INVESTIGATION OF 4H AND 6H-SiC THIN FILMS AND SCHOTTKY DIODES USING DEPTH-DEPENDENT CATHODOLUMINESCENCE SPECTROSCOPY

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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***************

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2006

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ABSTRACT

Replacing Si with wide band gap (WBG) semiconductors in power electronics is expected to have a major technological impact in the energy and transport industries. SiC-based devices have already been introduced, but their performance and development has been challenged by the material degradation and problems in further producing reliable contacts and high-quality interfaces.

This dissertation investigates the native defects on SiC surfaces and interfaces using nanoscale sensitive techniques. The effect of such defects on the performance of the devices is also investigated. The effect of the processing steps on the defect formation and structural changes is studied. Critical annealing conditions and doping levels are established for the spontaneous formation of stacking faults and associated deep level defects. Localized states at the metal-semiconductor interfaces are studied for both reactive and non-reactive metals. Analogous nanoscale studies of SiC defects and their correlation with Schottky diode electrical properties are planned on a diode-per-diode basis.

This research is expected to produce greater understanding of localized interface state formation and methods to control them. Such control is required for the SiC devices to achieve their expected performance.
Dedicated to Katya and myself
ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my advisor, Professor Leonard Brillson, for his guidance and support throughout my research at the Ohio State University. His never-ending enthusiasm and the ability to appreciate every result has been a constant source of encouragement. I am also grateful for a time, patience and tolerance Professor Brillson has afforded me.

I would also like to acknowledge my great high school teachers Alex Rosenwine and Isaac Kushnir who have helped to jumpstart my journey from winning science Olympiads to completing PhD degree.

I am grateful to my fellow graduate students and researchers in the group Yuri Strzhemechny, Gregg Jessen, Shawn Bradley, Brad White, Steve Goss, Min Gao and Dennis Walker for their various input and diverse experience they have shared with me. Thanks to all my friends including Andrey Bezugly, Helen Pushkarski, Vadim Stakhursrki, Zenya Tsurikova, Taras and Katya Kirichenko, Andrey and Larisa Stepanov, Julia Bezugla, Ruben and Katya Ter-Antonian, Sergey Knysh and many others for their support and making my graduate school experience a memorable and enjoyable. I am grateful to my family, and particularly my grandparents Julia and Vasillii Halimon, for their unconditional love and support. I also would like to thank my wife Katsiaryna for always being there for me and sharing all the joys and hardships during our graduate and professional school careers.
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L. J. Brillson, S. Tumakha, R. S. Okojie, M. Zhang, and P. Pirouz, “SiC studied

FIELDS OF STUDY

Major Field: Electrical Engineering
Physical Electronics
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CHAPTER 1: OVERVIEW

There is considerable interest in silicon carbide due to its favorable properties for a variety of demanding device applications involving high temperature, high frequency, and high power operation. SiC has a unique combination of high bandgap, high thermal conductivity, high critical electric field, and high saturated carrier mobility that makes it especially suitable for use in such device applications.

The mechanical and chemical properties of silicon carbide also make it attractive for micromechanical applications. The development of high temperature electronics and sensors is highly anticipated in the aircraft, aerospace, automotive, and power distribution industries. Replacing the conventional electronics that monitor performance in aircraft engines with SiC technology would eliminate the costly cooling and extra wiring interconnections associated with such monitors. In the automotive industry SiC could also improve reliability and cost by placing performance sensors in direct contact with hot parts of the engine. For vehicle utilizing electric power drive, whether it is as a hybrid car, subway system, or submarine, the higher stand off voltages, faster switching, lower weight and lower parasitic resistance offer considerable power efficiency improvements. Similar advantages are also expected for space probe applications and wireless communications.

The recent development of silicon carbide nanotubes offers the advantages of silicon carbide for the world of nanoapplications. Thus silicon carbide also becomes an
essential semiconductor for single-crystal harsh-environment nanoelectronics, nanosensors with a variety of applications including biological and chemical-sensing applications.

Power electronics, where the highest impact of SiC development is expected, is concerned with controlling and modifying the flow of electrical energy between source and loads. Such devices must be designed to handle the specific operating condition dictated by the voltage, current and dynamic parameters. Among various types of power control devices, switches and rectifiers are those that would benefit most from progress in solid-state technology.

SiC power devices now include Schottky diode, p-n diode, JBS diode (a variation of the two), unipolar transistors such as MOSFET, MESFET, JFET, and their variations, bipolar junction transistors, p-n-p-n devices such as thyristor and IGBT. Beyond the apparent favorable prospects of the SiC technology, depending on the technology used, such devices suffer from problems and defects that limit the full performance of SiC devices.

For bipolar devices, a major problem is the quality and stability of the material itself. Stacking fault formation under the forward-bias operation, during processing or even growth steps leads to device failures. The problems with producing the stable Schottky contacts affect the properties and reliability of Schottky diodes and MESFET based structures. For MOSFET, the challenge is in the low carries mobilities in the channel caused by the high density of traps on the oxide/SiC interface. In addition, the problems with low resistivity ohmic contacts degrade the performance of all such SiC devices.
Further progress in SiC microelectronics requires a fundamental understanding of several issues. What kinds of interface states are created at the metal-semiconductor junctions? How do they affect the electrical properties of the contacts? What are the conditions for the formation of structural defects such as stacking faults and how can these be avoided? What is the nature of the SiO₂/SiC interface states and what is the mechanism of their removal? The search for answers to these questions will be the subject of this dissertation.
CHAPTER 2: SIC PROPERTIES

2.1 Natural mineral Moissanite, the first synthesis of Carborundum

Unlike many minerals, SiC was largely unknown before the Industrial age because of its rare occurrence in nature. The first observation of SiC in nature belongs to Henri Moissan, who described the inclusions in the iron meteorite in Arizona as silicon carbide based on his previous experience with SiC synthesis in the lab. The mineral became to be known as Moissanite, and since then, the presence of SiC in other natural formations such as diamond pipes, or volcanic breccia, or in rock-forming material found as a beach pebble, has been described.

Although it is scarce on Earth, SiC compound can be found in stardust grains predating the solar system. Molecular condensation of SiC particles is thought to be possible in the atmospheres of the carbon red giants and material ejected from supernova. Isotope analysis of the Murray and the Murchison meteorite containing such SiC grains suggest their origin is closer to the center of the galaxy than the solar system.

It was only after Eugen G. Acheson produced SiC while trying to crystallize carbon to create diamonds and patented the process, that SiC became widely available and used in industry. However, the first suggestion about the possibility of having compounds with Si bonded to C belongs to Jöhn Jacob Berzelius who came to such
conclusion during his work on diamond synthesis\textsuperscript{16}. The crystals that Acheson obtained by dissolving carbon in aluminum silicate became known as “carborundum”. The word originates from “carbon” and “corundum” \(\text{Al}_2\text{O}_3\) used to synthesize the material. Under this trademark SiC is still used as the abrasive material for grinding and cutting purposes.

\textbf{2.2 Semiconductor properties of silicon carbide}

The acknowledgement of the useful electrical properties of SiC goes back to 1907, when H.J. Round observed the light emission of yellow, green, orange and blue colors near a negative electrical contact to the carborundum crystal\textsuperscript{17}, thus producing the first SiC light emitting diode.

\textbf{2.2.2 Potential advantages of SiC electronic applications. Comparison of SiC- and GaN-based power electronic devices}

Wide bandgap semiconductor materials have superior electric properties compared to Si. First of all, wide bandgap of SiC polytypes and GaN means that these semiconductors start showing intrinsic behavior at higher temperatures than conventional materials, such as Si and GaAs. When intrinsic behavior dominates, the electrical differences between the n and p regions vanish and the p-n junctions become ineffective in controlling carrier transport. Therefore devices need to be cooled to remain functional but devices using wide bandgap SiC and GaN need less cooling structures that maximize heat extraction.

The high bandgap also means high breakdown fields. A higher electric breakdown field results in higher breakdown voltage and therefore should eliminate the need for series stacking of devices and associated stacking difficulties. For example, p-n diode
breakdown voltage is expressed by \( V_{B,pn} = \frac{\epsilon_r E_c^2}{2qN_d} \). Therefore, for the similar doping density \( N_d \), 7.3 times higher critical field of 4H-SiC results in 46-fold increase in the breakdown voltage compared to Si diode, but, as follows from the basic material properties of GaN and two most used SiC polytypes in Table 1, the blocking voltage of GaN is higher, i.e., \( V_{B,pm}^{GaN} / V_{B,pm}^{4H-SiC} = 3 \). In addition, higher doping levels are possible with higher bandgap, thus, increasing breakdown voltage even further. 19

The two most widely used SiC polytypes have similar properties, but 4H-SiC has become more preferred since it does not exhibit the anisotropy of 6H-SiC. Therefore, 4H-SiC mobilities are identical along two crystallographic planes of the semiconductor.

<table>
<thead>
<tr>
<th>Property</th>
<th>Si</th>
<th>4H-SiC</th>
<th>6H-SiC</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap ( E_g ) (eV)</td>
<td>1.12</td>
<td>3.27</td>
<td>3.03</td>
<td>3.45</td>
</tr>
<tr>
<td>Breakdown field ( E_c ) (MV/cm)</td>
<td>0.25</td>
<td>2.2</td>
<td>2.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Electron mobility ( \mu_n ) (cm²/Vs)</td>
<td>135</td>
<td>650/0</td>
<td>370/370</td>
<td>900/2000(2D)</td>
</tr>
<tr>
<td>Thermal conductivity ( \chi ) (W/cm K)</td>
<td>1.5</td>
<td>4.5</td>
<td>4.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Dielectric constant ( \epsilon_r )</td>
<td>11.8</td>
<td>10.1</td>
<td>9.66</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table 1. Physical characteristics of SiC polytypes and GaN compared to Si. 20

Another advantage of the higher electric field is width reduction of drift region of the devices. The required drift region width could be estimated as \( W = \frac{2V_B}{E_c} \). 21

Comparing 4H-SiC and Si diodes with the same breakdown voltage, we get a 7.3-fold drift region width reduction, while \( W_{GaN}^{4H-SiC} / W_{Si}^{4H-SiC} = 0.55 \). If one neglects contact and
channel resistances, the on-resistance of the drift region in the unipolar devices can be estimated as 

\[ R_{on,sp} = \frac{4(V_g)^2}{\varepsilon_r(E_c)^3 \mu_n} \]

in the approximation of high breakdown voltage. Again, the on-resistance of the drift region of 4H-SiC devices is expected to be \( \sim 10 \) times less than in similar Si devices. Similarly, GaN and 4H-SiC on-resistances are related as 

\[ R_{on,sp}^{GaN} / R_{on,sp}^{4H-SiC} \approx 1.3 \]

Lower on-resistance means lower conduction losses and higher overall device efficiency.

Another useful way to quantify relative advantages of WBG materials for electronic performance is to compare figures of merit (FOM). Some of them are listed in Table 2, where \( E_C \) stands for critical field, \( V_G \) is the bandgap, \( T_{j,max} \) is the maximum junction temperature, and \( \lambda \) is thermal conductivity.
<table>
<thead>
<tr>
<th>Figure of Merit</th>
<th>Si</th>
<th>4H-SiC</th>
<th>6H-SiC</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>JFM (ultimate high frequency capability) ( (E_c \nu_{sat})^2 )</td>
<td>1</td>
<td>280</td>
<td>210</td>
<td><strong>756</strong></td>
</tr>
<tr>
<td>BFM (specific on resistance in FET drift reg.) ( \epsilon \mu E_c^3 \sim 1/R_{on,sp} )</td>
<td>1</td>
<td><strong>220</strong></td>
<td>125</td>
<td>190</td>
</tr>
<tr>
<td>FSFM (FET switching speed) ( \mu E_c^2 \sqrt{E_G} )</td>
<td>1</td>
<td>60</td>
<td>30</td>
<td><strong>65</strong></td>
</tr>
<tr>
<td>BSFM (bipolar switching speed) ( f_b = 1/RC_{in,sp}C_{in,sp} = \mu E_c^3 V_G^{1/2} / 2V_B^{3/2} )</td>
<td>1</td>
<td>13</td>
<td>13</td>
<td><strong>52.5</strong></td>
</tr>
<tr>
<td>FPFM (FET power handling capacity) ( \sqrt{\lambda(T_{J,max} - T_C)\mu E_c^3} )</td>
<td>1</td>
<td><strong>56</strong></td>
<td>48</td>
<td>30.5</td>
</tr>
<tr>
<td>FTFM (FET power switching product) ( \sqrt{\lambda(T_{J,max} - T_C)\mu E_c^3 E_G} )</td>
<td>1</td>
<td><strong>3500</strong></td>
<td>1500</td>
<td>2000</td>
</tr>
<tr>
<td>BPFM (bipolar power handling) ( \lambda E_c(T_{J,max} - T_C)/E_G )</td>
<td>1</td>
<td><strong>35.5</strong></td>
<td>57</td>
<td>11</td>
</tr>
<tr>
<td>BTFM (bipolar power switching product) ( \lambda D_{max}E_c^3(T_{J,max} - T_C)/E_G )</td>
<td>1</td>
<td>460</td>
<td>750</td>
<td><strong>560</strong></td>
</tr>
</tbody>
</table>

Table 2. Main figures of merit of SiC and GaN compared to Si. FOMs normalized to Si with larger number represent better performance. The best performing materials for each category are highlighted. Source –ref. 19,22

Based on the figures of merit above, the comparison of GaN Schottky diodes with SiC Schottky and Si p-n diodes at similar blocking voltages shows a performance advantage for the GaN Schottky diode. It is also an important property of the device to have negligible reverse recovery current and consequently lower switching loss.\(^2\) Lower switching losses also mean the device can operate at higher frequencies. GaN and SiC have similar switching properties and electron transport properties, including good
mobility and high saturated drift velocity; but, as the temperature increases, the switching performance of GaN diode surpasses the performance of SiC diode.\textsuperscript{23} Therefore, GaN can outperform SiC in microwave applications.

2.2.2.1 Device design flexibility

The strongest advantage of GaN over SiC is the heterostructure technology GaN can support. Quantum wells, modulation-doped heterointerfaces, and heterojunction structures can be realized using GaN and related nitrides giving access to new operation regimes for the electronic devices.\textsuperscript{2} Since SiC devices are hindered from the advantages of the high carrier mobility in a 2D confined electron gas, the use of silicon carbide MESFETs is limited to the applications below 3.5 GHz.\textsuperscript{24}

One of the most attractive properties of SiC is its excellent chemical stability and high melting point which make it a leading material for harsh chemical and high temperature conditions. GaN properties also include high mechanical and thermal stability, as well as large piezoelectric constants and the possibility of passivation by forming a thin layer of sapphire or gallium oxide.

When compared to other wide-bandgap semiconductors including GaN, silicon carbide has an additional advantage. Similarly to Si, silicon carbide’s native oxide is SiO\textsubscript{2}, which could be grown by simple thermal oxidation. That means that SiC can be processed in a similar way as Si. The only distinction is higher growth temperatures. For GaN the studies are under way to find a suitable oxide.
An additional strength of SiC is its thermal conductivity, which is roughly four times higher than that of GaN. This property is especially important in high-power, high-temperature applications. While growing GaN on SiC wafers may increase the overall thermal conductivity of GaN devices, it still does not equal the conductivity of SiC made devices.

Another property to consider in p-n diode structures is a forward voltage drop that is the voltage needed to collapse depletion region. Since the forward voltage required to overcome the p-n junction’s contact potential scales with band gap, it is higher in the GaN Schottky diode than a similar SiC diode because of GaN’s wider bandgap. The lower forward voltage drop is essential to minimize on-state losses in the power converter.

2.2.2.2 Wide Bandgap Device applications and reliability

2.2.2.2.1 SiC devices

SiC power devices now include Schottky diodes, p-n diodes, as well as JBS diodes as the variations of the two, unipolar transistors such as MOSFET, MESFET, JFET, and their variations, bipolar junction transistors, and p-n-p-n devices such as thyristor and IGBT.

In spite of the promising prospects of the SiC technologies, depending on the technology used, the devices suffer from problems that limit their full performance. For bipolar devices, a major problem is the quality and stability of the material itself. Stacking fault formation under the forward-bias operation, during processing or
even growth steps leads to device failures. The problems in producing the stable Schottky contacts affect the properties and reliability of Schottky diodes and MESFET based structures.

For MOSFET, the challenge is in the low carrier mobilities in the channel caused by the high density of traps on the oxide/SiC interface. The low mobility is considered to be related to the observed high density of the interface traps,\textsuperscript{28,29} which are especially high near 4H-SiC/SiO\textsubscript{2} interfaces. Interfacial defects do not only degrade the device performance, they also reduce reliability, especially under the extreme conditions the devices are expected to operate. The reduction of the interface states is therefore a prime task in the development of SiC MOS technology.

In addition, the problems with achieving low resistivity ohmic contacts degrade the performance of all such SiC devices. The stability of contacts under high temperature stress also needs to be addressed.

\textbf{2.2.2.2 GaN devices}

GaN-based devices now include AlGaN/GaN heterostructure field effect transistors (HFET), AlGaN/GaN heterojunction bipolar transistors (HBT), GaN metal-oxide semiconductor field effect transistors (MOSFET), and both Schottky and p-i-n AlGaN power rectifiers.

In the typical HFET structures, AlGaN is grown on top of GaN with the Ga face at the surface. The piezoelectric effect drives electrons towards the two dimensional electron gas at the interface. Putting strained InGaN quantum well between the strained AlGaN barrier and relaxed n-GaN layer could further enhance the sheet electron concentration.
The problems with HFET device development arise from the lack of understanding of and control over two-dimensional carrier sources. The carriers may originate from intentional and unintentional doping of the AlGaN layer as well as the polarization and piezoelectric effects.30

As it has been mentioned above, GaN unipolar devices have the potential for higher switching speed and larger standoff voltages than SiC. The combination of a switching device such as a thyristor with a power rectifier is a key component of inverter modules used in power control circuits. While metal-oxide-semiconductor turn-off thyristors made of SiC can be realized, the possibility of GaN/AlGaN that can provide superior performance is still in question. GaN is a direct gap material and therefore has a very short minority carrier lifetime. This presents a problem for devices with thick drift regions such as thyristors. Increasing Al concentration > 0.5 converts AlGaN to indirect semiconductor. Unfortunately, little is known about carrier lifetimes and the controlling doping for AlGaN with such high Al concentrations.16

Schottky and p-i-n GaN rectifiers are also of substantial interest. While p-i-n rectifiers are expected to have larger reverse blocking voltages, the Schottky rectifiers should have better switching speeds and higher forward turn-on voltages. However, the reverse leakage current in Schottky rectifiers is generally higher than expected from thermionic emission, due to defect states around the contact periphery. To reduce the leakage current and prevent breakdown, edge termination techniques are necessary. However, little has been studied about edge termination for GaN rectifiers.8

GaN MESFETs suffer from stability and gate sinking problems. Some of the difficulties may be overcome by using GaN-based MOSFET or metal-insulator-
semiconductor (MIS) FET. The GaN MOSFET and MISFET devices would provide lower leakage currents and reduce power consumption. The problem is to find the oxide or insulator that would produce the low interface states density. If the interface states density is high, the Fermi level will be pinned and inversion, i.e., accumulation of the carriers in the channel will be hindered.

2.2.2.3 Hybrid technology

Another promising technology is to use the advantages of both materials in hybrid GaN/SiC emitter/base approach. Since the minority carrier lifetime is much longer in the indirect band gap SiC, than in the direct band gap GaN, a higher base transport factor could be achieved. These devices would have a short base width, thus further enhancing the transport factor, and increasing the current gain. In addition SiC bipolar junction transistors with a wider bandgap emitter would have a large current gain due to larger emitter efficiency. The wider bandgap emitter restricts the diffusion of holes from the base to the emitter, resulting in high electron injection efficiency into the base. Additionally, the wider bandgap emitter allows the base to be heavily doped, thereby decreasing the base resistance and the sensitivity to the Early effect without sacrificing the emitter efficiency. Moreover, one avoids the current material difficulties associated with p-GaN by using the commercially available p-SiC. Gallium nitride is the natural choice for high bandgap emitter. Gallium nitride has not only higher bandgap (3.4eV) than SiC (2.9eV for 6H-SiC and 3.2eV for 4H-SiC), but it has a close lattice constant to SiC.

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\(^1\) The Early effect is caused by the reduction of base width in a bipolar transistor due to the widening of the base-collector junction at higher base-collector voltages. It can be observed on I-V characteristics as a slight increase of the collector current in the saturation region.
Admittedly, the growth of GaN directly on SiC is a challenge considering that great care must be taken to minimize minority carrier recombination at the emitter-base heterojunction, in order to obtain high emitter injection efficiency. However, n-p heterojunctions could be grown using n-type GaN directly on p-type SiC. Adding a SiC collector layer could provide high-temperature and high-power GaN/SiC HBTs that may achieve a high room temperature current gain of $>10^6$ and be able to operate at 520°C with a gain of 100.\textsuperscript{31,32,33} However, the presence of a deep defect level in the p-type SiC can significantly degrade the performance of GaN/SiC devices.\textsuperscript{34} Thus there are benefits and drawbacks in making GaN/SiC using 4H-SiC, which is favorable due to the larger energy band gap and superior electron mobility but unfavorable due to mid-gap state recombination at defects.

2.2.2.3 Availability

A critical parameter for a semiconductor’s commercial success is the availability of wafers. SiC wafers are available in diameters up to 7.5 cm. The best SiC wafers have less than one micropipe per square-centimeter; however, the most common wafers have fewer then ten micropipes per square-centimeter with less micropipes around the center of the wafer.

GaN boules are difficult to grow. Therefore, pure GaN wafers are not yet available. Instead GaN wafers are grown on sapphire or SiC. Silicon carbide is preferred substrate for power device applications, while sapphire for optical applications. The diameter and the thickness of the commercially available wafer is small in diameter and thickness.\textsuperscript{2}
There are no commercialized GaN-based devices yet. SiC Schottky diodes are available at ratings up to 20A at 600 V, or 10A at 1200 V. This is a significant improvement from Si diodes available at voltage ratings <300V, or GaAs Schottky diodes available at ratings up to 500V.

Overall SiC device technology is more advanced now than GaN technology. SiC device technology is leading both in research and commercialization. A lot of research needs to be done in order for GaN to become competitive with SiC in power applications. Commercial availability of GaN substrates would help in this regard.

