barrier height of a metal/semiconductor contact. The most common methods, which will be described here, are current-voltage (I-V) and capacitance-voltage (C-V) measurements. Other methods include measuring the current density as a function of temperature or measuring the current resulting from irradiation of the diode with photons. Photons with energy larger than the barrier height can excite carriers from the metal into the semiconductor.

Current-voltage (I-V) measurements

Ideal I-V measurements are based on the assumption that carriers are able to cross the barrier only by thermionic emission, meaning that the carriers must be thermally excited over the barrier and no tunneling takes place. When this occurs the current flowing across the barrier can be described by:

$$I = I_s \exp\left(\frac{qV}{nkT}\right) \left\{ 1 - \exp\left(\frac{-qV}{kT}\right) \right\} \quad \text{where} \quad (\text{B.1})$$

$$I_s = AA^{**}T^2 \exp\left(\frac{-q\phi_B}{kT}\right). \quad (\text{B.2})$$

In equation B.1, I is the measured current while I_s is the saturation current. The applied voltage is V , q represents the electron charge, k is the Boltzmann constant, T equals the temperature, A represents the contact area, n is the ideality factor and ϕ_B equals the barrier height. The Richardson's constant, A^{**} , can be calculated from materials constants. The ideality factor, n , should be one for an ideal Schottky diode, however it increases if the current is due to other mechanisms than just thermionic emission. When

the applied voltage, V , is much greater than kT/q then equation B.1 can be approximated by,

$$I \cong I_s \exp\left(\frac{qV}{nkT}\right) . \quad (\text{B.3})$$

The current is then measured as a function of the applied voltage and $\ln(I)$ is plotted versus the voltage and yields a straight line. The slope equals nkT/q and the intercept yields I_s . From this determination of I_s , the barrier height can be calculated, according to

$$\phi_b = \frac{kT}{q} \ln(AA^{**}T^2) - \ln(I_s) . \quad (\text{B.4})$$

For the determination of the barrier height to be accurate, the current must be primarily due to thermionic emission, i.e., the ideality factor must be close to one. An ideality factor greater than approximately 1.1 indicates that the diode is not ideal and there may be an interfacial layer or recombination in the depletion region. Difficulties also arise if the diode has a large series resistance. This results in a very short linear range in the $\ln(I)$ vs. V plot, thus making accurate extrapolation to I_s difficult. Mathematical methods have been developed which can compensate for the series resistance (see references at the end of the section). Finally, erroneous measurements can arise if the contact is not homogeneous. In some cases, the contact formed may have areas of higher and lower barrier heights in parallel, for example due to the presence of interfacial oxides. In this situation, the lower barrier height will be measured by this technique.

Capacitance-voltage (C-V) measurements

C-V measurements are not dependent on carrier transport across the barrier, rather the capacitance of the space charge region is measured as a function of the applied voltage.

The width of this space charge region changes with applied bias. In this measurement a reverse voltage is applied to the diode and the resulting capacitance is measured. The space charge region capacitance can be modeled using the simple planar capacitor. The width of the space charge region represents the distance between the plates in the capacitor. The capacitance is related to the voltage by

$$C^2 = \frac{q\epsilon_s N_D}{2\left(V_{bi} - V - \frac{kT}{q}\right)} \quad (B.5)$$

In this equation C is the capacitance, V the applied reverse voltage, q the charge on an electron, k the Boltzmann constant, T the temperature, ϵ_s the dielectric constant of the semiconductor, N_D the doping level, and V_{bi} the built-in potential. The width of the space charge region changes with applied bias, and it disappears if the applied bias equals the built-in potential. The built-in potential is the energy difference between the top of the conduction band in the bulk of the semiconductor and the top of the conduction band at the metal/semiconductor interface without any bias applied.

The capacitance is measured for various applied reverse biases and $1/C^2$ is plotted versus V . The intercept on the voltage axis is then V_{bi} and the barrier height is calculated by

$$\phi_B = V_{bi} + (E_C - E_F) + \frac{kT}{q} \quad (B.6)$$

$E_C - E_F$ is the difference in energy between the bottom of the conduction band and the Fermi level in the bulk semiconductor. This equation assumes that the semiconductor is n-type.

This determination of the barrier height assumes that the barrier height does not depend on the applied bias. This will not be true if there is an interfacial layer at the interface. Error in the barrier height will also result if the doping concentration, N_D , is not constant with depth. If the contact is not homogeneous the C-V method will measure the barrier height of the largest area. This may result in differences between I-V and C-V measurements. There are other more detailed reasons why C-V and I-V measurements will differ, as explained in the references below.

This section has given a brief overview of two Schottky barrier height measurement techniques. More detailed discussions can be found in the following references:

(Rhoderick and Williams, 1988)

(Schroeder, 1990)

(Sze, 1981)

Appendix C: Characterization methods

C.1 Rutherford backscattering spectrometry (RBS)

RBS is a very useful technique for thin film analysis because of its ability to provide quantitative information about composition, film thickness, and diffusion. Most importantly, this method is entirely quantitative and does not require any standards. A very comprehensive review of RBS can be found in (Chu et al., 1978). RBS uses the very simple principles of energy and momentum conservation during the elastic collision of two ions and the energy loss of an energetic ion traveling through a solid.

In a typical RBS experiment He^+ ions (or in special cases other light or heavy ions) are accelerated up to an energy of around 2 MeV. These ions collide with the nuclei of atoms in the sample. The energy of the incoming ions is large enough to easily penetrate the electron cloud of the atoms and leading to Coloumb interaction between the nuclei of the energetic ion and the target atoms. The direct Coloumb interaction between the He^{++} ions and the nucleus of the atoms leads to scattering of the He^{++} ion all the way from forward to backscattering. The backscattered ions are collected by a detector which measures the energy of the ion. There are three basic pieces of information about the target which can be determined from the energy of the backscattered ions. These are: the mass of the target atoms, the relative amounts of different atoms in the target (composition), and a depth profile of the elemental distribution.

C.1.1 Elemental analysis

The mass of the target atoms is the most basic piece of information derived from the experiment. The behavior of two particles in an elastic collision is governed by two

equations: the conservation of energy and the conservation of momentum. Using these two equations it is possible to find a relationship between the incoming energy of the ion, E_0 , and the backscattered energy of the ion, E_1 . This relationship, shown in equation C.1, is dependent only on the masses of the two atoms and the angle at which the ion is backscattered.

$$E_1 = E_0 \times \left[\frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{(M_2 + M_1)} \right]^2 = E_0 K \quad (\text{C.1})$$

Figure C.1: Schematic representation of an elastic collision between an ion of mass, M_1 , and energy, E_0 , and a target atom of mass, M_2 , which is initially at rest.

The masses, angles, and energies are defined in figure C.1. The square of the term in the brackets is called the kinematic factor, K . It is the ratio of the incoming energy and the backscattered energy. The incoming energy is set by the experimenter and the backscattered energy is measured by the detector. The detector is positioned at a specific backscatter angle, so θ is known. The mass of the ion, M_1 , is also known. Helium is the most common gas used and there are tables giving the kinematic factor for all elements at various backscatter angles assuming the incoming ion is He. Measuring the energy of the

backscattered ion provides a straightforward method of determining the mass of the target atom. If the target is a compound with more than one type of atom, backscattered ions will be measured at various energies corresponding to the different masses. Difficulties can arise if the elements in the target are heavy and close to the same mass. As the mass of the target atom increases, there is less differentiation in the energy of the backscattered ion between two neighboring elements in the periodic table. This can create difficulty when attempting to discern the presence of two heavy elements with similar masses. Heavy ion backscattering improves the mass resolution. (Yu et al., 1985; Yu et al., 1986)

C.1.2 Composition analysis

The previous calculation allowed the determination of the type of elements in the target; it is also possible to determine their relative quantities. Because atomic nuclei are so small, most of the incoming ions are not backscattered. The number of collisions is predictable based on the number and type of atoms in the target and the number of incident ions. This requires a knowledge of the differential scattering cross-section, $d\sigma/d\Omega$, equation C.2.

$$\frac{d\sigma}{d\Omega} = \left(\frac{Z_1 Z_2 e^2}{4E} \right)^2 \frac{4 \left\{ \left[1 - \left(\left(\frac{M_1}{M_2} \right) \sin \theta \right)^2 \right]^{\frac{1}{2}} + \cos \theta \right\}^2}{\sin^4 \theta \left[1 - \left(\left(\frac{M_1}{M_2} \right) \sin \theta \right)^2 \right]^{\frac{1}{2}}} \quad (C.2)$$

In equation 4.2 $d\Omega$ is the differential acceptance angle of the detector. The scattering cross-section can be interpreted as the probability that the incident ion will be scattered into the detector. The most important aspect of this equation is that the probability is

proportional to the square of the atomic numbers of the target and incident atoms. The total number of backscattered ions, A , can be determined using equation C.3.

$$A = \left(\frac{d\sigma}{d\Omega} \right) \times d\Omega \times Nt \times Q \quad (C.3)$$

N is the atomic density of target atoms, t is the thickness of the film, and Q is the total number of incident particles.

Figure C.2: Sample RBS spectrum of a compound thin film, A_mB_n .

Figure C.2 shows a sample RBS spectrum for a compound, A_mB_n , where the mass of element A is larger than the mass of element B. The area under each peak is the total number of backscattered ions. This is equal to the number of counts, H , at each energy times the energy width, ΔE .

In general, it is not necessary to calculate the total number of backscattered ions because the information desired is the relative amount of each element, i.e., the

composition. This can be derived from the ratio of the areas A and B in the spectrum above and equation C.3. The differential cross section, $d\sigma/d\Omega$, can be estimated as $(Z_1Z_2/E)^2$. Since Z_1 , E , t , and Q are the same for both areas these will cancel out in the ratio leaving the terms shown in equation C.4 for compound A_mB_n .

$$\frac{A_A}{A_B} = \left(\frac{Z_A}{Z_B}\right)^2 \left(\frac{N_A^{AB}}{N_B^{AB}}\right) = \left(\frac{Z_A}{Z_B}\right)^2 \left(\frac{m}{n}\right) \approx \frac{H_A}{H_B} \quad (C.4)$$

The area is calculated by multiplying the height of the peak times the width of the peak. Since the width will be approximately the same for both elements, a simplification can be made to equation C.4 by substituting the height of the peaks for the area. This calculation allows the composition to be determined without the use of any standard. Complications can arise if there are overlapping peaks in the spectrum.

C.1.3 Depth analysis

Finally, the width of the signal can also provide significant information. The measurement of the width allows the determination of the thickness of the film, or the depth distribution of elements in the structure. Very few of the ions are scattered by atoms at the surface of the target, many of them travel into the film before undergoing a collision. When the ion travels through the material it gradually loses energy through interactions with the electron clouds of the target atoms. This process is called electronic stopping. These are inelastic collisions where electrons valence and core electrons of the target atom are ionized or raised to excited states. The incoming ion does not significantly change its direction, but just loses a small amount of energy. The amount of energy lost depends on the atomic density in the target, N , and the element, which is characterized by

a stopping cross-section, ϵ . The energy loss per depth can be calculated as shown in equation C.5.

$$dE/dx = \epsilon N \quad (C.5)$$

The values of ϵ are tabulated for all of the elements for various He ion energies. When determining the thickness of a thin film the effective stopping cross-section must be used. This value, ϵ_0 , takes into consideration the fact that energy is lost as the ion travels into the film, and also as the ion travels out of the film, after the backscattering event. The thickness of the film is then calculated using the measured ΔE as shown in equation C.6.

$$t = \frac{\Delta E}{N \epsilon_0} \quad (C.6)$$

If the target is a compound, Bragg's law can be used to determine the stopping cross-section. The compound cross-section is an average of the stopping cross-sections for each element weighted by the composition ratio.

C.1.4 Strengths and weaknesses of RBS

RBS is a relatively simple, direct method to measure the composition and depth profile of a thin film system. It does not require quantitative standards and is a non-destructive measurement. No specimen preparation is required and data acquisition only takes 10-20 minutes per sample. Spectra can be quite complicated, however there are two RBS simulation computer programs, RUMP and GISA, which can aid in deconvoluting the signals. This is possible because of the quantitative nature of RBS.

Another advantage of RBS is the ability to measure damage to the crystal. When the incoming ion beam is aligned with a major axis of the crystal, the ions can travel down the open channels of the crystal. However if the crystal is damaged, these channels will be

blocked and there will be more backscattering of the ions. Thus a peak will be observed which corresponds to the degree and depth of the damage. This provides a method to determine damage caused by sputtering or ion implantation, for example.

There are, however, some pitfalls for RBS which must be considered. The sample must be laterally homogeneous on a fairly large scale because the ion beam diameter is approximately 1 mm. If the sample is not homogeneous, misinterpretation of the data is possible. This is shown in chapter 5 for the case of Pt on GaN. Often, signals from various parts of the sample may overlap, which also complicates data interpretation. This is especially a problem for films with two similar heavy mass elements or when a very light element, for example N, is present. In addition RBS does not provide any information on microstructure or crystal structure and has a depth resolution of approximately 50-100 Å.

C.2 X-ray diffraction (XRD)

XRD provides a method to determine whether interfacial changes are caused only by diffusion or if new phases are forming at the interface. A new phase can not be detected until it grows to an approximate thickness of 50 Å. Below this thickness the diffracted signal will be too weak to be detected. A good review of XRD can be found in (Cullity, 1978). The basis of XRD is the diffraction of electromagnetic radiation from a periodic structure, in this case the crystal lattice.

C.2.1 Theory of diffraction

When an x-ray is incident on an atom, some of the radiation is scattered coherently by the electrons of the atom. Some of the radiation is also scattered incoherently, however these scattered x-rays do not play a part in diffraction. When x-rays are incident on a

periodic array of atoms, such as in a crystal, some of the scattered x-rays will mutually reinforce each other and generate a diffracted beam. The condition for this to occur requires that the path length difference for the various scattered x-rays be an integral number of their wavelength, so that they will remain in phase. This requirement is shown graphically in figure C.3 and mathematically in equation C.7.