2.3 The existence of “polytypie” in SiC

Silicon carbide has the ability to form a number of crystalline structures, different in the stacking of layers of identical structure and composition. Such a property is defined by the International Union of Crystallography (IUCr) as polytypism and is essentially a one-dimensional form of the polymorphism. IUCr specifies that in polytypes two-dimensional translations within the layers are preserved, while the lattice spacing normal to the layers can vary among different polytypes and defines the stacking period for each one.

Verma and Krishna point out another important distinction between polytypism and polymorphism, which is related to the thermodynamic considerations. Namely, the polymorphic variations of the same chemical compound form under different conditions of temperature and pressure with different ranges of thermodynamic stability and with different physical properties such as density. Therefore they can be regarded as different
phases of the same compound. At the same time a range of SiC polytypes can form at nearly identical thermodynamic parameters, often producing several polytypes in the same chunk of grown SiC\textsuperscript{37}. The density of many of the polytypes is also nearly identical.

### 2.3.1 Crystallography and structure

SiC is a IV-IV semiconductor, meaning that both Si and C atom belong to group IV elements. Each carbon atom is bonded to four silicon atoms (and vice versa) forming a tetragonal building block. The C-Si sp\textsuperscript{3} bond is very strong and 12\% ionic. The distance between closest carbon (or silicon) atoms is $a = 3.08\text Å$ for all polytypes \textsuperscript{36}. The distance between the closest silicon and carbon atoms can be estimated as $a(3/8)^{1/2} = 1.89\text Å$. The height of unit cells varies among the polytypes; however, the distance between two Si (or C) layers is never too far from the tetragon height given as $a(2/3)^{1/2} = 2.52\text Å$.

![Figure 1. Tetrahedral structure of SiC building block.](image)

Many of the materials that have tetragonal bond form either diamond/zincblende, or wurtzite structures. Both these structures are close packed and can be described as close-packed arrangement of equal spheres held together by interatomic forces. In the case of SiC the positions of one kind of atoms (Si) resembles that of equal close-packed spheres with other atoms residing among the voids. This structure is also regarded as
close-packed, although, not ideally close-packed.\textsuperscript{38} Another way of describing such structure is in terms of two identical interpenetrating close packed lattices, one consisting of Si and another of C atoms. These two lattices are displaced one forth of a layer spacing along C-axis one from another.

Figure 2. Close-packed spheres. Letters B and C designate possible atom positions in layer stacked on top of the layer A.

Let us start the description of the stacking possibilities by considering the close-packed arrangement of equivalent spheres representing Si atoms on a plane (Fig 2) The position of this first layer we could call A. The next layer of Si atoms can be placed in the close-packed arrangement either in voids B or C. Likewise the layer above could be either in voids A or C (if the second layer is in B), or else in voids A or B (if the second layer is C). Carbon atoms reside in the voids formed between Si atoms. For each Si atom in a layer there is a corresponding carbon atom located \( \sim 1.89 \, \text{Å} \) below. Therefore the above description of stacking possibilities of layers of equal spheres should hold for bilayers of Si-C formed by corresponding layers of Si and C.
Depending on the stacking order of bilayers the bonding between Si and C atom positioned in adjacent bilayers can be either zinc-blend (cubic) or wurtzite (hexagonal). In hexagonal stacking the bonds in neighboring bilayers are staggered, so that they are rotated $60^\circ$ with respect to each other (Fig 3). In cubic stacking, corresponding bonds are eclipsed, so that they are mirror images of each other (Fig 3). The bonds configuration for each type of stacking results in a somewhat changed atomic environment, thus making atomic sites electronically inequivalent.

Figure 3. Staggered bonds on a) and b) vs. aligned on c) and d)

Figure 4. The arrangement of Si (white) and C (black) atoms in various polytypes.

a) 2H-SiC    b) 3C-SiC    c) 4H-SiC    d) 6H-SiC
Different polytypes are formed by any periodic sequence of bilayer positions A, B, and C. For example ABAB represents hexagonal polytype 2H-SiC which has hexagonal bonds only between the layers (Fig 4 a). Similarly ABCABC represents cubic polytype 3C-SiC and has cubic bonds only between the layers. (Fig 4 b) Other polytypes have a combination of both cubic and hexagonal bonds between the layers. Thus ABAC stacking forming hexagonal 4H-SiC has an equal share of cubic and hexagonal bonds, (Fig 4 c) while ABCACB forming 6H-SiC (Fig 4 d) has two third cubic bonds and a third of hexagonal bonds.

2.3.2 The notations used to describe polytypes

A compound is called polytypic if it occurs in structural modifications different from each other by stacking sequence of almost identical structure and composition. Among various notations systems developed to describe polytypes, International Union of Crystallography (IUCr) defines two categories.39

One category- indicative symbols- can be used without knowledge of the crystal structure, and relies on observable characteristics such as symmetry, interchange of axis and other. The second category- descriptive symbols- specifies the exact stacking sequence of layers and can provide information about unit cell and help identify matching structures described by different axis systems. Since most of notation systems were developed with a certain type of material or structure in mind, they may not be useful universally, or specifically, for SiC.
2.3.2.1 Indicative symbols

2.3.2.1.1 Ramsdell notation

Ramsdell notation introduced in 1947 is most commonly used to denote SiC polytypes. It specifies the number of layers in the unit cell followed by letter indicating lattice type. The cubic polytype repeats the stacking sequence every three layers and is designated as 3C. Analogously, the pure hexagonal polytype is designated as 2H. Other polytypes have the combination of the cubic and hexagonal stacking and their crystal symmetry is usually hexagonal (4H or 6H) or rhombohedral (15R).

Ramsdell notation is easy to use and can be applied to all close-packed structures. However it does not reveal the actual arrangement on the layers in the unit cell. Therefore, does not distinguish between the polytypes having the same lattice type and repeat period but different layer sequence. To distinguish such polytypes sharing the same Ramsdell notation subscripts a, b, c or 1, 2, 3 are used. The examples of such notations are 51R_a and 51R_b or 16H_1 and 16H_2. Although Ramsdell notation does not specify arrangement of layers in the unit cell, it is very convenient for polytypes with unknown structure, but known unit cell.

Ramsdell notation can be seen as the simplification of the modified Gard notation, which is used for the structures that have multiple periods along different axes. Modified Gard notation uses the same symbols as the Ramsdell notation to describe the crystal system, e.g. C for cubic, R for rhombohedral, followed by three lower case letters corresponding to unit-cell edges with corresponding numbers indicating periodicity. This notation reduces to Ramsdell notation in the case if the two periodicities along similar
Axes are the same. This is always true for SiC. In this case, modified Gard notation Haa4c simplifies to Ramsdell 4H by deleting the first two cell edges and placing the periodicity of the third direction in front of the symbol of crystal symmetry.

2.3.2.2 Descriptive symbols

2.3.2.2.1 ABC notation
The classical ABC notation describes the structure of polytypes by specifying the stacking sequence of successive layers in the hexagonal unit cell. Each layer in question is actually a bilayer of Si and C atoms separated by a distance ~1.89Å. In this notation the structure of 4H-SiC is described as ABCACB, 3C as ABC, 15R as ABCBACABACBCACB. Such representation provides a complete description of the structure, but it does not reveal the symmetry of the lattice. It also becomes more bulky for the polytypes with a large number of layers in the unit cell.

2.3.2.2.2 Hägg notation
The indicative symbols such as Ramsdell notation are easy to use. However, their assignment is not unique, and some polytypes with different stacking sequence may have identical Ramsdell symbols. Descriptive symbols specify exact stacking sequence of layers. Such symbols might indicate absolute orientation of each building layer and their relative displacement. In the case of equivalent building layers such as in SiC polytypes the layers may occupy only two alternative positions relative to the preceding layer. Therefore a complex description of layer orientations and displacements for a general case may be reduced to a sequence of characters of two kinds. Such symbolism is used in Hägg notation. Two possible stacking sequences follows either “cyclic” A→B→C order

14
corresponding to the translation 1/3, 2/3 in the basal plane, or “anticyclic” A→C→B order corresponding to a translation -1/3, -2/3. Hägg notation assigns symbol (+) to the “cyclic” order and (−) to “anticyclic” order. Therefore 2H (ABAB) may be represented as (+ − + −), 3C (ABC) as (+ + +), and 4H (ABCB) as (− + + −) or (+ + − −) if (+) is chosen as the starting symbol. For rhombohedral 15R we obtain (− + + − − + + − − + + − −). This sequence may be reduced to (+ + − −). Analogously, for all hexagonal polytypes the number of + and – symbols is the same as the number of layers in the unit cell, while for rhombohedral polytypes number of + and – signs is 3 time less than the number of layers in the units cell. Sometimes a subscript ‘3’ is used for notation of rhombohedral polytypes e.g. (+ + − −)3 to emphasize that three such repeats needed to complete the hexagonal unit cell. Another variation of notation is using ↑ ↓ symbols instead of + − to emphasize parallel vs. staggered bonds between the layers. (Fig 2.3.2)

2.3.2.2.3 Zhdanov notation

Zhdanov notation 40,41 is essentially a simplification of Hägg notation. The notation has a pair of numbers indicating the number of consecutive plus signs in the Hägg notation followed by the number of minus signs. Thus 4H is represented by (22), 6H as (33), and 15R as (32) or (23) or with a subscript (23)3 indicating that three such repeats complete a unit cell. This symbolism is especially convenient for describing stacking sequence of long period polytypes. Such 189R is written as (34)43 indicating that basic building block (34) of this polytype is 21R. The differences in the structure of polytypes 33H1 and 33H2 sharing the same Ramsdell notation is apparent from their Zhdanov symbols (33)2353334, (33)3(23)3.
2.3.2.2.4 Jagodzinski h-k notation

The h-k notation specifies the layer by the orientation of layers on either side of it. The layer is denoted as h if the layer is hexagonal-like i.e. preceded and followed by layers in the same orientation e.g. A-B-A or C-A-C. Otherwise if a layer is cubic-like and is surrounded by layers that are oriented differently, e.g. A-B-C, it is denoted as k. According to this notation 6H is hhkhhk or (hhk)_2, 3C is (k)_3 and 2H is (h)_2. This notation is especially useful for the calculation of interaction energy between layers.

2.3.2.2.5 Zigzag sequence

Another way to describe polytype structure takes advantage of the fact that Zhdanov symbols represent the step lengths in zigzag atom sequence in the (11\bar{2}0) plane. If a pair of atoms in bilayer is located in the A position, the next layer will be either to the left in B or to right in C. Similarly the atoms in the third layer will either continue the direction or change it. These repeated changes of direction result in the repeated zigzag pattern. The unit cell is repeated after the pattern arrives at the atom located in the same position e.g. A and has the same atomic environment as the starting atom. The examples of the zigzag pattern are give on Fig 4

2.4 Why there are so many polytypes?

The reasons for the abundance of stable polytypes are not yet completely understood. From thermodynamic point of view their existence and formation at similar temperatures seems anomalous. Indeed to minimize the free energy the system should favor the formation of less ordered polytypes. Therefore the existence of polytypes with very long ordering should require ordering forces with the range much longer than the interatomic forces.
In one of the earliest studies on the SiC polytypism, Baumhauer stated that occurrence of different polytypes correlates with their color. It was suggested later\textsuperscript{42} that such color variations are caused by impurities and that their accumulation\textsuperscript{43} on the growth surface may lead to periodic disturbances influencing the growth and the formation and different polytypes. The analysis of such impurities in three SiC polytypes have shown that the presence of Al has a correlation with the structure type while the presence of Mg, Mn or Fe has not\textsuperscript{44}. In spite of the fact that the evidence that Al impurities were shown to influence the growth of 4H, 6H and 15R polytypes, the impurity model could not easily be applied to explain, for example, the formation of longer period polytypes.

Most of the other theories explaining SiC polytypism can be divided into two categories. One deals with the effects screw dislocation may play in long range ordering, while the other involves thermodynamic investigation of polytypes stability depending on interaction energies between layers.

2.4.1 Screw dislocation theory of polytype formation

Applying screw dislocation theory of crystal growth to SiC Frank\textsuperscript{45} suggested that polytypism in SiC may be explained by spiral growth of crystals around such dislocations. The screw dislocations on a crystal phase would expose the crystal terrace and the growth on the edge of the terrace will create the structure with a period equal to the screw height. The screw dislocations with different Burgers would create different polytypes. Frank’s theory considered 6H or (33) polytype as the basic structure for the polytypes was able to account, for example, for the [(33)$_n$32] rhombohedral polytypes.
Mitchell \textsuperscript{46} has further developed these ideas by considering 6H (33), 15R (23) and 4H (22) polytypes as the basic building structures and investigating the stability of the gaps in the zig-zap pattern in [11\overline{2}1] direction caused by screw dislocations. This accounted for the most observable polytypes and predicted new structures. Krishna and Verma proposed further developments in a faulted matrix model.\textsuperscript{47} They considered the ABC sequence and horizontal slip planes or stacking faults and were able to account for all polytype structure including 2H.

Screw dislocation theory was able to explain the formation of various polytypes structures and received experimental support\textsuperscript{47} from the observation of growth spirals on the surfaces of polytypic materials whose step heights correlated with the heights of the unit cells. The theory failed to fully explain, however, the existence of polytypic structures that display no growth spiral on their surface, the coexistence of different polytypic structures in the same crystal or considerable concentration of random stacking faults in the structures. In addition, growth around a single screw dislocation could lead to a needle-shaped crystal \textsuperscript{48} and in order to get the growth of flat platelets, the crystal need to have the dislocations of opposite directions.

\textbf{2.4.2 Thermodynamic theories of polytypism}

Based on energy consideration Jagodzinski \textsuperscript{49} also questioned the screw dislocation origin of polytypes. He considered the formation of growth spiral and the polytype formation as two different phenomena and argued that the energy required to create the edge dislocations is less than that to create the screw dislocations. The stacking faults created by such dislocations should negate the ordering created by screw
dislocations. The low energy to create stacking faults should lead to formation of crystals with disordered stacking order. This is seldom observed and suggests the long-range ordering forces between layers. Let us consider free energy of polytype structure written as:

$$ F = U - TS, \quad (1) $$

where $F$ is the free energy, $U$ is internal energy, $S$ is the entropy, and $T$ is temperature. The internal energy component consists of potential energy and vibrational energy terms. Potential energy is expected to be close for different polytypes especially since their atoms have the same closest neighbors environment. The second term of free energy depends on system entropy and could be divided in configurational and vibration term. The configurational entropy is increasing with increasing disorder, thus favoring the formation of disordered structure. The vibrational entropy, however, should favor the ordering. Quantitative considerations show that the formation of small period polytypes like 4H, 6H and 15R is determined by internal energy considerations, but the formation of long ordered polytypes determined by vibrational energy. It follows from the theory that the formation of long ordered polytypes should be increasingly improbable and that ordered and the system has two stable phases, ordered and partially disordered. Both these results are in contrast with the experiment, but the theory laid out a ground for the thermodynamic approach to polytypism.

Many of the subsequent approaches used computational models to consider the energy interaction of various sequencing methods. Cheng at al have used ab initio pseudo potential and Ising spin array Hamiltonian calculations to derive the energy differences between the polytypes. They have found the energy differences between the
occurring and non-occurring polytype structures measuring roughly 0.01 eV per Si-C pair. Cheng’s work \textsuperscript{51} was one of the first to successes of axial next-nearest neighbor Ising (ANNNI) model. The Ising model \textsuperscript{53} was first developed to describe ferromagnetic materials. In the model the variables that describe the state of the structural unit of a material could take one of the two possible values (up or down) and can interact to either align to the same direction or be disordered. In the ANNNI model each such unit describes a Si-C pair and has two possible states $S=\pm1$, or $\uparrow \downarrow$. These pseudospins have the same meaning as the Hägg notation $+ -$ of layer stacking and are considered parallel for cubic stacking and anti parallel for hexagonal. Pseudospin interaction energy per unit cell could be written as:

$$\Delta E = -\frac{1}{N} \sum_{i,n} J_n S_i S_{i+n},$$

where layer index $i$ is summed over the total the number of layers $N$, and $J_n$, is an energy interaction between the units and its first, second and third neighbors ($n=1..3$). According to Heine and Cheng \textsuperscript{54} the interaction energy with the second nearest neighbors is opposite in sign and roughly half the value of the interaction energy with the first nearest neighbor $J_1 \approx -2J_2$. This means that twin boundaries are very likely to form. Heine’s work\textsuperscript{54} also suggests that 3C polytype patches are very likely to form during growth. For a growing surface layer where only one of the second neighbors is present the cubic stacking is preferential. This correlates very well with experimental observations.
In more recent calculations Lambrecht et al.\textsuperscript{55} found that value of $J_1$ and $J_2$ do not correspond to multi-degeneracy point, but rather $J_1 + 2J_2 < 0$, thus making the formation of twin boundaries even more favorable than in Heine et al. model. The twin boundaries occurrence every two or three layers can produce the structure of most common polytypes.
CHAPTER 3: EXPERIMENTAL TECHNIQUES

3.1 Ultra-high vacuum (UHV) condition.
Many surface science characterization techniques use ultra-high vacuum (UHV) conditions. There are two main reasons. Firstly, UHV allows preparing atomically clean surfaces and maintaining them in that state during duration of the experiment. Secondly, UHV enables using low-energy electron and ion based techniques without scattering from gas in the ambient environment.

<table>
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<th>Pressure (Torr)</th>
<th>Mean Free Path (cm)</th>
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<td>Rough (low) vacuum:</td>
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<td>&gt; 10^{-6}</td>
</tr>
<tr>
<td>Medium vacuum:</td>
<td>10^{-3} - 10^{-5}</td>
<td>&gt; 5</td>
<td>&gt; 10^{-3}</td>
</tr>
<tr>
<td>High vacuum (HV):</td>
<td>10^{-6} - 10^{-8}</td>
<td>&gt; 5 x 10^{3}</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>Ultrahigh vacuum (UHV):</td>
<td>&lt; 10^{-9}</td>
<td>&gt; 5 x 10^{8}</td>
<td>&gt; 10^{4}</td>
</tr>
</tbody>
</table>

Table 3. Typical classification of the pressure conditions.

The typical classification of pressure conditions with the corresponding mean free particle path and time for contaminant to complete one monolayer are shown in Table 3. For surface spectroscopy it is important that the mean free path of the particles of both probe and detected particles such as electrons, ions and molecules greatly exceeded the
dimension of the apparatus. This is achieved at pressures < $10^{-4}$ Torr corresponding medium vacuum conditions. However, because the background noise and the lifetime of the particle detectors such as the channeltrons and multiplier detectors significantly improves at pressures < $10^{-6}$ Torr, higher vacuum is typically used.

In order to sustain clean, unaltered due to interaction with ambient gases surface for the duration of the experiment, the background pressure must be such that the time for the contamination to buildup a monolayer was greater than the duration of the experiment. This conditions lead to the use of the UHV.

In order to achieve UHV, a multi-stage process is used. Initially, the vacuum chamber is pumped down to $10^{-5}$ Torr using a rotary “rough” pump. After that, the chamber is pumped down to about $10^{-8}$ using a turbomolecular pump. To achieve higher vacuum, the chamber is then heated (or “baked”) to a temperature about $180^0$ C while being continuously pumped out by turbo pump (sometimes together with ion pump). After a day or more of “baking”, the heaters are turned off, and the chamber is allowed to cool down. The “baking” is performed to desorbs gas atoms which are stuck to the chamber walls. Without the “baking” process UHV conditions are practically not achievable since it would have taken as long as months to desorb slowly “outgasing” water molecules from chamber walls. As the heaters are turned off, the chamber is sealed from “rough“ and turbo pumps and the pumping is completely switched to the ion pump. This pump is the most important for achieving UHV conditions. It works by accelerating electrons toward the positive anode down a spiral path in the electromagnetic field. The positive ions that are formed in the collisions of electrons with the gaseous particles strike the chemically active titanium cathode "getter" plate. This serves two purposes: the ions
combine with the cathode material (typically Ti) and they also eject more cathode material, which replenished the film of chemically active cathode material on the anodes. Inert gasses are buried in the pump surfaces after they are ionized by collisions and rammed into the cathode. After the chamber reaches room temperature the pressure should be at UHV conditions. To improve UHV vacuum the cryo pump that removes gaseous particles by freezing them to refrigerated plates may be started at this point, if available.

### 3.2 Cathodoluminescence

The interaction of electron beam with semiconductors produces a variety of processes that are used for material characterization techniques. Such techniques can provide a range of information including structural, chemical and charge collection properties of the semiconductors at high-resolution and in nondestructive manner. Cathodoluminescence further extends the capabilities of electron-beam characterization and can complement other measurements by providing information about electronic properties of the material. Its resolution is limited by the size of an electron beam to a few nanometers at best cases.

Cathodoluminescence uses an electron-beam to excite the electron-hole pairs. The light emitted by the excited carriers’ recombination is resolved spectroscopically using the monochromator and photodetector. Spectroscopic information should be relatively similar to that of photoluminescence (PL) and electroluminescence (EL) techniques after accounting for the differences associated mostly with different excitation volume and power density. One of the advantages of CL comes from the large rate of electron-hole
pair (EHP) generation. EHP generation rate could be estimated as $G = I_p V_b / E_i$ and depends on ionization energy $E_i$ of the material as $E_i = 2.8E_g + M$ \(^{57}\), where $E_g$ is a bandgap of the material and M is material-dependent parameter with the range 0-1 eV. Due to this large number of generated EHPs, electron beam excitation can produce emission by a variety of luminescence mechanisms. This allows one to detect states that otherwise would hard to excite. Another advantage of CL its ability to excite luminescence the wide range of energies which very useful for studying wide-bandgap semiconductor and dielectric materials that would require otherwise very deep UV photoexcitation source. CL can also be a nondestructive technique and could be used at energies up to 100 keV without producing atomic displacement.\(^{58}\) Another great advantage of CL is the ability to vary electron beam excitation depth under the sample surface. The next section will cover this aspect of CL in more details.

### 3.3 LEEN/DRCLS spectroscopy

Perhaps the most powerful property of CL is the ability to control the penetration depth of the beam by controlling electron beam energy $E_b$. This allows nondestructive probing electronic states as a function of depth.\(^{59}\) The CL performed varying electron beam energy in this fashion is referred to as Depth Resolved Cathodoluminescence Spectroscopy (DRCLS) to emphasize the depth dependent capability of the technique. A low energy variant of the technique is also referred to as Low- Energy Electron-Excited Nanoluminescence (LEEN) spectroscopy to highlight the surface-sensitive nature of the technique. Indeed, at $E_b$ energies less than 1 keV, the electron beam penetration can be
as shallow as few nanometers. This provides useful for many aspects of modern technology development. The formation of Schottky or ohmic contacts is dominated by the interactions in the metal-semiconductor interfacial layer limited to several monolayers. Similarly, the significant carrier mobility lowering in SiC MOS devices is caused by the large density of the interface states localized to nm-scale from the interface. The traps present in nm-scale thick high-k gate oxide dielectrics in Si devices cause the leakage and mobility degradation. LEEN spectroscopy provides means for probing such surfaces and interfaces on a nm scale.