Figure C.3: Diffraction of x-rays by a crystal. (Cullity, 1978)

$$\lambda = 2d_{hkl} \sin \theta_{hkl} \quad (C.7)$$

In this equation, λ indicates the wavelength of the incoming radiation, d_{hkl} is the spacing between the planes specified by the Miller indices, and 2θ is the angle between the incoming x-rays and the detector. If the detector is not placed at 2θ , then the diffracted beam will not be observed.

In order to determine the structure of a crystal, x-rays with a known wavelength are diffracted from a crystal. The most commonly used wavelength is 1.5404 Å which is due to the K_{α} characteristic x-rays generated by electrons impacting on Cu. The angles at which the diffracted beams occur are then measured by scanning the detector through a wide range of angles. This is called the θ - 2θ geometry. A large increase in x-ray intensity will be measured at an angle where there is a diffracted beam. By knowing the values of θ and λ , a sequence of d values can be calculated. These d values can then be compared to tabulated values for known crystal structures and used to calculate the lattice parameter of the crystal.

After an interfacial reaction, if a new phase is formed, new peaks should appear in the x-ray spectrum. These peaks can then be compared to observed or calculated peaks of known phases and the new phase can be identified. If only diffusion is taking place, no new peaks will be observed. Often, diffusion will result in the formation of a solid solution at the interface. The incorporation of the diffusing atoms into the crystal structure will result in a change in the lattice parameter of the crystal. This is observed as a shift in the diffraction peaks as the spacing, d , between lattice planes changes.

C.2.2 Strengths and weaknesses of XRD

XRD provides an excellent method for detecting the formation of new phases, after they have grown to a minimum volume. It is the easiest way to observe the crystal structure of the different layers. The need for an approximately 50Å thick film, means that the very first stages of reaction are not observable with this technique.

Sensitivity can be somewhat improved by using a glancing angle technique. In this technique the incoming x-ray angle is set at $1-3^{\circ}$ from the surface of the sample. The x-

rays then have a longer path length through the film. This method is also very useful if peaks from the substrate interfere with peaks from the new phase. Because the incoming angle is so small, the Bragg condition will not be satisfied for the epitaxial substrate planes parallel to the surface. If, however, the reacted phase is also epitaxial it will not be observed.

The presence of epitaxial films can create difficulties in the usual θ - 2θ geometry as well. If the sample is not correctly oriented with the beam, an epitaxial film may not be observed or the intensity of the signal may be reduced significantly. To overcome this it is necessary to use a diffractometer with the ability to tilt along other axes. The sample can then be placed at the correct orientation with respect to the incoming x-ray beam, so that the peaks from the epitaxial film are observed.

C.3 Auger Electron Spectroscopy (AES)

AES is used to determine the composition of the sample surface. The measurement depth is typically around $10\text{\AA}$, however in combination with ion beam sputtering it can be used to obtain a depth profile of the composition. A review of this technique can be found in (Slaughter et al., 1992). AES is an ultra-high vacuum technique which requires an electron beam as a probe.

C.3.1 Theory of AES

The Auger process is an atomic process which produces an energetic electron but no electromagnetic radiation. In this process an electron beam is incident on the sample and the electrons in this beam ionize the target atom leaving a vacancy in one of the inner shells. This inner shell vacancy is then filled by an electron from one of the higher levels.

The excess energy from this transition is transferred to a third electron, an Auger electron, which is ejected from the atom. The second and third electrons are from the same electron shell. The energy transferred to the third electron is characteristic of the transition energy for that element minus the binding energy of the third electron. A detector is used to measure the energies of the electrons ejected or scattered from the target. The peak in the energy spectrum caused by the Auger electrons is labeled by the shells that the three electrons initially occupied, i.e., KLL or LMM. This characteristic energy can be used to identify the element involved. Because the amount of energy transferred to the Auger electron is fairly small and the inelastic mean free path of electrons in solids is short, only electrons within the top 5-10Å of the surface usually escape. Thus this technique is very surface sensitive.

Auger spectra are usually not plotted as the number of electrons detected, $N(E)$, versus energy, E , rather, the derivative $dN(E)/dE$ is plotted. This is due to the properties of the energy analyzers and analog electronics used as detectors when this technique was first introduced. (Brundle et al., 1992) Observing the data in the derivative form also removes the background due to secondary, or inelastically scattered, electrons.

Determining which elements are on the sample surface is very straightforward. A peak energy will correspond to a tabulated characteristic energy for an element. Often more than one peak for each element may be observed, thus verifying the element's presence. The intensity of the peaks can be used to quantify the composition. For quantification the relative sensitivity factors for the elements must be known. These sensitivity factors are tabulated, although to make a very accurate determination the sensitivity factors should be determined in the same experimental system. The sensitivity factor accounts, in part, for

the fact that not all of the Auger electrons will escape from the sample without energy loss. The proportion that escape depends on the material.

A depth profile can be obtained by alternating measurement with sputtering by an ion beam. The ion beam is used to gradually sputter a crater in the sample so the composition can be analyzed versus depth. The sputter crater is generally much larger than the acquisition area. This prevents acquisition of signal from the side walls of the crater. The ion beam is not sputtering during data acquisition. The depth resolution is about 50Å, however the interface can be widened by knock-on of elements in the film by the ion beam. The energetic ions can actually push some target atoms deeper into the film, thus widening the interface.

C.3.2 Strengths and weaknesses of AES

AES is a very useful technique for identifying elemental composition, particularly because it can identify very light elements, such as N. It has very good lateral spatial resolution since the probe size can be as small as 500 Å. This is very useful when identifying the composition of different areas on the sample. The ability to do depth profiling with the use of an ion beam makes it a good technique for observing interfacial diffusion and phase formation.

One of the weaknesses of AES is that it is a destructive technique. In order to observe a depth profile, it is necessary to sputter away the material. In addition, it is possible to have preferential sputtering on a compound target which may leave the surface with an altered composition. Finally, to get truly quantitative information it is necessary to accurately determine the relative sensitivity factors. This involves using standards with a similar composition to that being measured and doing the measurements on the same

system being used for the experiments. Another disadvantage of AES is the occasional overlap of peaks. Generally, there is more than one peak which can be monitored for each element, so overlap is not a problem. One exception to this is the overlap of the Ti LMM and the N KLL peaks. The N KLL peak is the only Auger peak available for N, so the presence of Ti and N can not easily be distinguished.

C.4 X-ray photoelectron spectroscopy (XPS)

XPS has many similarities to AES. This technique has to be performed in ultra-high vacuum and detects an electron emitted from the sample. XPS is also used to determine the composition of the sample surface, however it can give more information on the bonding of the element than AES. It is very useful for measuring nonconductive samples. XPS can be used to perform depth profiling when combined with an ion beam sputtering system. A discussion of this technique can be found in (Slaughter et al., 1992)

C.4.1 Theory of XPS

In XPS an x-ray is used to ionize a core electron in the target atom. The kinetic energy of the ejected electron, the photoelectron, is measured. This energy is characteristic of the element since it is simply the energy of the incoming x-ray minus the binding energy of the electron in the atom. Thus this measured kinetic energy can be used to characterize the element on the sample surface. Often electrons from various shells (1s, 2p, etc.) will be ejected and this results in several characteristic peaks in the spectrum for each element. These peaks are labeled by the shell from which the electron escaped, e.g., 1s. These electrons can only travel a limited distance through the solid before being inelastically scattered, therefore only photoelectrons from the near surface region can escape with their

characteristic energy. The sampling depth for XPS is on the order of 25 Å. Obtaining quantitative information is difficult because sensitivity factors should be determined using known standards on the same instrument. Tabulated values of the sensitivity factors are available. Note that this process is simply the first step in the Auger process, therefore some of these inner shell vacancies will be filled through the Auger process and Auger electrons are also detected by this method.

When an atom bonds in a solid the energy levels of its core electrons change slightly due to the interaction. This change can be detected by a change in the energy of the photoelectron. The binding energy shifts for many compounds are tabulated and can be compared to the data obtained. Generally this shift is on the order of a few eV and can be difficult to resolve. XPS can also be used for depth profiling. The procedure used is the same as in AES, however a much larger area must be sputtered because the probe size for XPS is on the order of 1 mm.

C.4.2 Strengths and weaknesses of XPS

The main advantage of XPS is the ability to identify the chemical state of the element. This can help determine, for example, if the Ti in the sample is in the form of Ti or TiN. In addition, there is no overlap of the Ti and N peaks in XPS, however there are other overlapping signals. The ability to detect light elements is also advantageous. Since there is no electron beam incident on the sample, there are fewer sample charging problems and nonconductive samples can also be analyzed.

A disadvantage for XPS is that the probe size is rather large. It is not possible to identify and characterize small features on the surface of the sample. Accurate quantitative information is difficult to obtain because of the need for careful calibration. It

is much more accurate to compare relative compositions in similar samples. Depth profiling by XPS is a destructive technique because of the need to sputter.

C.5 Scanning electron microscopy (SEM)

SEM is one of the two imaging techniques used in this study. The scattering of electrons from the surface of the sample allows the formation of a topographical image of the surface. The resolution can be as low as a few nm and magnifications range from 10x to 300,000x. A complete review of the SEM technique can be found in (Postek et al., 1980).

C.5.1 Theory of SEM

An electron beam is focused on the sample and rastered over the surface. The energy of these electrons generally ranges from 5-25 kV. The electrons emitted or backscattered from the surface are detected and the output is mapped onto a cathode ray tube screen. The images are primarily formed from secondary electrons. These are low energy (<50V) electrons which were generated in the solid by inelastic collisions with the primary electrons. Because of their low energy, only electrons from near the surface can escape to form the image. The detector has a small bias on it to accelerate the secondary electrons toward the detector. The yield of secondary electrons does not depend on the atomic number of the elements in the sample, but it does increase with decreasing angle of incidence. This is one of the reasons why topography can be observed.

The interaction of the primary electrons with the sample also results in backscattered electrons. These are electrons which have undergone elastic interactions with the nucleus of an atom in the sample. These electrons have much more energy, therefore their

trajectories are not affected by the bias on the detector. Some of the backscattered electrons will be detected in the secondary electron image. Measurements of the backscattered electron yield are useful because the yield varies with the atomic number of the element from which the electron was scattered. The higher the atomic number, the higher the yield of backscattered electrons. A backscattered electron image can be made by putting a grid with a -50 V bias between the sample and the electron detector. This will repel all of the low energy secondary electrons. The contrast in the image will then be due primarily to the different atomic numbers of elements in the sample.

The interaction of the primary electrons with the sample also generates Auger electrons, photoelectrons, and x-rays. When an inner core electron is removed, the atom can relax via the Auger process or by emitting an x-ray with a characteristic energy. Many scanning electron microscopes are equipped with x-ray detectors in order to do elemental analysis. This technique is called energy dispersive spectroscopy (EDS). The primary electrons can generate x-rays quite deeply in the sample, thus the resolution of this type of elemental analysis is usually on the order of 0.5 μm .

C.5.2 Strengths and weaknesses of SEM

SEM is a good method for observing surface morphology of very small features. It is very intuitive because the observed image is similar to a visual image. The ability to do some elemental analysis using the backscattered electrons and x-rays is also useful.

One disadvantage is that the thin film/semiconductor interface can not be observed without significant sample preparation. In addition, composition gradients can not be determined on a small scale. Samples must be electrically conductive to form a good image. If only an image is desired, then the surface can be coated with a thin layer of

metal to aid in conduction. This metal coating, however, will interfere with elemental analysis.

C.6 Transmission electron microscopy (TEM)

TEM is a very complex and highly powerful technique, however sample preparation and analysis is very time consuming. It can provide a great deal of high resolution spatial information, but it is usually better to use other techniques to first determine the basic characteristics of the system. TEM is the only technique available to directly observe the microstructure at the interface, and it can also verify phase formation and epitaxial relationships. Because it is such a high magnification technique, only a small area of the interface can be observed, therefore the lateral homogeneity of the sample can not be determined unambiguously. There are many books explaining the technique, one which gives a good overview is (Thomas and Goringe, 1981). A very brief review will be given here.

In the TEM, a monoenergetic beam of electrons is incident upon a very thin sample. The electrons are diffracted as they travel through the material. Electromagnetic lenses are then used to focus the electron beams forming a diffraction pattern or an image. The diffraction pattern provides information about crystal structure, much in the same way as x-ray diffraction. The image of the sample can provide information about morphology, crystal structure, and epitaxy on an atomic scale. At the highest magnifications, the epitaxial relationships between the substrate and film can be observed. Atomic resolution TEM allows the direct imaging of columns of atoms down to approximately 1.5 Å.

Appendix D: Sputtering parameters

Metal	load	tune	forward power (W)	Target Bias (V)	Deposition Rate (Å/min)
Pt	860	995	300	1450	523
Pd	993	815	300	1350	475
Ni	870	979	300	1500	384
Au	870	957	300	1500	696
Ti	873	958	300	1450	230
Ta	925	850	300	1375	178
Mo	945	905	300	1350	287