A very useful approach modeling the penetration of the electron beam was introduced by Everhart and Hoff and is based on the analysis of electron energy loss as a function of the incident electron energy. This model is fairly accurate for the electron probe energies $1 < E_g < 25$ keV and for low atomic numbers. It uses the expression for general electron energy loss per unit path length, given as:

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

where $e$ is the electronic charge, $N_A$ is Avogadro’s number, $Z$ and $A$ are the atomic number and atomic weight, $\rho$ is the material density, $I = (9.76 + 58.8 Z - 1.19)Z$ (eV) is the mean excitation energy, $E$ is the electron energy, and $a$ is a constant equal to 1.1658. The theoretical maximum range for an incident electron with the energy $E_b$ is given by:

$$R_b = \int_0^E \left( \frac{\partial E}{\partial E} \right) = \int_0^E B \frac{\xi \partial(\xi)}{\ln(\xi)},$$
where $\xi = aE/I$. The parametr $\xi$ determines if empirical range formulas can be used since the model fails at low energies as $\ln(\xi) \xrightarrow{\xi \rightarrow \infty} -\infty$. The expression for $R_b$ could be further approximated as $R_b = C \xi^a$, with $C \approx 9.40 \times 10^{-12} (A/Z) c'/\rho = 1.597$, $a \approx 1.29$ and $c' = 1.48$ for $\xi < 10$. Figure 5 shows the penetration range $R_b$ and the depth of the maximum energy loss $U_0$ estimated using the Everhart-Hoff model with $Z$, $A$, and $\rho$ values for SiC.

The distribution of the electron beam energy loss as a function of a depth (or depth-dose function) is an important measure that indicates the density of EHP generation versus depth. The Everhart-Hoff model uses a third order polynomial
\[ g(z) = \alpha_0 + \alpha_1 z + \alpha_2 z^2 + \alpha_3 z^3 \]
with empirically determined coefficients to represent the depth-dose curve and $z$ normalized to $R_b$ such that $0 < z < 1$. Figure 6 shows the depth-dose curves for SiC based on the Everhart-Hoff model.

Modern methods of determining the depth-dose curve are based on the Monte-Carlo simulation of individual trajectories and energy loss of a large number of electrons. A random number generator is used is the equations that determine the electron scattering parameters such as the angle and electron energy loss. The simulation subtracts the energy from an electron until the electron stops and repeats the process for the next one. Such approach permits to simulate the scattering process not only for various kinds of bulk solids, but also for complex layered structures, which may include metal layers. One of the most commonly used simulation programs is CASINO that is the shareware program. It includes different models to simulate the scattering and can also models other
useful physical phenomena associated with high-energy electron interacting with solids e.g. X-ray emission. Figure 7 shows the depth-dose curves for SiC based on the CASINO simulation. Comparison with the Everhart-Hoff model indicated that later tends to underestimate the electron-beam penetration for low-energy electrons.
Figure 5. Electron penetration range $R_B$ and the depth of the maximum energy loss $U_0$ estimated using Everhart-Hoff model of electron beam interactions in SiC. Low energy electron beam generates electron-hole pairs within the topmost nanometers.
Figure 6. The depth-dose curves describe the electron beam loss based on the Everhart-Hoff model.

Figure 7. The depth-dose curves describe the electron beam loss based on the CASINO\textsuperscript{6} Monte-Carlo simulation.
3.4 Auger Electron Spectroscopy

Auger Electron Spectroscopy (AES) is the technique for probing the surface chemical composition of materials. It is based on measuring the core electron energies for particular atoms and involves three-electron process in which a core electron is removed by an incident electron beam. An electron in higher energy shell relaxes to the emptied state. In one of the possible processes that conserve the energy and momentum during this transition, the energy difference between two core levels is transferred to a third electron which is emitted from the solid at a precise energy. This electron is referred to as an Auger electron. An electron energy analyzer such as the Cylindrical Mirror Analyzer then analyzes the kinetic energy of all emitted electrons including both secondary and Auger electrons. The signal intensity of characteristic Auger peaks in the energy spectrum can then be used to measure the elemental composition of the sample. One of the major strengths of Auger spectroscopy is its surface sensitivity. The escape depth for the typical Auger electrons with the energies lower than 1600 eV is only \( \sim 30\text{Å} \). AES is sensitive to elemental composition on the order of 1%. Therefore it cannot be used to detect dopant or trace impurity concentration. However, it is useful in determining the surface contamination and molar composition of compound material with much more accuracy than mass-spectroscopy techniques can deliver. This is because the elemental sensitivity parameters are more reliable than in mass spectroscopy since they do not change significantly from material to material. By using AES together with inert gas sputtering, one can produce elemental composition depth profiles or control the decontamination of the surface before metal deposition or other processing.
3.5 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is another surface sensitive analytic tool that provides information about surface chemical composition. A major strength of XPS is that it can resolve the energy differences associated with electronic states of the atoms at the surface. In this method a sample is maintained under UHV and is bombarded with X-rays. While X-rays can penetrate a substantial depth into the sample, only a small fraction of these electrons, mostly at depth less then escape depth ~50Å make it outside the sample and are analyzed. The energy of escaped electrons depends on the core electron energy specific for each element. In addition small shifts in the binding energies can give the information about the chemical bonding of the atom.

The X-rays themselves are usually produced by accelerating electrons in order to collide with a metal target such as Mg or Al. These electrons can knock out electrons from the inner shell of the metal atom. As a result electrons from higher energy levels relax to the vacancy emitting extra energy as X-ray photons.

3.6 Secondary Ion Mass Spectrometry

A Secondary Ion Mass Spectroscopy (SIMS) is a powerful technique for chemical composition analysis. The technique can detect all chemical element and their isotopes as well as molecular species. SIMS is probably the most sensitive technique used in semiconductor characterization. It can detect dopant and impurities with the limits for some elements in the range of $10^{14}$ to $10^{15} \text{ cm}^{-3}$. In addition, it has wide enough dynamic range to keep track of the most abundant elements in the compound. The lateral
resolution is limited by analyzing ion beam size to as little as 120 nm, while the depth resolution can as small as 5 nm. SIMS method is destructive to the sample. It is based on the removing of material from the surface by ion beam sputtering and analyzing the masses of the removed particles using a mass analyzer. A very small fraction (~1%) of the ejected species is ionized either positively or negatively and can be analyzed by determining mass/charge ratio. This method of determining the mass/charge ratio can present a certain problem since various possible compounds form in the sputtering process. The presence of hydrogen and other light elements in the chamber increases multiplicity of particles with the same ratio. In addition, the possibility to detect multiply ionized particles complicates analysis further. Luckily, many elements are present in the nature (and in the material) at exactly known ratios of their isotopes. A thorough isotope analysis reduces many uncertainties in particle detection. During the sputtering process the primary ions lose their energy and come to rest within tens of nanometers of the sample surface. This leads to the ejection of the material from the surface, along with the implantation of the ion beam particles, knock-in of the surface particles deeper in the material and other destructive phenomena. The escape depth of the sputtered secondary ions is can be as low as few monolayers for typical primary ion energies. This shallow escape depth leads to a very surface sensitive measurement of composition. SIMS can be used in one of two modes: static or dynamic SIMS. Static SIMS uses very low primary ion currents and energies and has more surface depth sensitivity. Static SIMS is also less destructive than the dynamic SIMS since less surface material is removed. Dynamic SIMS uses a higher sputter rate to depth profile samples and to acquire a total mass spectrum or the ion yield of particular masses of interest versus sputter depth.
Only the charged species can be detected. This makes a secondary ion yield that can vary over five or more orders of magnitude a more important parameter than the total ion yield. Depending on the extraction plate bias, SIMS can detect positive or negative ions. The choice of detection depends on the sample and the positive/negative yield particular elements. Several factors influence the secondary ion yield of elemental and molecular species. Sputtering the sample with electropositive or electronegative ions, typically Cs+ (negative ion yield) or O2+ (positive ion yield), respectively, can enhance the secondary ion yield of species of opposite electronegativity. For example electronegative Au has a better yield when Cs+ beam is used, while Na when O+ beam is used. A Physical Electronics TRIFT III time-of-flight SIMS is used in the Electronic Materials and Nanostructures Laboratory at Ohio State University. The primary ion beam is 15 keV liquid metal ion gun (LMIG). It uses 69Ga+ to sputter the surface for the analysis cycle. Sputter column includes Cs+ and O2+ ions guns that also enhance either electropositive or electronegative secondary ion yield. The TOF-SIMS technique is generally believed to give a much better mass resolution when compared with other SIMS techniques, but has lower secondary ion signals because of the lower currents of analysis beam.

3.7 Secondary Electron Microscopy

A scanning electron microscope (SEM) is e-beam based techniques that is frequently used for surface analysis. SEM electron beam is rastered over the sample surface and generates the emission of secondary electrons that are collected by an Everhart-Thornley detector. The detector uses scintillation material to produce
photoemission signal that could be analyzed by photomultiplier tube detector (PMT). The PMT signal is used to create the secondary electron image of the sample. The resolution is limited by the size of the electron beam to <10 nm-scale. The major strength of SEM is that it could be used together with other e-beam based techniques such as cathodoluminescence (CL), Auger electron spectroscopy (AES), and electron beam induced current (EBIC).

A JEOL 7800F SEM Auger microprobe system in the Electronic Materials and Nanostructures Laboratory is equipped with an Oxford MonoCL cathodoluminescence attachment system and argon beam sputtering setup. The ion beam of the sputter gun is also aligned to the CL/Auger analysis position. SEM could be used with other attachments that extend its capabilities. These include a low-temperature stage, EBIC attachment, metal deposition and annealing system (in separated volume of the chamber). The electron beam current could be adjusted in the range $10^{-11}$-10$^{-8}$ A, while the beam energy can be in the range 0.1-25 keV. This range of energies allows cathodoluminescence probing in a wide range of depth under the surface (~2 nm to 2.5 µm). The CL attachment uses a parabolic mirror to collect the light and collimate it into the grating monochromator. There are two different monochromator gratings and two types of the detectors (PMT and Ge photodiode) that are chosen according to the spectral range of the interest.

The low-temperature stage uses liquid He to vary sample temperature from room temperature to as low as 8 K. The Auger part of the system uses a hemispherical analyzer to resolve the energies of electrons. Auger elemental composition analysis could be performed with the lateral resolution close to 25 nm in the same spots on the sample that
were characterized by CL. This created a powerful tool that allows correlating the electronic defects with the compositional changes due to contamination or nonuniformity of contacts and material.

3.8 Deposition of Metals and in situ Annealing

The deposition of the metals in the controlled environment is essential for producing clean metal-semiconductor interfaces in Schottky and ohmic contacts. The various methods of metal deposition include thermal and electron-beam evaporation, sputtering and CVD. Evaporation is very convenient for the high-vacuum systems. It allows one to control the deposition rates from very slow rates for thin films deposition to high rates for the contacts that can be electrically tested. In the e-beam deposition method a high-energy electron beam focused on the metal source in a crucible is used to heat up the metal until it evaporates. The deposition rate is monitored by the changes in quartz crystal oscillator resonant frequency. During e-beam evaporation the pressure in the chamber can reach $1 \times 10^{-8} - 1 \times 10^{-7}$ Torr. According to Table 1, such local pressures correspond to monolayer deposition rates on the order of seconds to minutes. The high temperatures involved in the process could lead to outgassing of contaminants present in the chamber that would be incorporated in the contacts. A thermal evaporation is another method for deposition of the contacts. In this method a tungsten filament is used to heat the crucible filled with the clean metal source. The method works best with the metals that have melting point less than 1000° C. After the initial outgassing of the source at temperatures below and then above melting, thermal evaporation could be performed at
$10^{-8}$ Torr or higher vacuum. This makes the thermal evaporation a very clean method for contact deposition. However, the thermal evaporation does not work well with refractory metals such as Pt, Ti and Ni that require e-beam evaporation.

The annealing step can improve the quality of interfaces for the Schottky contact reducing leakage and improving ideality factor. These improvements could be the results of breaking up silicon dioxide remaining at the interface and passivation of interface states. For ohmic contact the formation of a reaction layer at the interface is often needed which requires a high temperature ($600$-$900^\circ$ C) annealing. However, for Schottky contacts, the reaction needs to be avoided and the annealing is performed at lower temperatures and at shorter times.

To extract the cathodoluminescence signal from the metal-semiconductor interfaces one requires that metal layers did not exceed 5-10 nm nanometers. The annealing of such films ex-situ is connected with the possibility of metal-semiconductor contamination by diffusion of surface contaminants. The annealing in UHV removes the possibility of contamination.

Figure 8. The UVH compatible heater can anneal the samples at temperatures ranging from $500^\circ$ C Up to $1200^\circ$ C. It could be used for rapid 1 min contacts annealing as well as hours-long reliability and material degradation related annealing.
UHV annealing also permits CL characterization of the samples right after or even during annealing. This allows studying time-dependent phenomena connected to reaction, defect formation and diffusion.

### 3.9 Electrical Measurements

An HP 4145 semiconductor parameter analyzer was used for current-voltage (I-V) device characterization. Current-voltage measurements are conducted to determine electrical device characteristics by measuring current across the device as a function of applied voltage. Such measurements provide information about carrier injection and conduction of the material. I-V characterization of Schottky diodes yield the most common way to determine barrier height, however, its accuracy depends on the accuracy of Richardson constant that can significantly vary from its predicted value. The calculation of barrier height is done using an approximation of uniform barriers, which is rarely a case. The tunneling current along with the presence of traps and recombination centers at interface cause the current transport mechanism to diverge from thermionic film that further reduces accuracy of current-voltage barrier measurements. I-V measurements are also affected by image force at the interface and show a temperature dependence. Another way to characterize Schottky barrier is through capacitance-voltage (C-V) measurements. They are acquired by sweeping the DC voltage on top of AC voltage used to measure capacitance. In the case of nonuniform contacts, unlike I-V measurements dominated by lower barrier regions, C-V measurements are dominated by the regions having the highest area. For this reason C-V measurements of barrier height are considered more indicative of the barrier properties. The most reliable barrier height
measurements, however, can be achieved using photocurrent techniques such as internal photoemission (IPE). This technique relies on photoexcited current flow and is little influenced by tunneling current. In addition, IPE could also be used to detect contact non-uniformities.\textsuperscript{65}
CHAPTER 4 SIC PROPERTIES AND CHARACTERIZATION

4.1 Properties of SiC Surfaces

There are several reasons for the problems in obtaining SiC material with sufficient crystalline and electronic properties for producing reliable applications. One reason is the lack of understanding and control of surface properties of SiC surfaces. The atomic structure and defects of the surface influences the incorporation of defects into the grown material. One of the most severe problems with SiC growth is the propagation of micropipes and basal plane dislocations into the grown material.

It is logical that to obtain morphologically and electronically good quality interfaces, one requires clean and atomically ordered surfaces of the semiconductor. For the hexagonal surfaces this requirement presents a particular challenge as various cleaning and treatment techniques tend to change stoichiometry of the surface.

Some early studies 66 tried to investigate the work function and surface structure of the samples after the different degrease and acid etch chemical treatment. However, the differences of the surface properties were not observed possibly due to the high chemical inertness of SiC. When the samples were ion bombarded and annealed, the resultant surface was thought to be carbon rich. Yet, it was later shown 67 that the ion bombardment by itself could produce atomically clean surface with the stoichiometry similar to the bulk SiC. After the ion bombardment, the surface is disordered and needs to
be annealed. This causes the depletion of silicon, which has a higher vapor pressure than carbon. Therefore it is impossible to obtain the stoichiometric, well-ordered surface by combination of sputter and anneal preparation alone.

The disordered layer resulting from either the sputtering of the surface or the cutting and polishing procedure is difficult to remove by most chemical methods due to the inertness of SiC. The material might be removed by etching in molten hydroxides or peroxides. This however, tends to produce the rough surface. An alternative method to etch is to create the “sacrificial” oxide by thermally oxidizing SiC in similar way it is done with Si. The damaged layer is then consumed by oxide and removed by HF to reveal undamaged, stoichiometric surface. The material could also be removed by etching in hydrogen at elevated temperatures.

The removal of the disordered layers produces well-ordered uncontaminated surfaces. The surface exposure to the ambient atmosphere results in the formation of the surface oxides that need to be removed if the intimate interface between the deposited contacts is to be achieved. This “native” oxide can be removed by annealing the samples in an ultra-high vacuum (UHV). However, it can cause the surface to be silicon-depleted. While the evaporation of Si during the annealing can restore the Si stoichiometry, the balance of between the Si flux from and to the surface strongly affects the structure of the surface. Depending on the stoichiometry and orientation of the surface, several various ordered phases can be produced. 68
4.2 SiC-Metal Contacts

Metal--semiconductor contacts are present in every semiconductor device. The contacts can behave either as Schottky or as ohmic, depending on the characteristics of the interface. The formation of either type of contacts could be described using Schottky contact theory. 69 A good summary of recent views on Schottky contact formation mechanism can be found in review by Tung 70, which emphasizes their inhomogeneity. This section will start from describing the processing steps required to make a contact and continue with main points of Schottky barrier theory.

4.2.1 Four steps to produce the contact

In practice contact formation usually involves four steps. They are surface preparation, or cleaning, metal deposition, metal patterning, and annealing. 71

The purpose of the surface preparation and cleaning is to remove contamination and the damaged surface layer so that the metal could come into intimate contact with the semiconductor. Typical organic and inorganic contaminant can be removed by the various etchants, but if the surface is too damaged, a sacrificial layer of SiO2 could be also grown and removed. Whenever the clean surface is obtained, the native oxide will tend to form if the sample is not in UHV. To remove it before the metal is deposited, a short in-situ pre-clean annealing at least temperatures 900 °C or higher can be used to break down the oxide.

The following deposition of the metal is mostly performed using either sputtering, or evaporation. Sputtering is fast and utilizes the plasma discharge that sputters the metal from the target and deposits it on the sample. It allows compound targets and the pre-
cleaning using backspattering. Evaporation is very convenient for the high-vacuum systems. It allows controlling the deposition rates from very slow for thin films deposition to high for the contacts that can be electrically tested. In addition the use of a UHV system helps to produce atomically clean interfaces and deposit pure metal layers. The evaporation sources might be use thermal electron beam or in some cases effusion cells. In the thermal evaporator, the source is heated electrically and can be used only with the easier-to-melt metals. Electron beam evaporation uses the high current electron beam heating the source locally and can be used even with the hardest-to-melt metals. Effusion cells are used to evaporate metal in the atomic form rather than as small particles or molecules. It has both the evaporation zone to generate the beam flux and a separately heated higher temperature-cracking zone to thermally break apart particles and molecules.

Other methods, including chemical-vapor deposition, can be also used in special cases. One advantage of using CVD deposition is that epitaxial growth is easier to achieve.

The patterning of the metal could be done either by using lift-off or etching methods. The main difference between two is that the former involves the photoresist deposition and patterning before, rather than after metallization, as the later. In the lift-off process, the metal deposited on photoresist is removed after dissolving the acetone in the ultrasonic bath. It is preferred to have a metal layer thinner than the photoresist for a clean lift-off. Having photoresist with the sharp edges or with negative profile (wider at the bottom) is also helpful. Evaporation is well suited to lift-off since the metal deposition is directional and the metal deposition does not damage photoresist. Sputtering
may damage photoresist and, because it can cover the steps, may result in the metal layer with ragged edges or incomplete metal removal. CVD process also can be used to deposit metal for the lift-off process. However, photoresist, since it does not withstand CVD growth temperatures, should be then replaced with silicon dioxide or other dielectric. That requires an additional processing step.

The etching method of metal patterning is done by etching away the metal not covered by photoresist. This requires the wet or dry etch recipe that is not damaging for the photoresist or underlying material. In the case when multiple metallization layers are used or metals used are hard to etch, the lift-off is preferred.

In the final step the contact are annealed. For Schottky contacts the alloying and reaction that reduces barrier height should be avoided. Therefore, the annealing temperatures for such contacts do not exceed 500° C. The annealing step can improve the Schottky contact by reducing leakage and improving ideality factor. These improvements could be the results of breaking up silicon dioxide remaining at the interface and passivation of interface states. Such annealing could be performed in vacuum or inert atmosphere.

For the ohmic contact the formation of reaction layer at the interface is often desirable and the annealing is performed at higher temperatures (600-900° C) that promote such reaction. Specific attention should be spent on the investigation of reaction products. Some metals that form both silicides and carbides and reaction may completely incorporate consumed SiC in the alloy. Other metals may form silicides, but not carbides and the annealing may lead to the accumulation of carbon of the interface and be degrading for contact resistance. Some metal do not form either silicides or carbides, but
may diffuse in the semiconductor doping it or creating interstitials. The reaction between the metal and SiC produces the rough contact surface. Since this makes bonding more difficult, usually only a thin layer of metal is deposited for the reaction. Additional layers of metal could be deposited after high-temperature annealing.

4.2.2 Schottky contact physics

The Schottky barrier in a rectifying contact forms if the potential barrier is present on metal-semiconductor junctions. The effect that gave a name to the contact with such barrier was discovered by Schottky and comprises the reduction of work function under the applied electric field and is only part of broader explanation. In the simplest model the effects of the surface properties on the barrier height are ignored. Consider a band diagram of metal and n-type semiconductor as shown on Fig. 9a. After bringing the metal and the semiconductor together electrons flow from the semiconductor to the metal leaving the positive donor ions in the semiconductor and accumulating negative charge at the surface of the metal. The resulting electric field dipole resists further electron transfer. The metal and the semiconductor Fermi levels must align in the thermal equilibrium. Fig.(9 a and b) The barrier height is the energy difference between the Fermi level and the bottom of the conduction band in the semiconductor at the interface:

$$\Phi_b = \phi_m - \chi_s$$  \hspace{1cm} (5)

Such description of a metal-semiconductor contact is referred to as the Schottky limit. It follows from this model that it is possible to obtain it rectifying diode or ohmic contact by simply choosing a metal with the appropriate work function.
Equation above states that the barrier $\Phi_b$ is directly proportional to the metal work function $\phi_m$. Experimentally, however, there is a weak or little dependence on the metal work function:

$$S = \frac{\partial \Phi_b}{\partial \phi_m} < 1,$$

where $S$ is the interface behavior parameter. Therefore, the Schottky limit is not a complete description of all metal-semiconductor interfaces.

To account for the low dependence of contact barrier on $\phi_m$, Bardeen proposed that if a sufficient density of surface states exists at the metal-semiconductor interface, then the $\phi_b$ would be independent of $\phi_m$. These states can be occupied or empty.
depending on their position in energy relative to the Fermi level at the surface. Consider $\phi_0$, an energy level to which the surface states should be filled when the surface is neutral.

If the surface states are filled to a level above $\phi_0$, the surface has a net negative charge and the states behave acceptor-like. If the states are filled to a level below $\phi_0$, the surface has a net positive charge and the states behave donor-like.

If the number of surface states is large, then the Fermi level at the surface of the semiconductor will be at $\phi_0$. The charge in the surface states could now fully accommodate the potential difference $\phi_m - \phi_s$ that will appear entirely across the interfacial layer. Thus, no change in the charge within the depletion region of the semiconductor is required when a metal is brought into contact with the semiconductor. Therefore barrier height is independent of metal work function, and we obtain the barrier height is given as:

$$\phi_b = E_g - \phi_0$$  \hspace{1cm} (7)

This limitation when the Fermi level is pinned by the surface states to an energy level above the valence band is known as the Bardeen limit. For many semiconductors such as Si, Ge, GaAs, and GaP, the Schottky barrier heights for semiconductors are predicted more accurately by the Bardeen equation than by the Schottky limit, with the parameter $\phi_0$ estimated experimentally as $-(1/3)E_g$ so that the barrier height is close to the 2/3 of the band gap. One argument for this may be characteristic high density of states that is common to the diamond lattice and which pins the Fermi level at this energy. 73

In general the value of the barrier height will be between the Schottky limit and the Bardeen limit. For the metal-semiconductor interface where n-type semiconductor
permittivity $\varepsilon_s$, the interfacial layer thickness $\delta$ and permittivity $\varepsilon_i$, and the neutral level $\phi_0$ could be estimated as:

$$\phi_b = S(\phi_m - \chi_s) + (1 - S)(E_g - \phi_0),$$  \hspace{1cm} (8)

where the parameter $S$ depends in first approximation mostly on the density of surface states $D_s$, such as $S = \varepsilon_i/(\varepsilon_i + qD_s\delta)$ and varies between zero and unity. If $\varepsilon_i << qD_s\delta$ equation reduces to the Schottky limit. If $\varepsilon_i >> qD_s\delta$, then this equation reduces to the Bardeen limit.

**4.2.2 Current Transport Mechanisms**

There are four basic transport mechanisms across metal semiconductor junction.\(^\text{74}\)

For n-type semiconductor these mechanisms include: emission of electrons from the semiconductor over the top of the barrier into the metal (thermionic emission), quantum-mechanical tunneling through the barrier (field emission or Fowler-Nordheim tunneling), recombination in the space-charge region, and recombination in the neutral region (hole injection). For low-doped semiconductors the dominant transport is thermionic emission (TE). For the high doping range the tunneling or field emission (FE) becomes dominant. In the intermediate doping range thermionic field emission the transport is described as (TFE). A ratio of characteristic energy $E_{00}$ to the $kT$ parameter could be used to distinguish three regimes of conductivity. $E_{00}$ is defined as:

$$E_{00} = \left(\frac{q^2}{4\pi}\right)\sqrt{\frac{N_d}{m^*\varepsilon_s}},$$  \hspace{1cm} (9)
where $m^*$ is the effective tunneling mass, $\varepsilon_s$ is the dielectric constant, $q$ is the electronic charge and $k$ is the Boltzman constant. Thermionic emission dominates when $E_{00}/kT << 1$, field emission when $E_{00}/kT >> 1$, and for thermionic field emission $E_{00}/kT \approx 1$.

### 4.2.2.1 I-V measurements

The variations in the Schottky harrier height and applied voltage result in substantial changes in the current due to the exponential dependence of the current density on the harrier height and bias. As a result, one of the simplest methods to determine SBH is through current voltage measurements. The thermionic emission current density $J$ in terms of the applied voltage $V$ across Schottky barrier is given by:

$$J = A^*T^2 \left[ \exp \left( \frac{-q\phi_b}{kT} \right) \exp \left( \frac{qV}{nkT} \right) - 1 \right]$$  \hspace{1cm} (10)

where $A^*$ is the Richardson constant that can be approximated as $A^* \approx 120 (m^*/m)$, $\phi_b$ is the Schottky barrier height, and $n$ is the ideality factor. It now follows from thermionic emission current equation that the barrier height could be estimated from I-V plot as:

$$\phi_b^{IV} = \frac{kT}{q} \ln \left( \frac{SA^*T^2}{I_s} \right),$$  \hspace{1cm} (11)

where $S$ is the diode area, $I_s$ in the intersection of the linear fit to the I-V curve with the current axis on a log(I) plot. The slope of the linear fit to log(I) plot also provides the value of the ideality factor. One of the problems of this method comes from the uncertainty of the value of $A^*$. Also, as has been mentioned in experimental method section, I-V tends to provide the value of lower barrier height in the case of a inhomogeneous contact.
4.2.2.2 C-V measurements

Another method to measure Schottky barrier height is through capacitance voltage measurements. In the case of a uniformly doped semiconductor:

\[
\frac{1}{C^2} = \frac{2}{q \varepsilon_0 s^2 (N_D - N_A)} (V_{bi} - V),
\]

where \(N_D - N_A\) is the net donor concentration, \(V\) is the reverse voltage and \(V_{bi}\) is the intersection of the linear fit intercept with the voltage axis on the \(1/C^2\) plot. The barrier height can be evaluated now as:

\[
\varphi_{b}^{CV} = V_{bi} + V_n - \frac{kT}{q},
\]

where \(V_n\) is the Fermi level position under the conduction band edge without the contact. The slope of the curve provides the way to evaluate the net donor concentration. The value of Schottky barrier height extracted using C-V method depends less on the image force at the interface and the temperature and tends to be characteristic of the barrier height with the largest area in the case of inhomogeneous contacts.

4.3 Polytype interfaces: 3C inclusions, quantum well.

Inclusions in SiC are extended defects that are bound by stacking fault dislocations. The unique properties of the heterojunctions formed by such dislocations are that they and have a well ordered atomic structure with no broken bonds and that they consist of chemically identical materials. Therefore the interface is almost free of any interfacial states associated with impurities and lattice defects, artifacts which allow many theoretical calculations to be consistent with experiment.
The inclusions can form in the host material as the result of electrical stress\textsuperscript{26,75}, thermal processing\textsuperscript{76,5,6,7} or even form in as grown material. Most of the wafers that showed transformations with thermal processing have either highly n-type doped substrate or epilayer. The electrical stress, however, caused transformation in the lower doping material.

The common occurrence of stacking faults in adjacent basal planes rather than single faults scattered across the crystal can be understood in terms of the energy of formation of such defects. Iwata et al. \textsuperscript{77} have found that once a single stacking fault is produced a second one could be formed relatively easy. They have calculated that the energy of the formation of the second SF is about 4 times less than the energy required to produce single SF. In addition there might be a thermodynamically driven force behind the formation of double stacking faults. Liu et al. suggested that the transfer of electrons from the conduction band to the lower electronic state in the QW produced by double stacking faults would provide such drive by lowering system energy\textsuperscript{7}.

The presence of cubic inclusions in the 4H-SiC could be detected by luminescence methods. Our group measurements on thermally stressed samples have revealed cathodoluminescence peaks at 2.5 eV\textsuperscript{6}. Photoluminescence measurements on electrically stressed samples\textsuperscript{76} showed a photoluminescence peak at lower energy 2.42 eV. The photoluminescence of the 4H/3C/4H grown layers performed by Choyke\textsuperscript{78}, however, showed a series of peaks associated with 3C layers located at energies 2.17 eV and lower. Although in all three cases above the peaks were associated with the quantum well (QW) inclusions, the samples produced by thermal and electrical stress therefore show luminescence peaks at energies above the 3C bandgap of 2.39 eV, while grown
layered structures show luminescence peaks below the 3C bandgap. There is no contradiction, however. Because there is a spontaneous polarization difference between different polytypes, one expects an internal electric field in the quantum well. While the quantum confinement in the well should increase the energy of optical emission from the quantum well, the Stark effect should decrease emission energy. This is illustrated on Figure 10. In the case of low doping the electric field in the well lowers the bottom of conduction band with respects of the top of valence band in the well. This lowering may be larger than the higher energy shift of the ground state. In the case of high doping the electrical field is shielded by free carriers. This makes the QW a classic rectangular well with the ground state above the well bottom. In this case, optical emission is at an energy higher than the 3C-SiC bandgap.

Figure 10. (a) Spontaneous polarization causes the optical transition to happen at energy less than 3C bandgap. (b) In the case of shielded polarization, the quantum well is rectangular and the transition from the lowest QW state has an energy higher than the 3C bandgap.
4.4 SiO\textsubscript{2}/SiC interfaces

4.4.1 The interface states density of SiO\textsubscript{2}/SiC interfaces

When compared with other wide-bandgap semiconductors, silicon carbide has an additional advantage. Similar to Si, its native oxide is SiO\textsubscript{2}, which could be grown by simple thermal oxidation. That means that SiC can be processed in a similar way as Si, with the distinction of higher growth temperatures. The wide band gap, the high critical electric field, the high saturation electron velocity, and the high thermal conductivity of SiC could potentially extend the application of MOS devices to higher voltages, higher power levels, higher temperatures, and higher frequencies. However, SiC MOS devices developed so far suffer from the low minority carrier mobility and have not yet met expectations. The low mobility is considered to be related to the observed high density of the interface traps, \textsuperscript{79} which are especially high near 4H-SiC/SiO\textsubscript{2} interfaces. Interfacial defects not only degrade device performance, but also reduce reliability especially under the extreme conditions the devices are expected to operate. The reduction of the interface states is therefore prime task in the development of SiC MOS technology.

A good review of SiC/oxide interface states (D\textsubscript{it}) was written by Afanas’ev et al.\textsuperscript{80} The paper notes that the energy distribution of D\textsubscript{it} across the SiC bandgap obtained by admittance spectroscopy and deep level transient spectroscopy. D\textsubscript{it} on SiC/SiO\textsubscript{2} grown in dry O\textsubscript{2} measured by these methods has been shown\textsuperscript{81} to be above $10^{11}$ cm\textsuperscript{-2} eV\textsuperscript{-1} over the entire SiC bandgap energy range for all of the three most commonly used polytypes (4H-, 6H, and 3C-) and for both n- and p- conductivity types. Two regions have a particularly high D\textsubscript{it}. The lower half of the SiC bandgap density of states is in the range of $10^{12}$ cm\textsuperscript{-2}
eV$^{-1}$ for all polytypes. In the upper half of the band gap, near the conduction band, the
density of states is also enhanced, approaching the 10$^{13}$ cm$^{-2}$ eV$^{-1}$ in the case of 4H-SiC.

4.4.3.1 The interface states dependence on polytype

The polytype dependence of the density of states could indicate the structure of
the states contributing to D$_{it}$ near the band edges. For the lower bandgap 6H-SiC, such
density of states is lower then for the 4H-SiC. For 3C it is much lower, suggesting that
the interface traps are located in the particular range of energies, or are polytype
specific.\textsuperscript{80}

While the comparison of density of states close to the SiC valence band for the Si
faces shows little differences between 6H- and 4H-SiC \textsuperscript{80}, the D$_{it}$ near the conduction
band is significantly higher for 4H-SiC. In mid-gap region the density of states is notably
higher in 4H-SiC MOS structures as well. A low correlation between the defects
responsible for the interface states near conduction and valence band suggests the
different origins for these states.

The interface states density near the conduction band of 3C-SiC is about an order
of magnitude lower than the corresponding density of states in oxidized 4H-SiC. This can
be attributed to the $\sim$1 eV decrease in the SiC conduction band energy in the 3C
polytypes as compared to the 4H-SiC which shifts semiconductor Fermi level towards the
energy range of low D$_{it}$ values. \textsuperscript{80} A similar trend is observed when comparing oxidized
4H-SiC to other polytypes with lower bandgap value, such as 15R-SiC, after the same
processing.
The density of states is known to depend on the crystallographic orientation of the surface. In general, it is distinctly higher on the C- than on Si-face for both 6H- and 4H-SiC. For 6H-SiC, $D_{it}$ also increases with increasing crystal surface misalignment angle from the (0001) plane, which corresponds to Si-face. The MOS structures fabricated on other surfaces exhibit enhanced interface states density in the lower portion of the SiC bandgap, which is associated with higher availability of carbon atoms at the SiC surface planes. Similarly for the states located near the conduction band of 6H-SiC, the Si-face exhibits less $D_{it}$ than some other orientations. However, unlike for 6H-SiC, $D_{it}$ on (11\overline{2}0) and on some other orientation of 4H-SiC, has been shown to be reproducibly lower than on Si face (0001). Because the behavior of the density of traps in the lower and upper parts of 4H-SiC exhibits different trends, the corresponding defects might have a dissimilar nature.

### 4.4.3.2 The effect of various annealing treatments

In order to reduce the interface states density, various annealing procedures have been attempted. It was found that the conventional post-oxidation anneal of SiC/SiO$_2$ in the inert atmosphere similar to the one used in Si technology does not improve the interface states density. The annealing in H, which is known to passivate defects that have an unpaired electron, does produce some reduction in $D_{it}$ in 6H- and 4H-SiC, but at annealing temperatures exceeding 1000°C. Such reduction is seen only for n-type, but not p-type samples, which means that H annealing induces the changes in the $D_{it}$ only in upper part of band gap, and not in the lower part. The positive changes in the density of states can be diminished by the introduction of the significant amount of positive
charge near the interface associated with bound hydrogen. In comparison to the dry
grown oxides, wet oxidation seems to enhance the acceptor-type defects near the
conduction band of SiC.

In contrast, the growth in the presence of N$_2$, NO$_2$, and NO or the after-growth
annealing of oxides in such gases appears to improve transport properties near the
interface and significantly reduces the density of states on the SiC/SiO$_2$ interfaces. This
result is believed due to a double benefit of such treatment: (1) the enhanced removal of
the carbon from the interface region and (2) the passivation of dangling bonds. The
reduction of interface states seems to be both in the upper and lower parts of band gap
and works for 4H-SiC as well as 6H-SiC.

**4.5 Electronic Defects in 4H-SiC**

Different polytypes have significantly different bandgap energies so that small
bonding changes can provide large energy changes in localized and extended states.
Defects and their complexes play even more important role in SiC, since it is a compound
semiconductor. In addition to the impurities intentionally used to dope the material, the
electrical and optical properties are dependent on native defects. Such defects could be
introduced during growth or be formed during processing steps, such as irradiation
damage, annealing. Most native defects are either atomic in nature zero-dimensional,
two-dimensional planar defects or three-dimensional defects such as micropipes. Most
important atomic defects are vacancies, antisites, interstitials and their complexes.

Such native point defects can give rise to energy levels in the bandgap. Their
position with respect to the band edges depends on the polytype. Stacking faults (SF) and
grain boundaries (GB) are most important planar, two-dimensional native defects in the SiC. In crystals with stacking faults, the various lattice planes are not stacked in the same way as in ideal crystals, but certain planes are twisted by an angle. Two stacking variations, hexagonal and cubic, are possible between the adjacent planes. While their periodic arrangement results in the formation of a certain polytype, minor changes in stacking produce stacking fault defects. Grain boundaries occur in crystals that consist of differently oriented domains of the same polytype. Two notable cases of grain boundaries are twin and tilt boundaries. Two-dimensional native defects are believed to cause electrical effects in other semiconductors such as Si. In Si, they affect the device performance by generating electronic states in the band gap, causing the segregation of impurities or acting as electrical traps for charged carriers. In addition, the so-called micropipe defect - basically a tube propagating through the crystal - is known to cause device failure if present in the device active area. Closely related to micropipe defects are screw dislocations.

Appendix A lists the energies of many commonly observed defects in the SiC and their interpretation. Although the list does not intend to cover all possible defects observed via various spectroscopy methods, it provides a comprehensive reference of the defects that can be observed by cathodoluminescence and photoluminescence methods and is useful for quick identification of spectral features.
CHAPTER 5: RESULTS

5.1 Highly doped Metallized n- and p-type 4H-SiC and 6H-SiC samples

We have used low energy electron-excited nanoluminescence (LEEN) spectroscopy and X-ray photoemission spectroscopy (XPS) to probe deep level defect states at interfaces of 4H and 6H-SiC with Ti/Pt metallization. These studies aim to identify process conditions under which thermally-stable ohmic and Schottky contacts can be obtained on SiC while minimizing the formation of deep level electronic states. Depth-dependent LEEN measurements establish the presence of localized states and their spatial distribution on a nanometer scale. Spectra from the near interface region of 6H-SiC indicate the existence of a SiC polytype with a higher band gap of ~ 3.4 eV. Excitation of the intimate metal-SiC interface reveals a process-dependent discrete state deep within the SiC band gap. XPS measurements reveal consistent differences in the C 1s chemical bonding changes with specific process steps. Analogous chemical treatments of 4H-SiC also produce a lower band gap SiC polytype with ~ 2.5 eV energy extending tens of nanometers beyond the interface – confirmed by transmission electron microscopy (TEM). In this work we showed the first the effect of metal-semiconductor interactions not only on localized states but also on the lattice structure of the semiconductor near the interface.
5.1.1 Introduction

Although desirable ohmic or Schottky characteristics are obtainable for SiC devices, the interface properties depend significantly on specific process conditions used to prepare them. Localized electronic states at these interfaces are sensitive to such processing and can have substantial effects on barrier properties. However, relatively little is known about their properties compared with more conventional semiconductors.\textsuperscript{73,88} Such states can be formed by the altered atomic arrangements and chemical bonding often present near interfaces. These could be localized just a few monolayers from the semiconductor/metal junction or buried a few nanometers or more below the interface. Hence, techniques with sub-surface as well as surface sensitivity are required in order to probe such states.

The study of defect formation under controlled device processing conditions can be useful in understanding the origin of SiC interface states and the steps needed to minimize their density at electrical contacts. Furthermore, the polymorphic nature of SiC raises the possibility that structural relaxation, i.e., polytype phase transitions, can occur under certain conditions. Previously, it has been shown that phase changes may occur under applied stress\textsuperscript{89,90} or high-temperature doping diffusion.\textsuperscript{91} However, until now, there have been no studies of such changes with device processing or of their effect on interface transport properties. Titanium contacts to SiC are used generally to promote ohmic contact formation to single crystal SiC. Here we present results showing the effects of standard processing steps such as oxidation, HF strip, Piranha-clean and metallization on the formation of defect states and polytypic transformations near
Pt/Ti/6H-SiC and 4H-SiC interfaces. After describing the experimental techniques and processing in Section 2, we will present results for interface states and structural changes of 6H-SiC and 4H-SiC in Sections 3 and 4, respectively. Section 4 also contains results for extended polytype transformations at 4H-SiC surfaces and interfaces. Section 5 contains a discussion of our interface state results with those of previous studies. In addition, we show that the energies observed via LEEN spectroscopy are consistent with the structural features evident in cross sectional TEM images as well as their quantum-confined properties. Section 6 highlights the unique aspects of these SiC results relative to metal-semiconductor interface studies in general.

5.1.2 Experimental

All samples used for the LEEN analysis were processed and metallized at NASA-Glenn Research Center. In order to carry out optical studies on metal-SiC contacts, we used representative ohmic contact overlayers of Ti/Pt that were thin enough to transmit significantly in the visible wavelength region. Pt/Ti/6H-SiC and Pt/Ti/4H-SiC interfaces were formed by sputter deposition of 1-2 nm Ti followed by 2-3 nm Pt on chemically treated, SiC samples, all from the same wafer. The 6H-SiC wafers consisted of 2µm thick, n-type (Nd = 2 x 10^{19} cm^{-3}) epilayers grown 3.5° off the basal (0001) plane on high resistivity p-type substrates by chemical vapor deposition. The 4H-SiC wafers consisted of 2µm thick, n-type (Nd = 1.7 x 10^{19} cm^{-3}) epilayers grown 8° off the basal (0001) plane on high resistivity p-type substrates. All SiC wafers studied were supplied from Cree, Inc. Our studies followed the same sequence of process steps used conventionally to
remove surface contamination and structural damage prior to ohmic contact formation. This sequence of process steps appears in Table 1.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetone + Methanol</td>
</tr>
<tr>
<td>2</td>
<td>4-hr dry oxidation</td>
</tr>
<tr>
<td>3</td>
<td>HF-strip, DI water rinse and Piranha Clean (P-clean)</td>
</tr>
<tr>
<td>4</td>
<td>5-hr dry oxidation at 1150°C, HF strip, DI water rinse</td>
</tr>
<tr>
<td>5</td>
<td>Piranha Clean (P-clean)</td>
</tr>
</tbody>
</table>

Table 4. Specimen surface process steps.

First, the sample was cleaned with acetone and methanol. After this solvent clean, the sample was dry oxidized after at 1150°C for 4 hours, after which the oxide was stripped with HF and the surface rinsed with deionized (DI) water. In order to remove any non-organic contamination, the samples were then subjected to a Piranha-clean, consisting of 1:1 volume ratio of H₂SO₄ and H₂O₂ mixture. A sub-set of samples treated as above underwent a second dry oxidation, followed by a second HF strip and Piranha-clean (P-clean). Finally, all specimens were metallized by the sputter deposition of Ti and Pt and prepared for LEEN. Sample sets that were treated similarly as above, but not metallized, were analyzed by XPS, and TEM.

We used a low energy electron-excited nanoscale luminescence (LEEN) spectroscopy, a low energy form of cathodoluminescence spectroscopy (CLS) to
characterize the energies of electronic states as a function of distance from the SiC interfaces. This technique has provided similar information for a wide variety of semiconductor surfaces and interfaces.\textsuperscript{92,93,94,95} Base pressure in the LEEN ultrahigh vacuum (UHV) chamber was $10^{-10}$ Torr. At NASA-Glenn, we performed monochromatized, Mg K\textalpha\ X-ray photoemission spectroscopy (XPS) measurements of chemical bonding changes in SiC core levels on similarly processed, but not metallized, samples. Also, similarly processed, but non-metallized, samples were analyzed by transmission electron microscopy (TEM) at Case Western Reserve University and NASA-Glenn. CLS and LEEN spectroscopy involve the excitation of electron-hole pairs by an incident electron beam. The electron beam generates a cascade of secondary electrons that lose energy to plasmons and subsequently electron–hole pair generation. The optical signal results from radiative recombination of these free electrons and holes. Energy loss in electron cascade and, therefore excitation depth varies with incident beam voltage $E_B$. This is illustrated by the inset in Fig. 11.
Figure 11. LEEN depth-dose curve shows penetration depth versus $E_B$ for SiC. Inset graph shows corresponding energy loss in cascade versus depth.