8. References

- A.W. Adamson, *Physical Chemistry of Surfaces*, 5 ed. (John Wiley & Sons, 1990).
- K. Akimoto, T. Miyajima and Y. Mori, *Journal of Crystal Growth* **115**, 683 (1991).
- H. Amano, M. Kito, K. Hiramatsu and I. Akasaki, *Japanese Journal of Applied Physics* **28**, L2112 (1989).
- S.G. Anderson, F. Xu, M. Vos, J.H. Weaver and H. Cheng, *Physical Review B* **39**, 5079 (1989).
- J. Bardeen, *Physical Review* **71**, 717 (1947).
- V.M. Bermudez, T.M. Jung, K. Doverspike and A.E. Wickenden, *Journal of Applied Physics* **79**, 110 (1996).
- V.M. Bermudez, R. Kaplan, M.A. Khan and J.N. Kuznia, *Physical Review B* **48**, 2436 (1993).
- R. Beyers, *Journal of Applied Physics* **56**, 147 (1984).
- R. Beyers, K.B. Kim and R. Sinclair, *Journal of Applied Physics* **61**, 2195 (1987).
- R. Beyers, R. Sinclair and M.E. Thomas, *Journal of Vacuum Science and Technology B* **2**, 781 (1984).
- A.S. Bhansali, R. Sinclair and A.E. Morgan, *Journal of Applied Physics* **68**, 1043 (1990).
- S.C. Binari, H.B. Dietrich, G. Kelner, L.B. Rowland, K. Doverspike and D.K. Gaskill, *Electronics Letters* **30**, 909 (1994).
- J.B. Bindell, J.W. Colby, D.R. Wonsidler, J.M. Poate, D.K. Conley and T.C. Tisone, *Thin Solid Films* **37**, 441 (1976).
- C. Boney, Z. Yu, J. W.H. Rowland, W.C. Hughes, J. J.W. Cook and J.F. Schetzina, *Journal of Vacuum Science and Technology B* **14**, 2259 (1996).
- R.W. Bower, D. Sigurd and R.E. Scott, *Solid-State Electronics* **16**, 1461 (1973).
Smithells Metals Reference Book, Vol. , edited by E.A. Brandes and G.B. Brook (Butterworth-Heinemann Ltd., 1992).
- D. Briggs and M.P. Seah, *Practical Surface Analysis*, Vol. 1, 2 ed. (1990).

L.J. Brillson, Surface Science Reports **2**, 123 (1982).

L.J. Brillson, Surface Science **299/300**, 909 (1994).

R.K. Brow, R.E. Loehman and A.P. Tomsia, in *Metal-Ceramic Joining*, edited by P. Kumar and W. A. Greenhut (TMS, 1991), p. 229.

Encyclopedia of Materials Characterization, edited by C.R. Brundle, Jr., Charles A. Evans and S. Wilson (Butterworth-Heinemann, Boston, 1992).

W.D. Buckley and S.C. Moss, Solid-State Electronics **15**, 1331 (1972).

C. Canali, C. Catellani and M. Prudenziati, Applied Physics Letters **31**, 43 (1977).

C. Canali, F. Catellani, G. Ottaviani and M. Prudenziati, Applied Physics Letters **33**, 187 (1978).

R. Caron-Popowich, J. Washburn, T. Sands and A.S. Kaplan, Journal of Applied Physics **64**, 4909 (1988).

W.B. Carter and M.V. Papageorge, Journal of Vacuum Science and Technology A **10**, 3460 (1992).

J.D. Cawley, in *Metal-Ceramic Joining*, edited by P. Kumar and V. A. Greenhut (TMS, 1991), p. 3.

A.L. Chen, W. Walukiewicz, K. Duxstad and E.E. Haller, Applied Physics Letters **68**, 1522 (1996).

W. Chen, A. Kahn, P. Soukiassian, P.S. Mangat, J. Gaines, C. Ponzoni and D. Olego, Journal of Vacuum Science and Technology B **12**, 2639 (1994).

W.K. Chu, H. Kraütle, J.W. Mayer, H. Müller, M.-A. Nicolet and K.N. Tu, Applied Physics Letters **25**, 454 (1974).

W.K. Chu, J.W. Mayer and M.A. Nicolet, *Backscattering Spectrometry* (Academic Press, N.Y., 1978).

M. Clement, J.M. Sanz, A. Climent and J.M. Martinez-Duart, Surface and Interface Analysis **12**, 334 (1988).

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, Journal of Applied Physics **80**, 278 (1996).

- A. Continenza, S. Massidda and A.J. Freeman, *Physical Review B* **42**, 2904 (1990).
- R. Coratger, F. Ajuston, J. Beauvillain, I.M. Dharmadasa, C.J. Blomfield, K.A. Prior, J. Simpson and B.C. Cavenett, *Physical Review B* **51**, 2357 (1995).
- H. Cordes and Y.A. Chang, *MRS Internet Journal of Nitride Semiconductor Research* **2**, 2 (1997).
- C.A. Crider and J.M. Poate, *Applied Physics Letters* **36**, 417 (1980).
- B.D. Cullity, *Elements of X-ray Diffraction*, Second ed. (1978).
- F.R. deBoer, R. Boom, W.C.M. Mattens, A.R. Miedema and A.K. Niessen, *Cohesion in Metals: Transition Metal Alloys* (North-Holland, Amsterdam, 1958).
- L.R. Doolittle, *Nuclear Instrumentation Methods* **B15**, 227 (1986).
- D.L. Dreilus, B.P. Sneed, J. Ren, J.W. Cook, Jr., J.F. Schetzina and R.M. Kolbas, *Applied Physics Letters* **57**, 1663 (1990).
- J.-Y. Duboz, F. Binet, N. Laurent, E. Rosencher, F. Scholz, V. Harle, O. Briot, B. Gil and R.A. Aulombard, in *Study of GaN Schottky diodes*, Boston, 1996 (MRS).
- K.J. Duxstad, M.S. Thesis, University of California-Berkeley, 1994.
- N.V. Edwards, M.D. Bremser, J. T.W. Weeks, R.S. Kern, R.F. Davis and D.E. Aspnes, *Applied Physics Letters* **69**, 2065 (1996).
- T. Egawa, H. Ishikawa, T. Jimbo and M. Umeno, *Applied Physics Letters* **69**, 830 (1996).
- V.M. El-Boragy and K. Schubert, *Zeitschrift Fuer Metallkunde* **61**, 579 (1970).
- Y. Fan, J. Han, L. He, J. Saraie, R.L. Gunshor, M.M. Hagerott and A.V. Nurmikko, *Applied Physics Letters* **63**, 1812 (1993).
- Z. Fan, S.N. Mohammad, W. Kim, O. Aktas, A.E. Botchkarev and H. Morkoc, *Applied Physics Letters* **68**, 1672 (1996).
- D.J. Fertig and G.Y. Robinson, *Solid-State Electronics* **19**, 407 (1976).
- J.F. Fijol and P.H. Holloway, *Critical Reviews in Solid State and Materials Sciences* **21**, 77 (1996).