The two curves in the main graph also illustrate changes in the maximum cascade penetration, $R_B$, beyond the free surface and the maximum excitation depth $U_0 \sim \frac{1}{3} R_B$. Both curves represent low energy approximations to polynomial expressions derived by Everhart and Hoff expressions and depend on incident beam energy $E_B$ and material density. These theoretical expressions agree with Monte-Carlo simulations of backscattered electron trajectories that take into account the different densities of metal versus SiC and the angle of incidence. At $E_B$ of only a few hundred to several thousand volts, the Fig. 11 inset shows that the generation rate of electron-hole pairs peaks up in a depth range of nanometers. For example, with $E_B = 1$ keV in SiC, $R_B = 20$ nm and
maximum excitation is at $U_0 = 8$ nm. This nanoscale excitation permits one to selectively probe the semiconductor from the interface to the bulk. Particularly in the surface-sensitive regime, LEEN spectra must be acquired in UHV in order to prevent contamination and signal deterioration due to associated non-radiative transitions and rapid deterioration of radiative transitions close to the surface.

### 5.1.3 6H-SiC Results

LEEN spectroscopy provided information on the energies and spatial depth distribution of localized states near the SiC-metal interfaces. Figure 12 illustrates two families of LEEN spectra taken with increasing $E_B$ and peak excitation depth $U_0$. The spectra in Figure 12(a) represent a depth profile corresponding to 6H-SiC after a methanol-acetone clean and subsequent Pt/Ti metallization. The higher $E_B$ spectra corresponding to the bulk ($U_0 > 25$ nm) display the characteristic 2.9 eV near band edge (NBE) emission of the 6H-SiC polytype. For comparison, Figure 12(b) represents a depth profile corresponding to 6H-SiC after a methanol-acetone clean, a 4-hour oxidation at 1150°C followed by HF strip and DI water rinse, and a subsequent Pt/Ti metallization. Again, the higher $E_B$ spectra display the characteristic 6H-SiC polytype emission at 2.9 eV. Similarly, both figures show additional features at 3.3 eV for the lower $E_B$ spectra corresponding to the interface region ($U_0 < 20$ nm). Since these features have energies above the 6H-SiC band edge, they cannot be due to defect emission to or from states in the band gap. They can be instead attributed to broken 6H lattice periodicity resulting in polytype variation near the interface. Also near the interface, both Figs. 12(a) and 12(b) shows emission corresponding to a broad continuum of states below the bandgap.
Figure 12. LEEN spectra of 6H-SiC (a) after acetone-methanol clean and metallization, and (b) after acetone-methanol clean, 4-hour dry oxidation, HF oxide strip, DI water rinse, and metallization. New phase formation is apparent near the interface in both cases.
Figure 13. LEEN spectra of 6H SiC after Piranha-clean reveal new defect formation near the interface.

Figure 13 illustrates the depth-dependent LEEN features of the same surface following the P-cleaning step. Similar to Fig. 12, the 6H-SiC NBE feature at 2.9 eV dominates in the bulk, and the 3.3 eV local polytype feature is apparent near the interface. In addition, a 1.9 eV feature appears just below the metal/semiconductor interface. Note that 4 nm is the approximate metal overlayer thickness so that most electron excitation occurs within the metal layer. This variation in local electronic features near the
interface is illustrated in Fig. 14 for an entire sequence of process steps. Features at 2.9 eV and 3.3 eV and the continuum of states are relatively independent of surface treatment before metallization. The 1.9 eV feature first appears after the first oxidation step, then increases after P-cleaning. Significantly, it is not observed after the second oxidation, strip, and rinse, or the second P-clean.

Figure 14. LEEN spectra of 6H-SiC spectra directly under the metal show that 1.9 eV and 3.3 eV features are relatively independent of process, in contrast to the 1.9 eV feature that appears after the first p-clean.
Figure 15. XPS spectra of 6H-SiC surface treated after different process steps. The higher binding energy shoulder corresponds to higher chemical bond strength than that in bulk SiC.

XPS spectra of the bare (no metallization) 6H-SiC surface after different process steps appears in Fig. 15. Here, C 1s core level peaks exhibit a dominant peak corresponding to bulk SiC and a smaller shoulder corresponding to near-surface C with higher binding energy. The near-surface spectrum after acetone and methanol rinse (diamonds) exhibits pronounced secondary C 1s intensity that is reduced almost completely (squares) by the first oxidation, HF strip, and DI water rinse. This spectrum indicates that oxidation/strip removes carbon with bonding different from the SiC bulk.
Piranha cleaning of the surface (triangles) reintroduces the C 1s sideband and the second oxidation, HF strip, and DI rinse (x symbols) again reduces its intensity. Finally, the second P-clean (* symbols) produces no significant change. Assuming that the C 1s peak is indicative of surface states, then the reduction in the higher binding energy C 1s peak with oxidation is consistent with removal of adventitious C and any lattice damage.

The depth dependence of interface and bulk features shown in Figs. 12 and 13 is consistent with TEM cross sectional images of the Ti/6H-SiC interface. The TEM image in Fig. 16 for sputtered a 100 nm Ti film on 6H-SiC (not part of the sequence above) exhibits 6-fold periodicity characteristic of 6H-SiC layer stacking in the bulk semiconductor (right side). The periodicity of the deposited Ti’s crystal structure is apparent to the left of the interface. Within the interface region, the disruption of 6H periodicity and possible formation of other polytypic phases is apparent. Significantly, the ~ 5 nm width of this disrupted interface agrees qualitatively with the ~ 15-10 nm total depth beyond the ~4 nm metal thickness into the SiC over which the 3.3 eV and continuum of gap states are predominant.
5.1.4 4H-SiC Results

The LEEN spectral data for 4H-SiC yielded evidence for both localized states near the metal interface as well as a polytype transformation that extends at least 50 nm into the 4H-SiC bulk. Figure 17 illustrates depth-dependent LEEN spectra for a 4H-SiC sample after acetone and methanol cleaning. Analogous to the 6H-SiC results, we observe mostly
4H bandgap peak at 3.2 eV for $E_B$ corresponding to bulk excitation. Similarly, as $E_B$ decreases and excitation occurs closer to the interface, we observe additional emission at 3.4 eV and a broad continuum of states below the bandgap energy.

Figure 17. LEEN spectra of 4H-SiC prior to oxidation showing only 3.2 eV NBE peak dominant at bulk excitation energies and higher energy features at 3.4 eV near interface.

Figure 18 shows the spectra for 4H-SiC following the same 4-hour, 1150°C oxidation, HF strip, and DI water rinse as used with 6H-SiC in Fig. 12. For the 4H case, this process step introduces a dramatic change. Instead of increasing with increasing probe depth, the 4H-SiC NBE peak at 3.2 eV actually decreases. Furthermore, a new peak appears at 2.5 eV that increases with excitation depth and dominates the spectra in
the bulk. The appearance of this peak suggests the formation of a 3C polytype, whose band gap is 2.39 eV at room temperature.\textsuperscript{96} In addition, a broad spectral feature appears at \( \sim 2.0 \) eV with strong intensity for depths extending 20 nm in the bulk. Analogous to Figs. 12, 13, and 17, the interface region exhibits emission at \( \sim 3.3-3.4 \) eV as well as broad continuum of states below the bandgap.

![LEEN spectra of 4H-SiC after oxidation](image)

Figure 18. LEEN spectra of 4H-SiC after oxidation showing the appearance of a 2.5 eV NBE emission due to 3C-SiC and the near disappearance of the 3.2 eV 4H-SiC NBE emission at all excitation depths. Multiple scans at certain \( E_B \) illustrate the spectral variability.

In order to confirm the appearance of a new polytype phase within the 4H-SiC bulk, we obtained TEM images of the 4H SiC sample before and after oxidation. TEM images of 4H-SiC before oxidation show only the undisturbed bulk crystal. In contrast,
Figure 19 illustrates an image following oxidation. Here, 3C bands are evident in narrow bands running parallel to the basal plane, interchanging with 4H SiC layers and extending deep in the bulk. The thickness of these 3C layers ranges from two 3C lattice repeat distances to several nanometers. Figure 19 displays sets of discrete transformation bands (DTBs), each containing multiple alternating bands of 3C and 4H-SiC. In turn, these DTBs appear to be spaced several hundred nm apart and extend throughout the thickness of the epitaxial SiC layer. Nitrogen dopant redistribution is not detected by secondary ion mass spectrometry (SIMS). Nor is Si or C precipitation detected by AES, indicating no stoichiometric change in the Si/C ratio.
5.1.5 Discussion

The interface electronic properties of 6H-SiC LEEN spectra are consistent with previous measurements of Schottky barrier formation as well as with the XPS measurements of core level bonding. The 1.9 eV feature can be attributed to electronic states near midgap introduced by the Piranha cleaning. Fermi level “pinning” by discrete states located 1.9 eV below the conduction band edge would contribute to n-type Schottky barriers of the same energy. Previous work\textsuperscript{97,98} indicated Fermi level positions 1.8-2.0 eV above the valence bandedge for Ti on n-type 6H-SiC. The correspondence with the 1.9 eV emission provides modest evidence for the midgap state contributing to
Fermi level pinning. Alternatively, this 1.9 eV emission may be due to incomplete silicon dioxide removal after oxidation or an oxide layer introduced by Piranha-cleaning since a similar peak is found in studies of SiO$_2$ defects.$^{99}$ This is unlikely since such a defect is usually accompanied by comparable or stronger emission of an even more common SiO$_2$ feature at 2.7 eV$^{99}$ that is not obvious from these 6H-SiC spectra. The introduction of the 1.9 eV LEEN feature by p-cleaning coincides with the appearance of additional C 1s core level emission at higher binding energy associated with new carbon bonding sites. Its absence for p-cleaning after the second oxidation suggests that lattice damage and/or contamination removed by the second oxidation and strip may contribute to such states as well. The continuum of states within the band gap at the metal interfaces of both 6H-SiC and 4H-SiC is consistent with a disordered interface and a distribution of localized states.$^{100}$ The agreement between the depth range of the 3.3 eV LEEN peak feature and the width of the Ti/6H-SiC interface confirms the surface sensitivity and nanoscale discrimination of depth-variable features electronic transitions using this technique. Furthermore, the presence of the 1.9 eV mid-gap states, the continuum of gap states, as well as the new polytype evidenced by 3.3 eV emission imply several different factors that can significantly affect the Schottky barrier formation.

In Fig. 18, the appearance of a pronounced peak feature at 2.5 eV following the oxidation process step indicates a conversion of the 4H-SiC polytype to 3C-SiC. Lattice images similar to the cross sectional TEM micrographs in Fig. 19 with atomic scale resolution display the characteristic 3C stacking sequence. Such transformation bands may be the result of lattice strain in the epilayer and the subsequent formation of stacking faults. Polytype transformations have been reported for 6H-SiC subjected to mechanical
stress, and electrical stress has been shown to produce stacking faults near metal contacts to 4H-SiC and 6H-SiC. For the 4H-SiC studied here, such stress may result from impurity-induced lattice mismatch between the epilayer and substrate. The discrepancy in energy between the observed 2.5 eV peak and the usual bulk value of 2.39 eV can be accounted for by the confined nature of 3C inclusions. Figure 19 and other TEM images show that the thickness of the cubic 3C-SiC layers ranges from two 3C lattice parameters to many lattice parameters. The lowest thickness is most common and corresponds to a single stacking fault in the 4H-SiC lattice structure. At thicknesses of only a few nanometers, the conduction and valence band states can be described as quantum-confined states with new quantized energy states at the 3C/4H heterojunction that increase the NBE energy of recombination. In order to determine the transition energies associated with such confined states, we first calculated band offsets between 3C-SiC and 4H-SiC by comparing band offsets for 3C-SiC versus 6H-SiC and 4H-SiC versus 6H-SiC. This provides a cumulative 3C-SiC versus 4H-SiC conduction band offset value of $\Delta E_C = 0.84 \pm 0.1$ eV and a valence band offset value $\Delta E_V = 0.07 \pm 0.1$ eV. Here, the conduction band of 3C-SiC lies lower in energy than that of 4H-SiC, whereas the valence bands almost align. In this case, the positive conduction band offsets result in quantum wells for electrons inside the 3C band but no confinement for holes. For a quantum well of width 1.75 nm, corresponding to two 3C unit cell repeat distances normal to the basal plane, the lowest energy state for electrons with $m_{\text{eff}} = 0.66 m_0$ equals 0.11 eV from bottom of the well. Note that a $\pm 0.2$ eV error in $\Delta E_C$ produces $< 5\%$ change in this ground state energy. Also, the energy associated with any hole confinement is negligible. NBE emission in this structure would involve recombination.
of holes from the lowest quantum well state in the conduction band to the top of the valence band. The resulting emission would occur at: 2.39 eV (3C-SiC bandgap) + 0.11 eV (QW ground energy state) = 2.5 eV. This result is in excellent agreement with the LEEN spectra. Furthermore, since the joint density of states of the 3C-SiC quantum well is higher than that of bulk 4H-SiC and the quantum well is an efficient collector of free electrons, the latter serves as a more efficient source of carrier recombination. This accounts for the much stronger 3C-SiC NBE emission relative to that of 4H-SiC in Fig. 18.

The ultrathin nature of the 3C-SiC layers imbedded in 4H-SiC and the expected 3C-4H SiC band offsets indicate that these inclusions will form multiple quantum wells, and would therefore have a significant effect on Schottky barrier and ohmic contact properties. This is an unanticipated result, namely that standard device process steps can change the electronic and crystalline structure of conventional 4H-SiC. Structural changes observed in 4H-SiC Ti/Pt contacts manifest themselves in metal-4H-SiC current-voltage (I-V) measurements. Pt/Ti contacts to untransformed 4H-SiC exhibit rectifying behavior, whereas the same metals on transformed 4H-SiC show a linear I-V characteristic. The control of such 4H-to-3C conversions presents a challenge for current SiC microelectronics fabrication. Conversely, this finding opens the possibility for new structures that take advantage of the band gap changes and quantum-scale confinement induced by the transformation.
5.1.6 Conclusions

We have observed optical emission from discrete and continuum defect states on 6H-SiC/metal interfaces below the bandgap and polytypic features above the bandgap. The relative concentration of such features increases with proximity to the interface on a scale of nanometers. XPS core level spectra exhibit chemically-shifted C binding energies consistent with the different process steps and the changes in LEEN spectral features. TEM confirmed our results for polytypic formation within few nanometers from the interface. Analogous to 6H-SiC, 4H-SiC/metal interfaces displayed optical emission from discrete and continuum defect states, again increasing within a few nm of the interface. In contrast to 6H-SiC, 4H-SiC exhibits a pronounced polytype change to cubic 3C-SiC not only at the interface but extending hundreds of nm into the bulk. TEM cross sectional micrographs confirm the appearance and spatial extent of this 3C-SiC polytype transformation, revealing the presence of alternating layers of 3C-SiC and 4H-SiC in discrete transformation bands. These results have significant implications for the design and fabrication of SiC electronic devices.

5.2 Thermal and Doping Dependence of 4H-SiC Polytype Transformation

We have observed characteristic temperatures, anneal times, and doping densities that lead to stacking faults and 3C-SiC-like bands in 4H-SiC epilayers. Low energy cathodoluminescence spectroscopy measurements reveal a temperature threshold of 800°C for emergence of these features in thermally oxidized or argon annealed 4H-SiC with an activation energy $\approx 2.5$ eV. Stacking fault generation and polytype
transformation exhibits a strong doping dependence, appearing only in a range of highly doped n-type 4H-SiC. Systematics of these strain and/or electronic effects induced by high N concentrations can be used to control structural instabilities during SiC device fabrication.

5.2.1 Introduction

The structural properties of SiC and other wide band gap semiconductors (WBGS) are known to have a strong influence on their thin film and interface electronic properties. The interplay between crystal structure, strain, local bonding, and electronic states can strongly affect Schottky barriers, free carrier confinement, recombination and ultimately the power and speed of WBGS microelectronics. Recently, we showed that n-type, N-doped 4H-SiC epitaxial thin films on p-type SiC substrates can undergo polytypic transformation with thermal oxidation.5 Others have reported stacking fault (SF) generation and polytype changes in SiC with mechanical89 or electrical stress.26 We can observe electronic and structural features of these transitions using a combination of low energy electron-excited nanoluminescence (LEEN) spectroscopy and transmission electron microscopy (TEM) imaging. The near-surface capability of LEEN reveals that SiC can undergo polytypic transformations near metal or oxide interfaces. For Pt/Ti overlayers on both 4H-SiC and 6H-SiC, a higher band gap polytype106 appears, extending only a few nm into the SiC.6 This is consistent with TEM micrographs showing a disruption of the bulk lattice periodicity over a comparable nm-scale range. For Pt/Ti overlayers on 4H-SiC, thermal oxidation also induces a polytype transformation.
resembling 3C-SiC that extends well over a hundred nm into the otherwise 4H-SiC. TEM cross-sectional images reveal transformation bands several nm thick of alternating 4H and 3C-SiC stacking layers.

The driving force for this polytype change could be strain due to differences in thermal expansion between epilayer and substrate, injection of interstitials and stacking faults, doping-induced differences in lattice constant, or electronic effects. The 4H-SiC/3C-SiC/4H-SiC heterojunctions present device opportunities if they can be formed controllably. However, these transformations involve process steps often encountered in SiC microelectronic processing and are to be avoided. We have now explored the thermal, temporal, and doping parameters associated with the 4H-SiC transformation to understand the physical processes driving this structural change.

5.2.2 Experimental

Specimens consisted of high resistivity (4 Ω-cm), 8° off-axis (from the (0001) basal plane), Si-face, n -type 4H-SiC substrates with 2 µm thick n- (N) and p-type (Al) epilayers grown homoepitaxially by Cree, Inc. Wafers were cut into 1x1 cm² pieces, cleaned in acetone/methanol (“solvent cleaned”), then dry-oxidized at varying temperatures and times. Oxides were stripped in 49% HF acid and rinsed in deionized water and Piranha (50:50 volume ratio of sulfuric and peroxide solution) cleaned. A subset was thermally annealed in ULSI-grade argon versus oxygen. Another subset was analyzed with transmission electron microscopy (TEM). All were analyzed at room temperature by LEEN spectroscopy, a near-surface and depth-resolved form of cathodoluminescence spectroscopy that can excite luminescence selectively, either at the
metal/SiC interface, in the near surface region extending tens of nanometers into the SiC epilayer, or further into the SiC epilayer. Room temperature photoluminescence (PL) spectra with He-Cd (325 nm) laser excitation (7.5 µm penetration depth in 4H-SiC) exhibit features comparable to those of bulk LEEN spectra.
Figure 20. Sub-surface, 4 keV LEEN spectra of different $n = 1.7 \times 10^{19}$ cm$^{-3}$ 4H-SiC samples for various temperatures and times. The $\sim 2.5$ eV appears at 800$^\circ$C and grows with temperature up to 1150$^\circ$C. The inset Arrhenius plot yields $E_A = 2.5 \pm 0.35$ eV.

$E_B = 4$ keV

$U_0 = 50$ nm
The threshold for 4H-SiC polytype change depends both on anneal temperature and time. Figure 20 shows LEEN spectra of solvent cleaned, \( n = 1.7 \times 10^{19} \text{ cm}^{-3} \) 4H-SiC (measured by C-V and SIMS) for various oxidation and annealing conditions. Each spectrum is characteristic of multiple locations on several different samples. Shown here are 4 keV spectra with peak excitation depths \( U_0 = 50 \text{ nm} \) below the free surface. Similar features are apparent for excitation at lower depths. All spectra exhibit characteristic bulk 4H near band edge (NBE) emission at \( \sim 3.2 \text{ eV} \). The 1.75 nm width measured directly from TEM cross-sectional micrographs produces a 0.11 eV increase in NBE energy, almost exactly in agreement with the 2.47-2.48 eV energy expected for a quantum confined polytype with 2.36 eV band gap at room temperature.\(^6\) The lowest temperature oxidation temperature spectrum shows weak emission at 2.5 eV after 7 hours at 800\(^\circ\)C. At 1000\(^\circ\)C for 2.5 hours, the 2.47 and 3.2 eV features are comparable. After 2.5 hours at 1150\(^\circ\)C, the 2.47 eV feature is several times larger. This 2.47 eV peak signals the appearance of the 3C structural change.\(^5\) Little change occurs at a higher temperature of 1200\(^\circ\)C after comparable anneal time. A broad new feature appears at \( \sim 1.9 \text{ eV} \) that may also be present at lower intensity in the 1150\(^\circ\)C spectrum. At 1400\(^\circ\)C for much shorter time, the 2.5 eV and 1.9 eV peaks decrease, possibly due to electronic effects (see below), and the bulk 4H-SiC NBE peak reemerges. Thus any additional structural changes in the 1200- 1400\(^\circ\)C range do not contribute to further polytype transformation.
Figure 21. Subsurface, 4 keV LEEN spectra of different n= 1.7x10^{19} cm^{-3} 4H-SiC samples for a range of anneal times at 1150°C. The 2.47 eV peak appears after 1 hour. For this sample oxidized at 1150°C, a minimum anneal time is required for the 2.47 eV peak onset. With the same 50 nm probe depth, Fig. 21 spectra show no such emission for t < 1 hour. At one hour, I(2.47)/I(3.2) is low with significant broad emission at 1.9 eV. For a 1.5 hour anneal, the 2.47 eV peak dominates the spectrum. Only minor changes are evident for longer anneal times.
5.2.4 Discussion

The rapid growth of the intensity ratio \( I(2.47)/I(3.2) \) between 800°C and 1150°C and its time dependence suggest a thermally activated process. (The 3.2 eV NBE emission is used for normalization since the total excited 4H-SiC volume is large compared to that of the quantum confined polytype.) These temperatures are well below those required for dopant diffusion, but are consistent with previously reported deformation-induced polytype changes, since dislocation movement increases rapidly in this temperature regime.\(^{107}\) Indeed, an Arrhenius plot of the time-normalized LEEN intensity ratio \([I(2.5 \text{ eV})/I(3.2 \text{ eV})]^2/t\), assuming emission intensities proportional to diffusion length \( L = [D(T)\cdot t]^{1/2} \), where diffusion constant \( D(T) = D_0 e^{-E_A/kT} \) and \( D_0 \) is a constant, yields an activation energy \( E_A = 2.5 \pm 0.35 \text{ eV} \), as shown in the Fig. 20 inset. This is comparable to activation enthalpy changes for dislocation glide extracted from mechanical deformation rate studies.\(^{7}\)

To establish whether oxidation is responsible for the structural changes, we performed similar studies on solvent-cleaned 4H-SiC annealed in the same furnace in argon. A 4-hour 1150°C argon anneal produces the same strong 2.47 eV peak as in the oxidation experiments.\(^5\) As before, no such change occurs prior to annealing with solvent or P-cleaning. These results demonstrate that oxidation \textit{per se} is not required for the structural changes.
Figure 22. Sub-surface, 5 keV LEEN spectra of cleaned and oxidized 4H-SiC as a function of doping concentration. Only $n = 1.7 \times 10^{19}$ cm$^{-3}$ 4H-SiC exhibits a sharp peak at 2.48 eV.
Dopant type and concentration have a major effect on the polytype conversion. Figure 22 illustrates spectra for 4H-SiC specimens with different n- and p-type concentrations, all solvent-cleaned, then oxidized at 1150°C for 4 hours. These spectra show substantial differences in optical emission. Only the n=1.7x10^{19} cm^{-3} 4H-SiC exhibits a relatively sharp 3C band-like peak at 2.47-2.48 eV. Lower n-type doping specimens show broader emission shifted to 3C bulk-like energies of 2.31-2.37 eV, whereas the n=5.3x10^{18} cm^{-3} spectrum suggests two unresolved peaks centered at 2.31 and 2.48 eV. This progression from 4.1x10^{17} cm^{-3} to 1.7x10^{19} cm^{-3} suggests that the two spectral features are complementary. Significantly, no LEEN emissions in the 2.3-2.5 eV range are observable in p-type 4H-SiC at any doping level. The p-type NBE emission at 3.15 eV merely broadens toward 3.0 eV. At the highest dopings, both oxidation annealed n- and p-type SiC exhibit broad features around 1.9-2 eV or lower. At n=2.2x10^{19} cm^{-3}, the n-type SiC no longer exhibits 2.3-2.5 eV features. Besides observed lattice disruption, impurity and defect complexes may form that alter the effects of these high doping levels. In p-type 4H-SiC, a 2.09 eV feature has been attributed to N-Al complexes. Its appearance here in both n- and p-type 4H-SiC suggests new lattice defects. Thus only n-type 4H-SiC exhibits 3C-like features and only in the range of 4.x10^{17} cm^{-3} to 1.7x10^{19} cm^{-3}. The former is consistent with n-doped SiC’s tendency to favor cubic rather than hexagonal growth. Likewise, Miao et al. conclude that SFs should be energetically favorable in highly n-type 4H-SiC because the Fermi level in this case is above the SF level (~0.2 eV below the conduction band). The I(2.47)/I(3.2) decrease at 1400°C may be due to the Fermi level lowering with increased temperature, consistent with the Lambrecht and Miao model.
5.2.5 Conclusions

Significantly, the thermally-activated polytype transformation in 4H-SiC epilayers exhibit threshold temperatures, anneal times, and doping densities that are characteristic of SiC microelectronic processing. These results are consistent with dopant-induced strain and electronic effects, thermally-activated dislocation motion, and subsequent formation of polytype transformation bands. They suggest a tradeoff between high temperature annealing and high N doping in order to minimize structural instability.

5.3 Temperature-Dependent Photoluminescence and Cathodoluminescence Spectroscopies of Highly Doped 4H-SiC

We have measured the optical emission features of highly-doped n-type and p-type 4H-SiC epitaxial single crystals as a function of temperature from 10 to 300 K using photoluminescence and cathodoluminescence spectroscopies. In addition to the band edge features, we observe deep level emissions due to growing inclusions, the formation of stacking faults and polytype changes resulting from a combination of high doping and thermal annealing, as well as lattice disruption due to interface reaction. These multiple deep levels detected in highly doped 4H-SiC, depend strongly on dopant type and concentration. These results are used to distinguish between spectral features associated with structural versus chemical imperfections.
5.3.1 Introduction

SiC is a semiconductor of high current interest because of its unique electronic and thermal features. Due to its high band gap (high breakdown voltage, low intrinsic carrier concentration at high temperatures), high melting point (high thermal stability), and high thermal conductivity (excellent power dissipation), SiC may be used for wide variety of applications in high-temperature and high-power applications. 111

Recently it has been demonstrated that highly doped 4H-SiC exhibits structural changes under high-temperature annealing conditions5,112,7,76 or electrical stress, 26,102 resulting in stacking faults and the creation of transformation bands of 3C-SiC extending microns through the bulk of the epitaxial crystals. 5,75 Cathodoluminescence (CL) spectroscopy of these transformed polytype regions exhibit optical emission characteristic of 3C-SiC and corresponding to quantum-confined layers within the 4H-SiC host crystal.6 The driving force for such transformation may be internal stress caused by the difference in dopant concentration and the resultant difference in SiC bond length. Such a transformation could also be thermodynamic in nature, i.e., due to the formation of a new energy levels associated with stacking faults (SF).110,77 In either event, such transformations pose major problems for the processing and subsequent operation of 4H-SiC high temperature, high power devices.

In addition, low energy electron-excited nanoluminescence (LEEN) spectroscopy, a low energy (0.1 keV<EB<5 keV), depth-resolved form of cathodoluminescence spectroscopy), 113 reveals the presence of transformed layers with wider band gap (possibly 2H) near 4H-SiC interfaces with metal overlayers. 6 Although only a few nanometers in thickness, such intermediate layers can reduce the control of SiC Schottky
barriers or ohmic contacts. Both n-type and p-type 4H-SiC exhibit deep level features in addition to these transformation peaks that could be associated with strain, dopants, or unintentional impurities. Variable temperature photoluminescence (PL) spectroscopy can provide optical transition and activation energies that can be used to associate these features with particular physical imperfections of the 4H-SiC such as lattice defects, impurities, or morphological imperfections. The identification of these defects and other electrically active sites can improve our understanding of the forces driving SiC polytype transformations.

5.3.2 Experimental

Specimens consisted of high resistivity (4 Ω-cm), 8° off-axis (from the (0001) basal plane), Si-face, n-type 4H-SiC substrates with 2 μm thick n- (N) and p-type (Al) epilayers grown homoepitaxially by Cree, Inc. on nominally p-type bulk SiC wafers.

All samples were processed at the NASA-Glenn Research Center. Wafers were cut into 1x1 cm² pieces, cleaned in acetone/methanol (“solvent cleaned”), then dry-oxidized at varying temperatures and times. Oxides were stripped in 49% HF acid and rinsed in deionized water, then Piranha (50:50 volume ratio of sulfuric and peroxide solution) cleaned to remove any organic contaminants. N-type samples were N-doped, cleaned, oxidized for 4hr at 1000⁰ C and then oxide was stripped. This oxidation and strip process serves to remove damaged surface layers of SiC. P-type samples were Al –doped. Table 5 provides descriptions of the 4H-SiC samples, their doping concentrations and their processing treatments.
Table 5. Descriptions of the 4H-SiC samples, their doping concentrations and processing treatments.

Photoluminescence spectra were performed using a 325 nm, 200 mW He-Cd laser as an excitation source. The absorption coefficient $\alpha$ for 325 nm He-Cd laser excitation in 4H-SiC is 1330 cm$^{-1}$, corresponding to an absorption length of 7.5 $\mu$m at RT. At 2K, $\alpha = 1190$ cm and $\alpha^{-1} = 8.4$ $\mu$m is even longer.\textsuperscript{114} Samples were mounted in a Janis Research CCS-100-EB variable temperature (9-325K) cryostat with sapphire window access.

LEEN spectroscopy measurements were performed using a glancing incidence electron gun in ultrahigh vacuum (UHV). Incident beam current was $\sim$3 $\mu$m with energies $E_B$ ranging from 0.5 keV to 5 keV. Monte Carlo simulations\textsuperscript{61} as well as Everhart-Hoff\textsuperscript{60} polynomial approximations yield corresponding depths of maximum excitation ($V_0$) ranging from 3 to 60 nm, increasing with increasing $E_B$. A Carl-Leiss prism monochromator positioned at a sapphire window port of the UHV chamber coupled with
a quartz lens and an external optical fiber provided the optical train for the LEEN spectra. PL spectral resolution was 20 meV in the energy ranges measured. Corresponding spectral resolution for LEEN measurements was 40 meV.

5.3.3 N-type 4H-SiC Luminescence Spectroscopy Results

PL spectra for all samples exhibit similar sets of peak features in the near band edge (NBE) region at low temperatures. As shown in Figure 23, there are several main features common to all spectra: a broad shoulder at 2.835 eV, plus partially-resolved peaks at 2.905 eV, 2.94 eV, 3.005 eV and 3.05 eV. The free exciton features (3.16 eV, 3.17 eV, 3.19 eV at 2 K)\textsuperscript{108} are not present in these low temperature spectra. With increasing temperature from 10 K to 160 K, the 2.9 eV features drop in intensity but their lineshapes remain approximately unchanged. The intensity of 2.9 eV emission does not have a strong dependence on the n-type doping level of the epilayer.
Figure 23. PL spectra of n-type 4H-SiC at 9 K in the 2.9 eV region with different N
doping. Similar sets of near band edge features are evident, independent of doping.

Figures 24 – 27 illustrate temperature-dependent PL spectra for the same samples
as in Fig. 23. For these and all other samples, both n- and p-type, a broad feature at 2.45
eV appears at ~160 K, increases in intensity relative to the 2.9 eV features with
increasing temperature up to 240 K, then gradually decreases with further temperature
increases. NBE features at 3.09, 3.16 and 3.22 eV appear along with this 2.45 eV peak.
With increasing temperature, these NBE peak features merge into a broad peak at 3.16
eV and a shoulder at ~3.05 eV that dominate the RT spectrum. The 2.905 and 2.94 eV features decrease with increasing temperature and are completely quenched above 200 K. Figures 24–27 show that the 2.45 eV peak persists at 300 K for all but the $1.7 \times 10^{19}$ cm$^{-3}$ sample. For this crystal, Fig. 26 shows the appearance of a 2.5 eV shoulder, starting at around 90 K, that evolves into a sharper 2.5 eV peak at around 200 K. At around 280 K, an additional, broad feature appears at 1.87 eV that increases with increasing temperature. The spectrum for the $n=2.2 \times 10^{19}$ cm$^{-3}$ doped sample Fig. 27 also indicates emission around 2.0 eV. These features are not evident in the spectra of the lower doped specimens.
Figure 24. Temperature-dependent spectra of $n = 4.1 \times 10^{17}$ cm$^{-3}$ N 4H-SiC PL from 10 to 325 K. Fine structure in the 2.9 eV region is replaced by near band edge ($\sim$3.16 eV and 3.22 eV) emissions above $T \sim 160$ K. A broad emission at 2.45 eV also emerges at $\sim$160 K and shifts to $\sim$2.5 eV with increasing temperature.
Figure 25. Temperature-dependent spectra of $n = 1.7 \times 10^{19}$ cm$^{-3}$ N 4H-SiC PL from 10 to 325 K. A broad emission at 2.5 eV emerges at ~160 K that sharpens with increasing temperature up to 325 K. At ~280 K and above, a new broad peak appears at 1.9 eV.
Figure 26. Temperature-dependent spectra of $n = 2.6 \times 10^{18}$ cm$^{-3}$ N 4H-SiC PL from 10 to 325 K.
Figure 27. Temperature-dependent spectra of \( n = 2.2 \times 10^{19} \) cm\(^{-3}\) N 4H-SiC PL from 10 to 325 K.

Figure 28 shows low energy cathodoluminescence (LEEN) spectra at 300 K taken with \( E_B = 4 \) keV for the same four n-type specimens. Each spectrum shows similarities and differences with its PL counterpart in Figs. 23 - 27. The \( n = 4.1 \times 10^{17} \) cm\(^{-3}\) crystal exhibits the same NBE peak at 3.16 eV but an even stronger emission at 2.36 eV. This
2.36 eV feature is absent in the corresponding Fig. 24. Similarly, the n=2.6 x 10^{18} \text{ cm}^{-3} crystal exhibits the same NBE peak at 3.16 eV as in Fig. 25, and a much stronger set of broad, unresolved features at 1.9 eV and 2.25 eV. The n=1.7 x 10^{19} \text{ cm}^{-3} sample displays a much more pronounced 2.5 eV feature than the PL spectrum in Fig. 26, along with a NBE peak at 3.16 eV. These features are clearly stronger in LEEN than in PL. For the n=2.2 x 10^{19} \text{ cm}^{-3}, both LEEN and PL show similar peak emissions at 3.16 eV and broad features from below h\nu=2 eV to above 2.5 eV, weaker in PL than in CL spectra.
Figure 28. Comparison of 300K CL spectra with incident beam $E_b = 4$ keV versus n-type doping level. The $n = 1.7 \times 10^{19}$ cm$^{-3}$ N 4H-SiC spectrum exhibits a pronounced 2.5 eV peak as well as the 3.2 eV NBE peak. Other n-type doping levels exhibit features at $\sim 1.9$ eV and 2.25-2.35 eV.
Figure 29. Temperature-dependent PL spectra of $p > 2 \times 10^{19}$ cm$^{-3}$ Al 4H-SiC from 8 to 325 K. For temperatures above ~120 K, the broad 2.16 eV peak weakens and is replaced with a broad 2.4 eV peak. Near band edge and 2.9 eV region emissions are absent above 100 K but reappears for $T > 200$ K.
Figure 30. Temperature-dependent PL spectra of $p = 1.7 \times 10^{19}$ cm$^{-3}$ Al 4H-SiC from 8 to 325 K.
Figure 31. Temperature-dependent PL spectra of $p = 5 \times 10^{18}$ cm$^{-3}$ Al 4H-SiC from 8 to 325 K.
5.3.4 P-Type 4H-SiC Luminescence Spectroscopy Results

4H-SiC crystals doped p-type with Al display PL and LEEN spectra that differ significantly from the n-type spectra described in Sec. IIIA. The 9K spectra in Figs. 29-31 show multiple NBE features at 2.94, 3.0, 3.06, 3.16, and 3.22 eV. Unlike the n-type spectra in Fig. 24, free exciton features appear at the lowest temperatures. Each spectrum also shows a broad peak feature at 2.15 eV. No such 2.15 eV peak appears for the n-type samples in Figs. 24 - 27. With increasing temperature, the emission peaks appear to shift to lower energy (Fig. 31), or remain unchanged (Fig. 30). Also unlike the n-type spectra in Figs. 24- 27 , NBE emissions are weak or absent for 100 K<T<200 K for the p-type 4H-SiC in Figs. 29-31. With the exception of n=1.7 x 10^{19} cm^{-3}, all n- and p-type 4H-SiC display a clear NBE peak at 3.16 eV at 300 K. Only the p-type spectra display a 2.15 eV feature. The intensity of this feature decreases with increasing temperature above ~ 100 K, gradually merging into the 2.4 eV feature common to all n- and p-type samples.
Figure 32. Comparison of 300K CL spectra with incident beam $E_B = 4$ keV as a function of p-type doping level. Peaks appear at 2.45, 3, and 3.2 eV. With increasing Al doping, the 3.0 eV feature grows and a broad peak appears at $\sim$1.9 eV.
Figure 33. Depth-dependent LEEN spectra of p-type, $5 \times 10^{18}$ cm$^{-3}$ Al-doped 4H-SiC showing only broad near band edge and deep level emission features at $\sim$2.5 and 3.2 eV. With increasing excitation depth, these features appear sharper.
Figure 34. Depth-dependent LEEN spectra of p-type, $1.7 \times 10^{19}$ cm$^{-3}$ Al-doped 4H-SiC.
Figure 35. Depth-dependent LEEN spectra of p-type, >2 x 10^{19} cm^{-3} Al-doped 4H-SiC
Figures 32 – 35 show CL and LEEN spectra respectively for acceptor-doped 4H-SiC. CL spectra at 300 K in Fig. 32 of the same p-type 4H-SiC samples measured in Fig. 26 show a dominant 3.22 eV NBE for \( p = 5 \times 10^{18} \text{ cm}^{-3} \) 4H-SiC and a 3.06 eV emission whose intensity increases with increased Al doping. LEEN spectra in Figs. 33 - 35 show that with lower \( E_B \) and \( U_0 \), the 3.2 eV NBE intensity decreases, and broad features at 3.4 eV, \( \sim 2.45 \) eV, and 2.0 eV increase. For the samples with higher Al doping concentration, the 3.06 eV peak intensity increases and its energy shifts to 3.0 eV at all depths probed. The broad emission at \( \sim 2.45 \) eV is similar for all Al doping concentrations.

5.3.5 Discussion

4.3.5.1 N-type 4H-SiC Luminescence

The NBE and deep level luminescence features in Figs. 23-35 can be associated with a variety of localized states with energies in the 4H-SiC band gap. The physical origins of these states range from donor and acceptor impurity levels to point defect complexes, and include various extended defects. Indeed, some of these features appear to be similar to those reported previously for stacking faults and polytype changes induced by thermal or electrical stress.

5.3.5.1.1 Luminescence features at 2.8-3.1 eV

The multiple narrow spectral features from 2.8 eV to 3.1 eV can be associated with antisite pairs \(^{115}\) and N-bound excitons. \(^{116}\) The 2.9 eV peaks could be attributed to N donor sites or a thermodynamically induced state associated with stacking faults proposed by Miao \textit{et al.} \(^{110}\) and Iwata \textit{et al.} \(^{77}\) NBE emission peaks at 3.16 eV and 3.22 eV at temperatures above 180 K have energies corresponding to N donor levels at \( E_c - \)}
0.092 eV and $E_c-0.052$ eV. However, there is no significant dependence of their intensity on N concentration. Nevertheless, in support of their N-related origin, the temperature quenching of the ~2.9 eV peaks is similar to the DAP peak quenching in B-doped samples due to thermal ionization of the N – donor. When temperature is increased from 60 K to 120 K, the intensity of DAP decreases as shallow N donors are ionized and conduction-electron-to-deep-B transitions begin to dominate. If the 2.9 eV features are related to N donor sites in our samples and the 2.45 peak involves a transition from the conduction band, the N ionization process in the same range of temperatures can explain the decline of 2.9 eV features and the simultaneous increase of NBE and 2.45 eV peak intensities at intermediate temperatures.

Additionally, the $h\nu=2.8-2.9$ eV peaks may be due to point defects. It has been found that 2 MeV $10^{15} - 10^{18}$ cm$^{-2}$ electron irradiation can produce a series of sharp PL lines in this same 2.8-2.9 eV energy interval for both n-type and p-type 4H-SiC. Egilsson et al. and Eberlein et al. have attributed these features to recombination of a delocalized electron with a localized hole bound to a Si antisite defect.

The NBE PL peak features at 2.905 eV, 2.94 eV, 3.005 eV and 3.05 eV in Fig.23 may also have a morphological origin. S.G. Sridhara et al. reported similar peaks for electrically-stressed 4H-SiC. They observed a peak at 2.90 eV, sharper peaks at 2.93 eV, 2.94 eV, 2.95 eV, 2.96 eV, and 2.99 eV, in addition to very sharp lines at 2.97 and 2.98 eV. These lines were attributed to exciton recombination at local potential fluctuations caused by stacking faults induced by electrical stress. S. Bai et al. have also observed sharp PL features under FreD laser excitation in 4H-SiC grown by a hot wall CVD reactor that are associated with stacking faults observed via TEM. These peaks
appear at 2.877, 2.881, 2.885, 2.908, and 2.941 eV, the higher two of which agree with Sridhara’s and our work. We extracted the activation energy of 2.9 eV integrated peak intensities as shown in Fig. 36 for \( n = 2.6 \times 10^{18} \) cm\(^{-3}\) using the expression 
\[
I(T) = I_0 \left/ \left(1 + \alpha \exp\left(-E_A / kT\right) \right) \right.
\]
to describe the quenching behavior. A value of \( \sim 254 \pm 10 \) meV was calculated for most samples. This is consistent with the result reported by Sridhara, where a corresponding \( E_A \) of 282 meV was calculated.\(^{120}\)

![Figure 36. Activation energy plot of the broad 2.5 eV peak for \( n = 2.2 \times 10^{19} \) cm\(^{-3}\) N 4H-SiC.](image)

As Fig. 23 shows, peak features in this 2.8-2.9 eV energy range appear for all samples after several hours annealing at temperatures \( T > 1000^\circ \)C. They are present in
samples with lower doping ($< 10^{19}$ cm$^{-3}$), for which LEEN spectra show no pronounced 2.5 eV peak associated with stacking faults. Nor are stacking faults evident in TEM images, in contrast to highly doped specimens after high temperature annealing that do exhibit stacking faults and 2.5 eV LEEN peaks. LEEN spectra taken at 100 K (not shown) demonstrate that such 2.8-2.9 eV features are observed in the substrate and not in the epilayer.

5.3.5.1.2 Luminescence features at 2.45, 2.15, and 1.9 eV

The broad feature at 2.45 eV discussed here is also common to all n-type and p-type samples studied, indicating that it could be an inherent property of the material as grown. In n-type 4H-SiC, it appears at intermediate temperatures. In p-type 4H-SiC, it appears at high temperatures, growing in intensity with increasing temperature as the 2.15 eV feature diminishes. Sridhara et al. observed a RT PL peak in B-doped samples located at 2.4 eV with the shape similar to those in spectra of Figs. 24 - 32. Furthermore, Kakanova-Georgieva et al. observed CL spectral features ranging from 2.45 to 2.1 eV, which they attributed to transitions involving N donor - B acceptor recombination. One such defect could be associated with B occupying a C site, and another with B centered in a vacancy cluster. Galeckas et al. also found strong emission at 2.43 eV with a shoulder at ~2.3 eV, which they attributed to B impurities based on previous studies of B-doped 4H-SiC. It should be noted that SIMS depth profiles of our samples yielded very low signals attributable to B. Nevertheless, their absolute concentrations could not be determined for lack of a standard. Thus, B contributions to PL can not be ruled out.
In our spectra, the N doping concentration could be affecting both the number of B-N pairs and the amount of lattice stress, thereby changing the balance between the 2.45eV, 1.9-2.0 eV and other peak emission intensities. The fact that the highly N-doped 1.7x10^{19} cm^{-3} sample exhibits the strongest 1.9 eV PL feature is consistent with its relation to stress and polytype change induced by high N concentration. The only sample with a higher N doping exhibits a highly disordered domain structure according to X-ray diffraction, possibly reducing the formation of these morphological defects.