- J.J. Fijol, L.C. Calhoun, R.M. Park and P.H. Holloway, *Journal of Electronic Materials* **24**, 143 (1995).
- C. Fontaine, T. Okumura and K.N. Tu, *Journal of Applied Physics* **54**, 1404 (1983).
- J.S. Foresi and T.D. Moustakas, *Applied Physics Letters* **62**, 2859 (1993).
- U. Gösele and K.N. Tu, *Journal of Applied Physics* **53**, 3252 (1982).
- W. Götz, N.M. Johnson, D.P. Bour, M.D. McCluskey and E.E. Haller, *Applied Physics Letters* **69**, 3725 (1996).
- W. Götz, N.M. Johnson, R.A. Street, H. Amano and I. Akasaki, *Applied Physics Letters* **66**, 1340 (1995).
- R.L. Gunshor, J. Han, A.V. Nurmikko and A. Salokatve, *Journal of Crystal Growth* **150**, 790 (1995).
- J.D. Guo, M.S. Feng, R.J. Guo, F.M. Pan and C.Y. Chang, *Applied Physics Letters* **67**, 2657 (1995).
- J.D. Guo, C.I. Lin, M.S. Feng, F.M. Pan, G.C. Chi and C.T. Lee, *Applied Physics Letters* **68**, 235 (1996a).
- J.D. Guo, F.M. Pan, M.S. Feng, R.J. Guo, P.F. Chou and C.Y. Chang, *Journal of Applied Physics* **80**, 1623 (1996b).
- M.A. Haase, J. Qiu, J.M. DePuydt and H. Cheng, *Applied Physics Letters* **59**, 1272 (1991).
- P. Hacke, T. Detchprohm, K. Hiramatsu and N. Sawaki, *Applied Physics Letters* **63**, 2676 (1993).
- J. Han, R.L. Gunshor and A.V. Nurmikko, *Journal of Electronic Materials* **24**, 151 (1995).
- X. He, K. Tao and Y. Fan, *Journal of Vacuum Science and Technology A* **14**, 2564 (1996).
- V. Heine, *Physical Review A* **138**, 1689 (1965).
- B. Heying, X.H. Wu, S. Keller, Y. Li, D. Kapolnek, B.P. Keller, S.P. DenBaars and J.S. Speck, *Applied Physics Letters* **68**, 643 (1996).

F. Hiei, M. Ikeda, M. Ozawa, T. Miyajima, A. Ishibashi and K. Akimoto, *Electronics Letters* **29**, 878 (1993).

M.T. Hirsch, unpublished (1997).

M.T. Hirsch, K.J. Duxstad and E.E. Haller, *Electronics Letters* **33**, 95(1996).

P.S. Ho, T.Y. Tan, J.E. Lewis and G.W. Rubloff, *Journal of Vacuum Science and Technology* **16**, 1120 (1979).

B.D. Hunt, L.J. Schowalter, N. Lewis, E.L. Hall, R.J. Hauenstein, T.E. Schlesinger, T.C. McGill, M. Okamoto and S. Hashimoto, in *Thin Films Interfaces and Phenomena; Vol. 54*, edited by R. J. Nemanich, P. S. Ho, and S. S. Lau (Materials Research Society, 1986), p. 479.

G.A. Hutchins and A. Shepela, *Thin Solid Films* **18**, 343 (1973).

D.B. Ingerly, Y.A. Chang, N.R. Perkins and T.F. Kuech, *Applied Physics Letters* **70**, 108 (1997).

H. Ishikawa, S. Kobayashi, Y. Koide, S. Yamasaki, S. Nagai, J. Umezaki, M. Koike and M. Murakami, *Journal of Applied Physics* **81**, 1315 (1997).

H. Ishikawa, K. Tsukui, Y. Koide, N. Teraguchi, Y. Tomomura, A. Suzuki and M. Murakami, *Journal of Vacuum Science and Technology B* **14**, 1812 (1996).

E.V. Kalinina, N.I. Kuznetsov, V.A. Dmitriev, K.G. Irvine and J. C.H. Carter, *Journal of Electronic Materials* **25**, 831 (1996).

T.U. Kampen and W. Mönch, *MRS Internet Journal of Nitride Semiconductor Research* **1**, 41 (1996).

R. Kaplan, S.M. Prokes, S.C. Binari and G. Kelner, *Applied Physics Letters* **68**, 3248 (1996).

J. Karpinski, J. Jun and S. Porowski, *Journal of Crystal Growth* **66**, 1 (1984).

M.R.H. Khan, T. Detchprohm, P. Hacke, K. Hiramatsu and N. Sawaki, *Journal of Physics D: Applied Physics* **28**, 1169 (1995).

T.S. Kuan, J.L. Freeouf, P.E. Batson and E.L. Wilkie, *Journal of Applied Physics* **58**, 1519 (1985).

- O. Kubaschewski, C.B. Alcock and P.J. Spencer, *Materials Thermochemistry*, 6 ed. (Pergamon Press, Oxford, 1993).
- Metal-Ceramic Joining*, edited by P. Kumar and V.A. Greenhut (TMS, 1991).
- V. Kumar, *Journal of Physical Chemistry of Solids* **36**, 535 (1975).
- S. Kurtin, T.C. McGill and C.A. Mead, *Physical Review Letters* **22**, 1433 (1969).
- N.I. Kuzntsov, E.V. Kalinina, V.A. Soloviev and V.A. Dmitriev, in *Schottky barriers on p-GaN*, Boston, 1995 (MRS), p. 837.
- O. Lagerstedt, B. Monemar and H. Gislason, *Journal of Applied Physics* **49**, 2953 (1978).
- Y. Lansari, J. Ren, B. Sneed, K.A. Bowers, J.W. Cook, Jr. and J.F. Schetzina, *Applied Physics Letters* **61**, 2554 (1992).
- H. Lee, D.B. Oberman and J. James S. Harris, *Journal of Electronic Materials* **25**, 835 (1996).
- L.F. Lester, J.M. Brown, J.C. Ramer, L. Zhang, S.D. Hersee and J.C. Zolper, *Applied Physics Letters* **69**, 2737 (1996).
- S.D. Lester, F.A. Ponce, M.B. Craford and D.A. Steigerwald, *Applied Physics Letters* **66**, 1249 (1995).
- J.-C. Lin, K.-C. Hsieh, K.J. Schulz and Y.A. Chang, *Journal of Materials Research* **3**, 148 (1988a).
- J.-C. Lin, X.-Y. Zheng, K.-C. Hsieh and Y.A. Chang, in *Interfacial reactions between Ni and GaAs*, 1988b, p. 233.
- M.E. Lin, Z. Ma, F.Y. Huang, Z.F. Fan, L.H. Allen and H. Morkoc, *Applied Physics Letters* **64**, 1003 (1994).
- L.-M. Liu, G. Lindauer, W.B. Alexander and P.H. Holloway, *Journal of Vacuum Science and Technology B* **13**, 2238 (1995).
- Q.Z. Liu, K.V. Smith, E.T. Yu, S.S. Lau, N.R. Perkins and T.F. Kuech, in *On the epitaxy of metal films on GaN*, Boston, 1996 (MRS).
- S.G. Louie, J.R. Chelikowsky and M.L. Cohen, *Physical Review B* **15**, 2154 (1977).
- G.W. Ludwig and M. Aven, *Journal of Applied Physics* **38**, 5326 (1967).