Previous work showed that a critical doping level of 1.7x10^{19} cm^{-3} N, results in stacking faults after extended annealing, yielding a layered structure of 3C-SiC lattice polytype. Figures 25 and 28 show that this is accompanied by the appearance of a 2.5 eV peak. Our results here also show that this is the only sample that demonstrates the sharp PL feature at 2.5 eV. See Fig. 26. The activation energy estimated from an Arrhenius plot is ~ 0.25 eV, consistent with the 2.9 eV activation energy and a level 0.2-0.3 eV below E_c.

Figure 25 illustrated LEEN spectra with deep level emissions at 1.9, 2.25, and 2.36 eV that are most prominent for the lowest doping concentrations. Increased N doping may increase NBE transitions involving N donor levels relative to the lower energy transitions. For the n=1.7 x 10^{19} cm^{-3} 4H-SiC in Fig. 28, the transformation bands observed by TEM have a lower band gap and the effective quantum wells act as sinks for carrier recombination. The competition for free carriers introduced by these quantum wells effectively reduces the deep level defect intensities. The higher doped n=2.2 x 10^{19} cm^{-3} SiC exhibits X-ray diffraction peak broadening indicative of grain boundaries and
lower induced stacking faults. Hence, less prominent 3C-like emission at 2.5 eV is expected. Furthermore, the additional crystalline disorder may induce additional recombination that competes with the 1.9 – 2.3 eV transitions shown.

A more probable explanation of the broad ~ 2.4 eV feature is in terms of 3C inclusions rather than B in the 4H-SiC host crystal. Bulk 3C NBE emission is below 2.39 eV. But for small enough inclusions, this energy increases due to quantum confinement. Furthermore, if these inclusions have variable size, they will exhibit a broad range of energies. Approximating such inclusions as platelets whose layer thickness defines the maximum emission energy, a simple finite well calculation yields a range of sizes from 1.5 to 5 nm that can account for the range of energies contained within the ~ 2.4 eV shoulder.

The 2.15 eV broad feature can also be accounted for in terms of 3C-SiC inclusions. Choyke and Patrick ascribed broad emission from 2.14 to 2.22 eV to N-Al donor-acceptor pairs in 3C-SiC with a limiting photon energy for distant pairs at 2.09 eV at 1.8 K. 125 Thermal dissociation of such pairs is consistent with a T-dependent shift to ~2.4 eV at intermediate temperatures. There is also considerable evidence for the presence of 3C inclusions in TEM cross- sectional studies. 126,127

Thermal activation of free carriers at spatially localized sites can account for the temperature dependence of PL spectra in Figs. 24 and 26. For temperatures from 10 to ~ 90 K, recombination involving NBE bound excitons and donor-acceptor pairs dominates the PL spectra. With increasing temperature, these conventional features broaden and higher energy peaks appear as carriers are thermally excited from these shallow states to
the band edge. Such free exciton emission is most pronounced for the lowest doped sample in Fig. 24, appearing at 3.22 eV at $T = 140$-$160$ K. Similar emission appears in Figs. 25 and 27 but is remarkably absent in Fig. 26. For this $n = 1.7 \times 10^{19} \text{ cm}^{-3}$ specimen, no band edge emission is detectable at any temperatures. This absence can be attributed to competition for free carriers with other recombination channels. Recombination at 2.45-2.47 eV is common to all of the 4H-SiC samples shown in Figs. 24 - 31, becoming the dominant luminescence feature for temperatures from 140 K to above 200 K. In the case of the $n = 1.7 \times 10^{19} \text{ cm}^{-3}$ sample, this 2.47 eV recombination appears dominant at temperatures as low as 90 K, thereby quenching any NBE recombination at higher temperatures. Significantly, 4H-SiC with this doping concentration forms the most pronounced transformation bands with thermal stress, suggesting a relatively high concentration of 3C inclusions.

The appearance of this 2.45-2.47 eV feature at temperatures for which free carrier recombination takes place is consistent with its assignment to 3C inclusions spatially separated by distances exceeding bound exciton radii. Based on the band alignment of 3C and 4H-SiC, almost the entire band offset should appear in the conduction band, corresponding to a deep level $\sim 3.2 - 2.4 = 0.8$ eV below the 4H-SiC conduction band edge. Significant recombination at these 3C inclusions requires a supply of free carriers that is available only at intermediate temperatures. At relatively low temperatures and free carrier densities, such carriers recombine preferentially at the more closely spaced shallow level sites. As temperature increases and more free carriers are thermally generated, Shockley-Read-Hall (SRH) statistics favor recombination at the deeper level.
The same argument can account for the emergence of the 2.5 eV peak in Fig. 26. As mentioned above, the activation energy for this peak is \( \sim 0.25 \) eV, consistent with thermal activation from a NBE level. Even higher temperatures and carrier densities are required for this recombination channel to become dominant since the associated transformation bands are even less numerous and more spatially separated.

The reported sizes of 3C inclusions and transformation bands are consistent with the spectral line widths shown in Figs. 24 - 31. As already mentioned, quantum confinement and DAP features associated with 3C domains can account for the broad \( \sim 2.4 \) eV feature. The narrower line width and higher energy of the 2.5 eV feature in Fig. 26 is consistent with the uniformly thin (1.5 nm) dimension of the 3C transformation bands. The presence of such features and presumably such inclusions for all 4H-SiC samples studied suggests that they are naturally occurring defects and that they can provide the nucleation sites responsible for formation of stacking faults and 3C-SiC transformation bands.

Features at 1.9 eV-2.0 eV are observed both in PL and LEEN spectra (Figs. 24 - 28) of annealed n-type samples and are not observed in unannealed samples. For the \( n=1.7 \times 10^{19} \) N sample in Figs. 24 - 26, a 1.87 eV peak appears near room temperature following a 4-hour, 1150\(^{0}\) C anneal. A similar PL peak appears in bare 4H-SiC with this dopant concentration following 1150\(^{0}\) C annealing in UHV. \(^{126}\) In the \( >2.2 \times 10^{19} \) N specimen, a weak 1.9 eV peak appeared after 4 hr of 1150C anneal. Both followed appearance of 3C-like bands that are produced by the double stacking fault formation. This is direct evidence that the 1.9-2.0 eV line in our PL and LEEN spectra is associated with structural defects.
Galeckas et al. also found significant emission at \( \sim 1.8 \) eV that appeared localized at partial dislocations bordering the stacking faults as well as at screw and/or edge threading dislocations.\(^{133}\) Hence, the identification of the 1.9 – 2 eV feature with partial, screw and/or edge threading dislocations is consistent with both thermally and electrically-driven experiments.

Varying the power density of the 3.8 eV He-Cd laser over two orders of magnitude (not shown), one finds a corresponding variation of the 2.5 eV PL peak intensity. In contrast, the 1.9/ 2.5 eV PL peak intensity ratio decreases by 3.5x with increasing power, suggesting saturation of a lower density of states associated with the 1.9 eV transition. This is consistent with the assignment of the 2.5 eV peak to 2-dimensional stacking fault domains and the 1.9 eV feature to the correspondingly lower density of states at the 1-dimensional boundaries of such domains.

5.3.5.2 P-type 4H-SiC Luminescence

5.3.5.2.1 Luminescence features at 2.0 – 3.2 eV

P-type PL and CL features are consistent with the interpretation of features in n-type spectra in Sec. IV A. LEEN spectra in Fig. 32 show that the features at 3.0-3.2 eV increase with Al content. Since Al forms an acceptor level at 3.0 eV,\(^ {128}\) this peak can be attributed to a conduction band-to-acceptor transition. PL spectra also demonstrate enhancement of 3.16 eV and 3.22 eV features with Al doping level. These features may be due to DAP recombination involving residual N donor levels at \( E_c - 0.052 \) eV and \( E_c - 0.092 \) eV.\(^ {117}\) This can explain why such a N-related peak is enhanced with Al content. Spectra for p-type 4H-SiC with doping in excess of \( 10^{18} \) cm\(^{-3} \) exhibit broadening of the
NBE peak, consistent with band tail states. None of the n-type specimens exhibit such features, regardless of doping concentration - presumably because its donor levels lie closer to the band edge.

Temperature dependent spectra in Fig. 29 - 31 show that a broad feature consisting of two peaks at 2.15 eV and 2.40 eV. The 2.15 eV peak may be due to acceptors in the proposed 3C inclusions. As mentioned above, both 2.1 and 2.45 eV features can be attributed to B-related centers in 4H-SiC. 122, 123 Since B is a common contaminant 118 that it is present in carbide components of growth systems, it may not be unusual to observe it in both n-type and p-type samples. With increasing temperature, ionization of these acceptors would increase the emission energy to that of 3C-SiC band gap, i.e., 2.3-2.4 eV. This would account for the gradual shift of the 2.15 eV feature to 2.4 eV at intermediate temperatures.

5.3.5.3 Comparison Between Cathodoluminescence and Photoluminescence

Significant differences are evident between our PL and CL spectra. Thus, for n-type 4H-SiC, emissions at 2.45 eV are observed more readily in PL than CL, while 2.5 eV emissions due to 3C-SiC layers associated with stacking faults are more evident with CL. In p-type 4H-SiC, emissions at 2.15 and 2.4 eV are more pronounced in PL than in CL, while CL shows more intense NBE and 3.0 eV features than PL spectra. These differences can provide additional information on the nature of the excitations.

Different penetration depth and excited free carrier densities can account for some of the PL vs. CL spectral changes. The penetration depth of PL is 7.5 µm versus 50 nm
for CL at 4 keV and even less at lower excitation energies. Since the thickness of our 4H-SiC epilayer is 2 µm, the CL spectra measure contributions only from the epilayer, whereas the PL spectra include significant contributions from energy levels at the substrate/epilayer interface and the 4H-SiC substrate. The 3.16, 2.5, 2.25-2.36, and 1.9 eV features in n-type and the 3.2, 3.0, and 2.45 eV features in p-type CL spectra can therefore be associated with at least the epilayer. On the other hand, the pronounced 2.4 eV, room temperature PL feature in p-type and low n-type samples indicates a contribution primarily from the substrate. This is reasonable given the nominal p-type doping known for the substrate. Certainly, the absence of above-band-gap emissions in the PL spectra confirm their epilayer origin. At the same time 2.8-2.9 eV features are also observed in all samples, and are shown to be of the substrate origin. Low temperature LEEN shows no such features in the epilayer and strong presence in the substrate.

5.3.6 Conclusions

We have analyzed the major spectral features of temperature-dependent PL and CL spectra of 4H-SiC. Previous work suggests that the 2.9 eV features in n-type samples can originate from multiple factors - stacking fault luminescence as well as Al-N DAP transitions. The 3.0 eV features in p-type material are very similar to 2.9 eV features in n-type samples, whereas 3.22 eV NBE emission is due to shallow N levels. Likewise, previous work shows that the 2.5 eV peak is associated with 3C-SiC layer formation originated by double stacking faults. The 2.4 and 2.15 eV features can be associated with B doping, especially since the 2.4 eV peak dominates substrate-excited spectra. Based on their identification in electroluminescence spectra and their association with 2.5 eV...
stacking fault features, the 1.9 eV feature can be identified with the formation of partial
dislocations. The temperature-dependent PL and CL spectra reported here illustrate the
diverse nature of electronic states in commercial 4H-SiC epilayers and the relative
contributions of point imperfections versus extended defects to the temperature-
dependent optical emission.

5.4 Electronic Defect States at Annealed Metal/4H-SiC Interfaces

We have used low energy electron-excited nanoscale luminescence spectroscopy (LEEN) to study the formation of electronic surface states at metal/4H-SiC contacts. These junctions were formed using both low and high reactivity metals to study how the nature of interface chemical bonding affects the interface state formation. We observe evidence for the formation and removal of localized states at energies that have been associated with morphological SiC defects. Metals such as Au and Ag with no strong chemical reactivity exhibited the most pronounced changes. Conversely, chemically-reactive metals such as Ti and Ni exhibited only minor changes and only with high temperature annealing. These observations suggest that native defects rather then metal-specific chemical bonding dominate the interface electronic features.

5.4.1 Introduction

Localized electronic states play a central role in the formation of Schottky barriers, ohmic contacts and heterojunctions. Such states can form as a result of localized
charge transfer, chemical bonding, impurity diffusion, or point defect formation. In SiC, local polytype changes, dislocation and stacking faults can produce electrically active sites as well. To measure interface states, one requires a probe of chemical, structural and electronic properties on nanometer scale. This is a particular challenge for the conventional techniques such as photoluminescence, where optical penetration depth is typically microns, or capacitance spectroscopies, where probe depth are limited by depletion width to hundreds of microns. A variant of cathodoluminescence, low energy electron-excited nanoluminescence spectroscopy (LEEN) provides a depth-resolved technique for measuring electronic properties of semiconductor surfaces, interfaces and thin films. Depending on the electron beam energy (E_b), the electron cascade generated by an incident beam peaks at different depths under the surface. As E_b decreases below 1 keV, excitation of electron-hole pairs occurs less than several nanometers below the free surface. By varying the energy and excitation depth, one can use LEEN spectroscopy for depth-resolved probe of buried interfaces. In this work we have used LEEN spectroscopy to provide evidence for localized states at metal-SiC junctions. Such states have a significant influence on the charge transfer properties of such contacts. Until recently, these states at SiC-metal junctions have only been inferred, based on the variations in Fermi level position with metal work function, rather than from more direct measurements. Schottky barrier height (SBH) studies of 4H-SiC with a wide range of metals show no strong Fermi level “pinning” in a narrow range of energies, suggesting only a moderate influence of localized states. Previously, we reported 1.9 eV process-dependent interface state emission at Pt/Ti/4H-SiC interfaces. Furthermore, high temperature annealing can produce stacking faults and effective gap states in highly-
doped n-type 4H-SiC. At issue is whether these and other interface states due to chemical bonding and/or diffusion are present at metal-SiC interfaces and play a role in barrier formation. Here we present low energy, electron-excited nanoluminescence (LEEN) spectroscopy measurements of both free and metallized 4H-SiC Si-face surfaces at room and elevated temperatures.

5.4.2 Experiment

Specimens consisted of 8° off-axis [from the (0001) plane], Si-face substrates with 2 µm thick n-type [N], 2.2 x 10¹⁹ cm⁻³ doped epilayer grown homoepitaxially by Cree, Inc (Research Triangle Park, NC). LEEN spectra were acquired with energies ranging from 0.5 keV to 5 keV, corresponding to peak excitation depths U₀ of 3 nm to 60 nm respectively. The experiments were conducted in four steps: (1) ~ 2-4 nm of metal were thermally evaporated on solvent-cleaned (acetone, methanol, DI water) SiC surface. Metal thickness was limited in order to permit detection of light emission through the overlayer; (2) This was followed by LEEN analysis (in a different chamber) both in the region exposed to metal deposition and the adjacent bare SiC; (3) The sample was then annealed in ultrahigh vacuum (UHV) at a given temperature for one hour. Temperatures were measured with an optical pyrometer focused directly on the sample surface; (4) After a sufficient time for the sample to cool down to room temperature in ultrahigh vacuum (UHV), LEEN spectra were retaken. This LEEN measurement / anneal cycle was
repeated with increased temperatures. LEEN spectra are acquired using a glancing incidence electron gun, quartz window and lens, an Oriel monochromator, and Andor CCD detector. Secondary ion mass spectrometry (SIMS) measurements were performed using a time-of-flight (TOF) SIMS instrument (PHI Trift III). Depth profiles were performed with Ga ions at a rate of 1 nm per sec.

5.4.3 Results

Figure 37 presents LEEN spectra for Au, an unreactive metal on the SiC (0001) surface. Deposition of 2-4 nm Au introduced a new, near surface luminescence at 1.7- 2.1 eV without any other processing steps. The changes are most evident in the spectra shown for $E_B=0.5$ keV, corresponding to an electron cascade peak at $U_0= 2-4$ nm below the free surface. For direct comparison, spectra before and after Au deposition were normalized to the near-band edge (NBE) peak to emphasize the changes taking place within the same sample volume. The increase in luminescence was apparent on an absolute scale as well. The difference of the two LEEN curves from the same area before and after Au deposition appears as a broad peak centered at 1.9 eV with a range of energies indicated.
Figure 37. $E_B = 0.5$ keV LEEN spectra of 4 nm Au on SiC vs. bare SiC, normalized to NBE emission. Curve subtraction yields a broad peak at $\sim 1.9$ eV.

Increasing $E_B=1$ keV, corresponding to $U_0=4$-6 nm, one probes deeper into the epilayer and further away from the interface. Fig. 38 shows a set of spectra taken at 1 keV analogous to those in Fig 37. The changes in the 1.9 eV peak induced by Au deposition are similar to those at $E_B=0.5$ keV but appear less intense. The analogous set of spectra for $E_B=2$ keV ($U_0=15$ nm) showed no significant changes with Au deposition. Therefore the changes did not extend beyond the first several nanometers below the interface. It should be noted that LEEN spectra taken at 2 keV and higher accelerating voltages displayed a close correspondence, indicating that the Au film introduces no significant spectral changes due to any wavelength-dependent absorption.
Figure 38. $E_B = 1$ keV LEEN spectra of 4 nm Au on SiC vs. bare SiC, normalized to NBE emission. The 1.9 eV difference curve has less intensity at $E_B=1$ keV vs. 0.5 keV and lacks the 2.3 eV shoulder.

Figure 39. Annealing removes the 1.9 eV, $E_B=0.5$ keV LEEN feature at the Au-SiC interface, reversing changes induced by Au deposition.
Figure 40. These changes are less pronounced with deeper $E_B=1$ keV excitation.

Annealing of the Au on 4H-SiC sample in UHV at 800° C for 1 hr. produced well-pronounced changes as well. Figures 39 and 40 show the comparison of the spectra obtained before and after anneal. The spectra were normalized to the same NBE emission level. Similar to the changes with Au deposition, the most pronounced effect was seen in lowest penetration depth spectra taken with $E_B=0.5$ keV beam penetrating $U_0=2-4$ nm. Again, these changes were located in the 1.7-2.1 eV range. The subtraction of the two curves taken before and after annealing revealed a removal of the broad peak at 1.7-2.1 eV nearly identical (see Fig. 41) to that introduced by deposition. As with Figs. 37 and 38, the $E_B=1$ keV data showed similar but less pronounced changes centered around 1.9 eV. Likewise, a deeper probing 2 keV beam showed no significant changes in LEEN spectra. Background changes due to sample positioning are noticeable only above 3.2 eV.
In general, the induced changes were nearly equal and opposite to those produced after the gold deposition alone. This is illustrated in Fig. 41, comparing such changes for $E_B = 0.5$ keV due to Au deposition vs. Au deposition plus annealing.

![Figure 41. Comparison of $E_B=0.5$ keV LEEN difference spectra from Figs.37, 39 and 40 showing near complete reversibility of 1.9 eV emission changes. Annealing also reduces pre-existing 2.3 eV emission.](image)

This figure demonstrates the near-complete reversibility of 1.9 eV emission by $800 \, ^\circ C$ annealing. Comparison of these difference spectra also shows that annealing removes additional emission in the 2.3 eV range. In contrast, the annealing does not cause any pronounced changes in the adjacent SiC bare surface with no Au deposited (not shown). The 2.3 eV emission also exhibits a strong depth dependence, showing the most pronounced decrease with annealing right at the interface and less change with increasing distance from the interface.
A negative SIMS, Cs depth profile of the annealed Au-on-SiC surface indicates a small but significant diffusion of Au into the SiC lattice. Figure 42 illustrates a SIMS depth profile obtained from a SiC sample after Au deposition, annealing, followed by an aqua regia etch to remove the metal and thereby eliminate any knock-on effects from the overlayer Au. As shown, the Au diffuses ~ 15 nm into the SiC. Note also the ~ 40% decrease in Si within the first few nm of the interface.

The LEEN features of other metals on 4H-SiC further characterize the nature of the near-interface states. In the case of Ag, no strong chemical bonding is expected. This is analogous to the chemical nature of the Au/SiC interface. $E_B = 0.5$ keV excitation probes the first few nm below the ~ 3 nm thick Ag layer. For this SiC specimen, 1.9 eV emission was evident in selected areas of a sample even before deposition and extended ~200 nm into the SiC. This indicates the intrinsic nature of the defects associated with the emission. Unlike the Au/SiC interface, there were no changes induced by Ag deposition alone. Annealing at temperatures up to 500°C also had little effect on emission, as shown in Fig. 43. However, consistent with the Au/SiC interface, Ag/4H-SC LEEN spectra show an apparent decrease in 1.9 eV emission with 700 °C annealing. Also similar to the Au/SiC case, the changes due to annealing with $E_B = 1$ keV excitation are less apparent than at 0.5 keV. These changes diminish further with deeper excitation, again consistent with the Au-SiC results.
Figure 42. Negative SIMS profile of SiC after Au deposition, annealing and removal by aqua regia etch. Sputter rate was ~ 1 nm/s. Au has diffused into the first 10-15 nm.

Figure 43. LEEN spectra of 3 nm Ag on SiC. Analogous to the Au/4H-SiC interface, 1.9 eV emission is reduced by 700 °C annealing.
In the case of Ti, strong chemical bonding can occur that should not be reversible with annealing. We used $E_B = 1$ keV excitation to probe the first 4-5 nm, i.e., the metal and the first few nm below the metal. Indeed, comparison of the Ti /SiC plus 800 °C anneal vs. Ti /SiC before anneal in Fig. 44b showed apparent changes only in the ~ 2.9-3 eV range, i.e., an emission increase, as illustrated by the difference spectrum. Emission at that energy has been attributed to single stacking faults as well as native defects. There were no changes in the 1.9 eV region after annealing, in contrast to the Au-SiC or Ag-SiC junctions.

In the case of Ni also, strong chemical bonding is expected that should not be reversible with annealing. As with Ti, there are no observed reversible changes due to annealing of the Ni/4H-SiC interface. In fact, comparison of the Ni/4H-SiC vs. the bare SiC surface both after a 500 °C anneal showed no differences. Similarly, only minor changes occur above 900 °C, and these are confined in the ~ 2.8 eV range. See difference curve. Therefore, these spectra show that the Ni on 4H-SiC interface exhibits emission behavior analogous to that of Ti.
Figure 44. LEEN spectra of 3 nm (a) Ni and (b) Ti on SiC. No significant changes observed for 900 °C annealing of Ni film. For Ti film, changes appear at 2.85 eV at 800 °C annealing.