- B.P. Luther, S.E. Mohny, T.N. Jackson, M.A. Khan, Q. Chen and J.W. Yang, *Applied Physics Letters* **70**, 57 (1997).
- R. Madar, G. Jacob, J. Hallais and R. Fruchart, *Journal of Crystal Growth* **31**, 197 (1975).
- T. Marshall, S. Colak and D. Cammack, *Journal of Applied Physics* **66**, 1753 (1989).
- W.C. Maskell, N.M. Sammes and B.C.H. Steele, *Journal of Physics D: Applied Physics* **20**, 99 (1987).
- T. Matsuoka, A. Ohki, T. Ohno and Y. Kawaguchi, *Journal of Crystal Growth* **138**, 727 (1994).
- C.A. Mead, *Physics Letters* **18**, 218 (1965).
- C.A. Mead, in *Symposium on Ohmic Contacts: Ohmic Contacts on Semiconductors*, edited by B. Schwartz (Electronics Division Electrochemical Society, New York, 1969), p. 3.
- S. Miller and P.H. Holloway, *Journal of Electronic Materials* **25**, 1709 (1996).
- S.N. Mohammad, Z. Fan, A.E. Botchkarev, W. Kim, O. Aktas, A. Salavador and H. Morkoc, *Electronics Letters* **32**, 598 (1996).
- S.E. Mohny and X. Lin, *Journal of Electronic Materials* **25**, 811 (1996).
- W. Mönch, *Semiconductor Surfaces and Interfaces* (Springer-Verlag, Berlin, 1993).
- B.A. Morgan, K.M. Ring, K.L. Kavanagh, A.A. Talin, R.S. Williams, R. Yasuda, T. Yasui and Y. Segawa, *Journal of Vacuum Science and Technology B* **14**, 1238 (1996).
- T. Mori, T. Kozawa, T. Ohwaki, Y. Taga, S. Nagai, S. Yamasaki, S. Asami, N. Shibata and M. Koike, *Applied Physics Letters* **69**, 3537 (1996).
- N.F. Mott, *Proceedings of the Cambridge Philosophical Society* **34**, 568 (1938).
- Z.A. Munir and A.W. Searcy, *The Journal of Chemical Physics* **42**, 4223 (1965).
- S.P. Murarka, *Solid-State Electronics* **17**, 869 (1974).
- H. Muta and D. Shinoda, *Journal of Applied Physics* **43**, 2913 (1972).
- J.V. Naidich, *Progress in Surface and Membrane Science* **14**, 354 (1981).

S. Nakamura, in *III-V Nitrides*, edited by T. Moustakas, I. Akasaki, B. Monemar, and F. Ponce (Materials Research Society, 1996).

S. Nakamura, N. Iwasa, M. Senoh and T. Mukai, *Japanese Journal of Applied Physics* **31**, 1258 (1992).

S. Nakamura, T. Mukai and M. Senoh, *Japanese Journal of Applied Physics* **30**, L1998 (1991).

Shuji Nakamura, Takashi Mukai and Masayuki Senoh, *Applied Physics Letters* **64**, 1687 (1994).

S. Nakamura, M. Senoh, S.-I. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku and Y. Sugimoto, *Japanese Journal of Applied Physics* **35**, L74 (1996a).

S. Nakamura, M. Senoh, S.-I. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto and H. Kiyoku, *Applied Physics Letters* **69**, 1477 (1996b).

K. Nakano, unpublished (1996).

R.J. Nemanich, C.C. Tsai, B.L. Stafford, J.R. Abelson and T.W. Sigmon, in *Thin Films and Interfaces II; Vol. 25*, edited by J. E. E. Baglin, D. R. Campbell, and W. K. Chu (Materials Research Society, 1984), p. 9.

Gertrude F. Neumark, Robert M. Peck and James M. DePuydt, *Physics Today* **June**, 26 (1994).

N. Newman, J. Ross and M. Rubin, *Applied Physics Letters* **62**, 1242 (1993).

Joining of Ceramics, edited by M.G. Nicholas (Chapman and Hall, 1990).

M.G. Nicholas and D.A. Mortimer, *Materials Science and Technology* **1**, 657 (1985).

M. Ogawa, *Thin Solid Films* **70**, 181 (1980).

K. Ohkawa, T. Karasawa and T. Mitsuyu, *Japanese Journal of Applied Physics* **30**, L152 (1991).

M. Ohring, *The Materials Science of Thin Films* (Academic Press, Inc., Boston, 1992).

H. Okuyama, S. Itoh, E. Kato, M. Ozawa, N. Nakayama, K. Nakano, M. Ikeda, A. Ishibashi and Y. Mori, *Electronics Letters* **30**, 4 (1994).

- J.O. Olowolafe, P.S. Ho, H.J. Hovel, J.E. Lewis and J.M. Woodall, *Journal of Applied Physics* **50**, 955 (1979).
- M. Osinski, J. Zeller, P.-C. Chiu, B.S. Phillips and D.L. Barton, *Applied Physics Letters* **69**, 898 (1996).
- G. Ottaviani, *Journal of Vacuum Science and Technology* **16**, 1112 (1979).
- C.J. Palmstrom and T.D. Sands, in *Contacts to Semiconductors*, edited by L. J. Brillson (Noyes Publications, Park Ridge, NJ, 1993), p. 67.
- R.M. Park, T.M. Troffer, C.M. Rouleau, J.M. DePuydt and M.A. Haase, *Applied Physics Letters* **57**, 2127 (1990).
- L. Pauling, *The nature of the chemical bond*, 3 ed. (Cornell University Press, Ithaca, New York, 1960).
- S. Pearton, C.R. Abernathy, F. Ren and J.R. Lothian, *Journal of Applied Physics* **76**, 1210 (1994).
- S.J. Pearton, V.K. Chakrabarti, A. Perley and K.S. Jones, *Journal of Applied Physics* **68**, 2760 (1990).
- R. Peddada, K. Sengupta, I.M. Robertson and H.K. Birnbaum, in *Metal-Ceramic Interfaces; Vol. 4*, edited by M. Ruhle, A. G. Evans, M. F. Ashby, and J. P. Hirth (Pergamon Press, New York, 1990), p. 115.
- J.C. Phillips, *Bonds and bands in semiconductors* (Academic Press, New York, 1973).
- A.T. Ping, A.C. Schmitz, M.A. Khan and I. Adesida, in *Effects of Reactive Ion Etching on the Electrical Properties of n-GaN Surfaces*, Boston, 1995 (MRS), p. 769.
- J.M. Poate and T.C. Tisone, *Applied Physics Letters* **24**, 391 (1974).
- M.T. Postek, K.S. Howard, A.H. Johnson and K.L. McMichael, *Scanning Electron Microscopy: A Student's Handbook* (Ladd Research Industries, Inc., 1980).
- R. Pretorius, *Journal of the Electrochemical Society* **128**, 107 (1981).
- J. Qiu, H. Cheng, J.M. DePuydt and M.A. Haase, *Journal of Crystal Growth* **127**, 279 (1993).
- E.H. Rhoderick and R.H. Williams, *Metal-Semiconductor Contacts*, Vol. 19, 2 ed. (Clarendon Press, Oxford, 1988).

- S. Ruvimov, Z. Liliental-Weber, W. Swider, J. Washburn, E. Bourret, K.J. Duxstad and E.E. Haller, *Journal of Vacuum Science and Technology* (1996a).
- S. Ruvimov, Z. Liliental-Weber, J. Washburn, K.J. Duxstad, E.E. Haller, Z.-F. Fan, S.N. Mohammad, W. Kim, A.E. Botchkarev and H. Morkoc, *Applied Physics Letters* **69**, 1556 (1996b).
- T. Sands, *Materials Science and Engineering B* **1**, 289 (1989).
- T. Sands and V.G. Keramidas, in *Handbook on Semiconductors; Vol. 3*, edited by T. S. Moss and S. Mahajan (Elsevier Science Publishers, 1994).
- T. Sands, V.G. Keramidas, A.J. Yu, K.-M. Yu, R. Gronsby and J. Washburn, *Journal of Materials Research* **2**, 262 (1987a).
- T. Sands, V.G. Keramidas, K.M. Yu, J. Washburn and K. Krishnan, *Journal of Applied Physics* **62**, 2070 (1987b).
- R. Schmid-Fetzer, *Journal of Electronic Materials* **17**, 193 (1988).
- A.C. Schmitz, A.T. Ping, M.A. Khan and I. Adesida, in *Schottky barrier heights of Ni, Pt, Pd, and Au on n-type GaN*, Boston, 1995 (MRS), p. 831.
- A.C. Schmitz, A.T. Ping, M.A. Khan, Q. Chen, J.W. Yang and I. Adesida, *Electronics Letters* (1996a).
- A.C. Schmitz, A.T. Ping, M.A. Khan, Q. Chen, J.W. Yang and I. Adesida, *Semiconductor Science and Technology* **11**, 1464 (1996b).
- W. Schottky, *Zeitschrift für Physik* **14**, 63 (1923).
- W. Schottky, *Naturwissenschaften* **26**, 843 (1938).
- W. Schottky and W. Deutschmann, *Physikalische Zeitschrift* **30**, 839 (1929).
- D.K. Schroeder, *Semiconductor Material and Device Characterization* (1990).
- R.J. Shul, G.B. McClellan, S.J. Pearton, C.R. Abernathy, C. Constantine and C. Barratt, *Electronics Letters* **32**, 1408 (1996).
- D. Sigurd, R.W. Bower, W.F. VanDerWeg and J.W. Mayer, *Thin Solid Films* **19**, 319 (1974).

- A.K. Singh, M.M. Srivastava and O.N. Srivastava, *Journal of the Less-Common Metals* **57**, 225 (1978).
- J.M. Slaughter, W. Weber, G. Guntherodt and C.M. Falco, *MRS Bulletin* **December** (1992).
- L.L. Smith, M.D. Bremser, E.P. Carlson, J. T.W. Weeks, Y. Huang, M.J. Kim, R.W. Carpenter and R.F. Davis, in *Ohmic contacts formation to doped GaN*, Boston, 1995 (MRS), p. 861.
- L.L. Smith, R.F. Davis, M.J. Kim, R.W. Carpenter and Y. Huang, *Journal of Materials Research* **11**, 2257 (1996a).
- L.L. Smith, S.W. King, R.J. Nemanich and R.F. Davis, *Journal of Electronic Materials* **25**, 805 (1996b).
- W.E. Spicer, P.W. Chye, P.R. Skeath, C.Y. Su and I. Lindau, *Journal of Vacuum Science and Technology* **16**, 1422 (1979).
- K. Suganuma, in *Joining of Ceramics*, edited by M. G. Nichols (Chapman and Hall, London, 1990), p. 173.
- R.A. Swalin, *Thermodynamics of Solids* (John Wiley and Sons, Inc., New York, 1962).
- S.M. Sze, *Physics of Semiconductor Devices*, 2 ed. (John Wiley & Sons, Inc., 1981).
- G. Thomas and M.J. Goringe, *Transmission Electron Microscopy of Materials* (John Wiley & Sons, 1981).
- J.A. Thornton and D.V. Hoffman, *Thin Solid Films* **171**, 5 (1989).
- C.D. Thurmond and R.A. Logan, *Journal of the Electrochemical Society* **119**, 622 (1972).
- S. Tomiya, E. Morita, M. Ukita, H. Okuyama, S. Itoh, K. Nakano and A. Ishibashi, *Applied Physics Letters* **66**, 1208 (1995).
- J.T. Trexler, S.J. Miller, P.H. Holloway and M.A. Khan, in *Interfacial reactions between metal thin films and p-GaN*, Boston, 1995 (MRS), p. 819.
- J.T. Trexler, S.J. Pearton, P.H. Holloway, M.G. Mier, K.R. Evans and R.F. Karlicek, in *Comparison of Ni/Au, Pd/Au, and Cr/Au metallizations for ohmic contacts to p-GaN*, Boston, 1996 (MRS).
- K.N. Tu, *Applied Physics Letters* **27**, 221 (1975).

- K.N. Tu, Annual Reviews of Materials Science **15**, 147 (1985).
- C.B. Vartuli, S.J. Pearton, C.R. Abernathy, J.D. MacKenzie, E.S. Lambers and J.C. Zolper, Journal of Vacuum Science and Technology B **14**, 3523 (1996).
- M. Vos, F. Xu, S.G. Anderson, J.H. Weaver and H. Cheng, Physical Review B **39**, 10744 (1989).
- L. Wang, M.I. Nathan, T.-H. Lim, M.A. Khan and Q. Chen, Applied Physics Letters **68**, 1267 (1996).
- L.C. Wang, P.H. Hao and B.J. Wu, Applied Physics Letters **67**, 509 (1995).
- Y.X. Wang and P.H. Holloway, Vacuum **43**, 1149 (1992).
- Y.-X. Wang and P.H. Holloway, Journal of Vacuum Science and Technology B **2**, 613 (1984).
- A.D. Westwood and M.R. Notis, in *Advances in Ceramics, Vol. 26*, 171 (1989).
- W.D. Westwood, MRS Bulletin **December**, 46 (1988).
- J.A. Wolk, J.W. Ager III, K.J. Duxstad, E.E. Haller, N.R. Taskar, D.R. Dorman and D.J. Olego, Applied Physics Letters **63**, 2756 (1993).
- Y. Wu, W. Jiang, B. Keller, S. Keller, D. Kapolnek, S. Denbaars and U. Mishra, in *Low resistance Ohmic contact to GaN with a separate layer method*, Nagoya, Japan, 1995 (IEEE), p. D.
- W. Xie, D.C. Grillo, R.L. Gunshor, M. Kobayashi, G.C. Hua, N. Otsuka, H. Jeon, J. Ding and A.V. Nurmikko, Applied Physics Letters **60**, 463 (1992a).
- W. Xie, D.C. Grillo, R.L. Gunshor, M. Kobayashi, H. Jeon, J. Ding, A.V. Nurmikko, G.C. Hua and N. Otsuka, Applied Physics Letters **60**, 1999 (1992b).
- T. Yasuda, I. Mitsuishi and H. Kukimoto, Applied Physics Letters **55**, 1103 (1988).
- K.M. Yu, J.M. Jaklevic and E.E. Haller, Nuclear Instruments and Methods, **B10/11**, 606 (1985).
- K.M. Yu, J.M. Jaklevic and E.E. Haller, in *Investigation of metal/GaAs reactions by heavy ion Rutherford backscattering spectrometry (RBS)*, 1986, p. 281.

L.R. Zheng, L.S. Hung and J.W. Mayer, in *Thin Films Interfaces and Phenomena*; Vol. 54, edited by R. J. Nemanich, P. S. Ho, and S. S. Lau (Materials Research Society, 1986), p. 45.