5.4.4 Discussion

The LEEN spectra above demonstrate the presence of electronic states localized within nanometers of metal/4H-SiC interfaces. Furthermore, the energies and intensities of the emissions associated with these states as well as their changes with annealing and
chemical reactivity provide an indication of their physical origin. Previously we reported the emergence of a 2.47 eV midgap emission due to stacking faults for bare 4H-SiC surfaces annealed in UHV at 1150°C for 2 hours. Additional 2 hour, 1150°C anneals increased this emission along with a 2.2 eV shoulder and a broad 1.7-1.9 eV shoulder. Electroluminescence measurements by Galeckas et al. of electrically-stressed 4H-SiC diodes show that broad 1.8 eV emission can be associated with partial dislocations that decorate stacking faults and 2.8 eV emission with the stacking faults themselves. Liu et al. showed that the structure of such stacking faults were isolated single-layer Shockley faults bound by partial dislocations. Previously, Okojie et al. showed that the structure of the stacking faults formed by high temperature annealing of highly n-doped 4H-SiC were double stacking faults with optical emission at 2.5 eV. Thus, optical emissions at 1.8, 2.5 and 2.8 eV are all characteristic of either stacking faults or the dislocations that bound them.

For Au deposited on bare SiC in UHV, similar 1.9 eV and 2.3 eV emissions appear at room temperature under the metal. Depth-resolved spectra with increasing incident beam energy $E_B$ and excitation depth show that the 1.9 eV emission is localized within the first 10 nm. A 1 hour, 800 °C anneal removes this 1.9 eV feature, along with some 2.3 eV emission. These changes may be related to Au-Si interdiffusion, as indicated by Fig. 42. For Ag deposited on bare 4H-SiC in UHV, the interface state emissions again involve a 1.9 eV transition. As with Au, annealing decreased its intensity. Furthermore, these changes are all localized to within nanometers of the metal/SiC junction.
The more reactive metals Ti and Ni exhibit qualitatively different behavior, showing changes only at energies associated previously with stacking fault formation. The samples were annealed up to 900° C, in the range of the temperatures known to produce Ohmic contacts due to metal-silicide compound formation. The changes induced by Ni after 900° C annealing appearing in Figs. 44 a) and b) are negligible compared to minor spatial variations in LEEN features across the sample. The changes induced by Ti after 900° C are more pronounced. They indicate increased emission in the 2.9-3 eV range, consistent with single stacking fault formation. The absence of new defect emission features under these conditions is surprising, given the movement and bonding of Si and C atoms expected at reacted interfaces. However, even though such silicide and carbide reactions are favorable, they may consume Si and C at the surface equally, resulting in no net defect formation. Alternatively, reaction and diffusion may be inhibited by residual surface O contamination, since the thermodynamic driving force for metal oxide formation is much larger than those of the silicide or carbide counterparts and the high bond strength of such oxides could result in barriers to further chemical interaction.

The LEEN results show the appearance of emissions only at energies of 1.9, 2.5, and 2.8 eV as well as the absence of any emissions due to new gap states related to particular metals. They indicate that extrinsic metal-induced states do not dominate interface state behavior. Instead, the similarities between the interface features and those associated with morphological defects suggest a physical mechanism common to both. Native point defects associated with both SiC interfaces and dislocations can provide a
mechanism consistent with the observations presented here. Such defects are known to
diffuse at temperatures comparable to those used here\textsuperscript{136} and to form with metal-
semiconductor interdiffusion.\textsuperscript{129} Furthermore, point defects can coalesce around
dislocations due to strain fields or charging. If such defects are responsible for the 1.9 eV
emission at 4H-SiC dislocations, then their spatial redistribution with metal-SiC
interdiffusion and annealing could account for the localized changes in 1.9 eV emission
in the Au or Ag LEEN spectra. For example, Au intermixes with Si in the outermost layer
of SiC. This process is possible without intentional annealing since Au forms a eutectic
with Si at relatively low (363\textdegree C) temperatures.\textsuperscript{137} Likewise, Ag forms a eutectic with Si,
albeit at higher temperature (840\textdegree C).\textsuperscript{138} Both result in the formation of interfacial defects
such as V\textsubscript{Si}, and metal interstitials. Such intermixing is relatively localized, even after
multiple, high temperature anneals. The depth profile in Fig. 42 showed that
interdiffusion occurs at Au-SiC interfaces. Si vacancies are a strong candidate for the
deep levels controlling the barrier height\textsuperscript{138} and they have been shown\textsuperscript{139} to produce
photoluminescence features at \(\sim 1.35 - 1.44\) eV. The complementary optical transition
within the 3.26 eV 4H-SiC band gap\textsuperscript{140} would fall into the 1.8-1.9 eV range, in agreement
with both our spectra and with the Galeckas \textit{et al.} assignment.\textsuperscript{133} While the peak observed
in this work is significantly broader than the features observed by Wagner \textit{et al.}\textsuperscript{139} in low-
doped samples, this might be expected due to defect complexing with other lattice
imperfections as well as the higher doping. Carbon vacancy complexes may also play a
role since annealing is known to convert V\textsubscript{Si} to the V\textsubscript{C}-C\textsubscript{Si} pair with optical emission in
the 1.1 –1.15 eV range.\textsuperscript{141} The complement of this optical transition is \(\sim 2.2\) eV, near the
peak energy of emission reduced by annealing. The smaller reduction of this emission is
consistent with the higher thermal stability of carbon complexes vs. $V_{Si}$. The decrease in 1.9 eV emission with annealing may be the result of vacancy removal at the metal interface or free surface. Alternatively, the diffusion promotes atomic Au diffusion, complex formation, and passivation with other chemical impurities or morphological defects such as stacking and dislocations.

Finally, the energies of these metal- and annealing-induced interface features can account for the range of 4H-SiC (0001) SBH’s measured previously. In general, $1.0 \leq \Phi_{SB}^{n} \leq 1.8$ eV, i.e., 1.45-2.25 eV above the valence band. This range of SBH corresponds to energy positions in the band gap of $E_C -1.8$ eV and $E_V +2.25$ eV. Significantly, the near interface changes in CLS emission with metallization and annealing reported here appear at similar energies of ~1.9 eV and 2.3 eV, indicating transitions to or from deep levels and the SiC band edges. Since the filling and unfilling of such states during metal-semiconductor charge transfer acts to constrain the range of Fermi level movement, our results suggest that defects rather than metal-specific localized states play a primary role in SiC Schottky barrier formation.

5.3.5. Conclusions

LEEN spectroscopy of different metals on 4H-SiC reveals interface states localized to within only a few nanometers of the intimate junction. These metal- and thermally-induced interface state observations suggest that native defects rather than any metal-specific chemical bonding or impurity dominate the interface electronic states. There is a good correspondence between the Schottky barrier height limits and changes in the interface features. These states appear to be of two distinct types, depending on the
metal reactivity with the SiC. Those metals that have no strong chemical reactivity exhibit states whose intensities vary with annealing. Those metals that chemically react with SiC show qualitatively different behavior and exhibit these changes only at high temperatures.

5.5 Defect-Driven Inhomogeneities in Ni/4H-SiC Schottky Barriers

Nanoscale depth-resolved cathodoluminescence spectroscopy (DRCLS) of Ni diode arrays on 4H-SiC epitaxial wafers reveals a striking correspondence between deep level defects and electrical transport measurements on a diode-by-diode basis. Current-voltage measurements display both ideal and non-ideal diode characteristics due to multiple barriers within individual contacts. Near-interface DRCLS demonstrates the presence of three discrete midgap defect levels with 2.2, 2.45, and 2.65 eV emission energies whose concentrations vary on a submicron scale among and within individual diodes, correlating with barrier inhomogeneity. These results also suggest that SiC native defect levels can account for the maximum range of n-type barrier heights.

5.5.1 Introduction

Silicon carbide represents an excellent candidate for high-temperature electronic device applications because of its high breakdown voltage, low series resistance, and stability under harsh chemical and high temperature conditions. SiC Schottky diodes are of special interest since these unipolar devices avoid reverse recovery effects of bipolar devices, thereby offering higher frequency operation. Although commercialized, 4H-SiC
diodes still face problems of device reproducibility and high reverse currents. Previous Schottky barrier $\phi_B$ studies showed a moderate dependence on metal work function $\phi_M$ with slope $d\phi_B/d\phi_M = 0.2 < S < 0.7^{143,131}$, indicating only partial Fermi level $E_F$ pinning by interface states. The nature of these states remains under debate with significant evidence for the role of native defects such as C$^{144}$ or Si$^{138}$ vacancies, with significant densities near interfaces$^{145}$. Previous work showed that native defects can limit $E_F$ movement in GaAs$^{146}$. However, until now, there has been no direct correlation between bulk defect states at metal-SiC interfaces and their diode characteristics. We have used depth-resolved cathodoluminescence spectroscopy (DRCLS) to measure the optical emissions of mid-gap states localized at 4H-SiC interfaces with a range of diode behavior on the same wafer. These measurements demonstrate the presence of multiple barriers among and within diodes and the correlation of these barriers with multiple bulk defect states.

5.5.2 Experimental

A 2” N-doped, 4H-SiC single-crystal wafer (Cree Research) oriented $\sim 8^\circ$ off [0001] supported a n-type, $2.5 \times 10^{15}$ cm$^{-3}$ 26-µm epi-layer grown by chemical vapor deposition$^{147}$ (CVD), on which a $\sim 150$ nm sacrificial oxide layer was grown in dry O$_2$ at a temperature of 1150 °C and removed using 10% HF. Backside ohmic contacts were formed by Ni evaporation and annealing in an Ar+H$_2$ mixture for 10 min. at 950 °C. An SiO$_2$ layer 1-2 µm thick was deposited using plasma enhanced CVD, patterned and etched using a buffered oxide etch (BOE) solution to provide 500 and 300 µm diode holes. Nickel was deposited by thermal evaporation at room temperature and patterned into diodes for I-V analysis; the diodes were later removed for room temperature
DRCLS. 5 kV electron beam excitation rastered over the diode area in a JEOL 7800F Auger microprobe excited electron-hole pair recombination within the SiC’s outer ~250 nm for each diode, generating luminescence collected with an grating monochromator and photomultiplier. The relatively low excitation energy enables surface-sensitive measurements of the contact region.  

5.5.3 Results

Of the 500 diodes characterized by I-V, 85% of the 500 μm diameter diodes and 93% of the 300 μm diameter diodes displayed characteristics represented in Fig. 45 a). As reported previously for 4H-SiC, the diodes that displayed excess current at low voltages can be modeled using thermionic emission theory as two Schottky barriers in parallel.

\[
J = J_{\text{sat}}^H \exp \left( \frac{q(V - IR_s^H)}{n^H kT} \right) + J_{\text{sat}}^L \exp \left( \frac{q(V - IR_s^L)}{n^L kT} \right)
\]

where the superscripts L and H denote the low and high barrier regions, respectively, \( n \) is the ideality factor, and \( R_s \) accounts for the series resistance.

Except for a slightly higher tendency for the non-ideal diodes to be located towards the perimeter of the wafer, the wafer locations of these “double-barrier” diodes have no significant spatial relationship with each other. Areas of 10 mm² typically contain single-barrier diodes, with a few double-barrier diodes distributed at random. The higher \( \phi_{BH} \) (lower \( \phi_{BL} \)) of the dual barriers ranged from 1.31-1.55 (0.60-0.87) eV.
Figure 45. I-V (a-b), XRT (c-d) and PLM (e-f) of ideal and non-ideal 500- and 300 µm diameter Ni Schottky contacts to n-type 4H-SiC at room temperature: (a, c, and e) diode containing micropipes displaying single barrier characteristic and (b, d, and f) diode containing no micropipes or screw dislocations displaying double-barrier characteristic. Dashed lines in (a-b) show predicted thermionic emission currents. Micropipe locations are marked with letters ‘MP.’ Screw dislocations appear as white dots.
X-ray topography (XRT) and polarized light microscopy (PLM) were performed after metal contact removal. Screw dislocations and micropipes were detected in ~100 diodes. However, no correlations were found between the ideality factors, barrier heights or reverse leakage currents at −10 V and the numbers of screw dislocations or micropipes under each diode. For example, Figs. 45 c) and 45 d) display XRT images of diodes with both single- and double-barrier characteristics. Although the diode marked with an arrow in Fig. 45 c), (diode 2151) contains three micropipes and six screw dislocations, it displays single-barrier I-V characteristics Fig. 45 a). Moreover, no micropipes or screw dislocations were detected within diode 3696 Fig. 45 d), yet Fig. 45 b) displays a double barrier characteristic. Plots of ideality factors, barrier heights, and reverse leakage currents (not shown) vs. numbers of dislocations or micropipes showed no correlation between these structural defects and the low-voltage electrical characteristics.
Figure 46. Comparison between DRCLS a) and b), and I-V c) and d) characteristics of two strongly non-ideal diodes. Subtraction of broad 2.45 eV features reveals additional 2.2 and 2.65 eV peaks whose intensities vary between diodes.

Multiple DRCLS spectra were obtained for 37 of the 500µm and 14 of the 300µm diodes, the majority of which exhibited double barriers. Figures 46 a) and b) show CL characteristics of the exposed contact footprints for two Ni/4H-SiC diodes that exhibited the double diode I-V characteristics shown in Figs. 46 c) and 46 d), respectively. Besides weak near band edge emission at ~ 3.2 eV, solid lines on Figs. 46 a) and b) represent Gaussian fits to the broad 2.45 eV CL emission commonly observed for most diodes (not shown). The lower curves show the difference between the measured curves and the Gaussian fits, revealing two additional peaks at 2.2 eV and 2.65 eV. These features
become more apparent in local areas within a single diode. Figure 47 shows spectra from two separate 50x50 µm areas within one such double diode. In addition to the broad 2.45 eV feature, Figs. 47 a) and b) exhibit spectra with dominant peak features at 2.65 eV and 2.2 eV, respectively. DRCLS of the entire 500x500 µm diode area in Fig. 47 c) exhibit features that represent a weighted average of the two more localized spectra. These local variations demonstrate that the overall diode area encompasses regions containing spatially varying densities of at least 3 deep level defects.

Figure 47. CL spectra a) and b) from different 50x50 µm areas vs. entire diode area c) shows that 2.2 eV and 2.65 eV peaks are distributed nonuniformly within diodes.
An additional peak at 2.5 eV is occasionally observed due to 3C-SiC inclusions generated by double stacking faults. However, these show no strong correspondence with I-V characteristics, as expected, since the thin double stacking faults forming the 3C-like inclusions propagate to the surface at 8° vicinal angle and cannot be in direct contact with Ni over extended surface areas. Nevertheless, they may contribute to increased recombination and $n$ values.

5.5.4 Discussion

For n-type 4H-SiC with a 3.27 eV band gap, the 2.2, 2.45, and 2.65 eV emissions are likely due to transitions from states 1.07, 0.82, and 0.62 eV above the valence band $E_V$, respectively - in striking agreement with component $\Phi_B^n$ values of 1.05, 0.87, and 0.6 eV typically observed in pronounced double barrier diodes. The broad 2.45 eV peak is usually attributed to B-related defects but may also originate from nanosize distributions of 3C inclusions frequently incorporated in the material during growth. Indeed, recent PL studies of variable sized 3C-SiC nanocrystals exhibited very similar luminescence in this energy range. The 2.65 eV peak has been observed only in the diodes that exhibited double barrier behavior. The lower of these dual Schottky barrier heights (LSBH) extracted from I-V was ~0.6-0.8 eV, corresponding to $E_F$ pinning ~2.6-2.4 eV above the SiC valence band $E_V$. Although the origin of this defect is not yet clear, its bandgap position is in the range of the commonly observed $Z_{1/2}$ defect at $E_C$-0.63-0.68 eV, possibly related to C vacancy complexes, nonaxial C-Si nearest-neighbor divacancy $V_C-V_{Si}$, Si antisites or 8H-SiC inclusions. The 2.2 eV peak was most evident in diodes with pronounced double barrier I-V curves. A $\Phi_B^n$ value of ~1 eV was
extracted for many of such diodes. This peak appeared in some single barrier diodes as well. The nature of 2.2 eV is not yet clear, although several studies reported energy levels falling into the same range. Possible candidates are $P_1$ and $X$ vacancy related centers at $E_C$-1.15 eV, UD-1, UD-2 related to $(V_{C-}\text{Cs})$, UD-3 at energies 1.06 eV, 1.10 eV, 1.35 eV respectively, implantation-induced defects RD$_{1/2}$ at 0.89-0.97 eV, and RD$_3$ at 0.98-1.08 eV or Ec-1.1 eV.

Considerable evidence exists for barrier inhomogeneities within individual diodes including SiC. For our $\Phi_n^B$ vs. ideality $n$ graphs that extrapolate to nearly ideal barriers characteristics, $\Phi_n^B$ uniform $\approx$ 1.47 eV, close to the 1.60 eV value of Skromme et al., who proposed discrete crystal defects at localized barrier patches leading to non-ideal behavior. Our results demonstrate that localized native defect states pinning $E_F$ at surface areas are responsible for such inhomogeneities. Similarly, the 0.6 eV $V_{Si}$-$V_C$ and 1.8 eV $V_C$ native defect levels may account for the minimum and maximum values, respectively, of $\Phi_n^B$ reported for 4H-SiC.

5.5.5 Conclusions

In summary, Ni- 4H-SiC diodes with double barrier I-V characteristics showed relatively strong near-surface defect emission at 2.65 eV and/or 2.2 eV, corresponding to the lowest barriers observed for these diodes. These defects rather than any morphological features can account for the diode barrier inhomogeneities. The pronounced influence of common native defects near SiC surfaces may also account for its limited range of $\Phi_B$ values, underscoring the importance of sub-surface gap state measurements.
CHAPTER 6: CONCLUSIONS

We have observed optical emission from discrete and continuum defect states on 6H-SiC/metal interfaces below the bandgap and polytypic features above the bandgap. The relative concentration of such features increases with proximity to the interface on a scale of nanometers, which correlates with TEM results showing polytypic formation within few nanometers from the interface. 4H-SiC/metal interfaces displayed optical emission from discrete and continuum defect states analogous to 6H-SiC. In addition, in contrast to 6H-SiC, 4H-SiC exhibits a pronounced polytype change to cubic 3C-SiC not only at the interface but extending hundreds of nm into the bulk. TEM cross sectional micrographs confirm the appearance of this 3C-SiC polytype transformation, revealing the presence of alternating layers of 3C-SiC and 4H-SiC in discrete transformation bands.

The characterization of a set of n- and p- type samples with a range of doping levels that were annealed at different temperatures and times revealed that thermally-activated polytype transformation in n-type 4H-SiC epilayers exhibit threshold temperatures, anneal times, and doping densities that are characteristic of SiC microelectronic processing. This indicates the processing limits within which stacking fault generation could be avoided. No polytype transformations were detected in p-type samples. These results are consistent with dopant-induced strain and electronic effects,
thermally-activated dislocation motion, and subsequent formation of polytype transformation bands. They suggest a tradeoff between high temperature annealing and high N doping in order to minimize structural instability.

We have analyzed the major spectral features of temperature-dependent PL and CL spectra of 4H-SiC. The temperature-dependent PL and CL spectra reported illustrate the diverse nature of electronic states in commercial 4H-SiC epilayers and the relative contributions of point imperfections versus extended defects to the temperature-dependent optical emission.

LEEN spectroscopy of different metals on 4H-SiC revealed interface states localized to within only a few nanometers of the intimate junction. These metal- and thermally-induced interface state observations suggest that native defects rather than any metal-specific chemical bonding or impurity dominates the interface electronic states. These states appear to be of two distinct types, depending on the metal reactivity with the SiC. Those metals that have no strong chemical reactivity exhibit states whose intensities vary with annealing. Those metals that chemically react with SiC show qualitatively different behavior and exhibit these changes only at high temperatures.

We have investigated several dozen rectifying contacts from the same silicon carbide wafer. The results indicate that multi-phase contacts and/or intrinsic or growth-related defects provide important sources of variability. Measurements of nickel Schottky contacts showed a variety of behavior. For example, the barrier heights ranged from 0.88 - 1.36 eV and displayed an inverse correlation with the measured deep-level defect concentrations. In particular, Ni- 4H-SiC diodes with double barrier I-V characteristics showed relatively strong near-surface defect emission at 2.65 eV and/or 2.2 eV,
corresponding to the lowest barriers observed for these diodes. These defects rather than any morphological features can account for the diode barrier inhomogeneities. The pronounced influence of common native defects near SiC surfaces may also account for the limited range of Schottky barrier heights. Therefore monitoring sub-surface can be used to account for and predict Schottky barrier behavior.

The results presentment in the dissertation underscore the importance of defects for controlling SiC contact properties, particularly in nanoscale region just below surface and across the contact. The characterization of defects in these regions requires local probe techniques of electronic and chemical properties. The combination of LEEN spectroscopy in the same instrument with Auger microprobe allows probing and correlating such properties on nanoscale. To produce clean intimate interfaces between the metal and semiconductor the deposition of metal in UHV is performed. Electrical measurements of such contacts provide information about Schottky barrier heights and their uniformity. SIMS can detect interdiffusion at metal-semiconductor interfaces that is connected to the interfacial defect generation. The combination of these techniques provides a powerful research approach to investigating metal-semiconductor interfaces.

Future work should further investigate the indications that the native defects can be generated at metal-semiconductor interfaces. A thorough understanding of the local chemistry including reaction, diffusion and alloying is required to control the formation of such defects. The ultimate goal of the research is understanding and control of interface chemistry and native defects that should allow the control of contact properties including Schottky barrier heights and thermostability of SiC contacts.
APPENDIX A

The table of commonly observed 4H-SiC spectral features.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Width</th>
<th>Associated with</th>
<th>Designation</th>
<th>Technique</th>
<th>Sample</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.16 eV to 3.194 eV</td>
<td></td>
<td>free exciton lines</td>
<td>I</td>
<td>LT PL at 2K</td>
<td>CVD grown</td>
<td>108</td>
</tr>
<tr>
<td>3.246 eV</td>
<td></td>
<td>neutral nitrogen donor</td>
<td>Q</td>
<td>LT PL at 2K</td>
<td>CVD grown</td>
<td>108</td>
</tr>
<tr>
<td>3.162 eV and 3.18 eV</td>
<td></td>
<td>four particle bound complex</td>
<td>P</td>
<td>LT PL at 2K</td>
<td>CVD grown</td>
<td>108</td>
</tr>
<tr>
<td>3.24* eV</td>
<td></td>
<td>no-phonon lines of the neutral Al acceptor four-particle complex</td>
<td>4Al o</td>
<td>LT PL at 2K</td>
<td>CVD grown</td>
<td>108</td>
</tr>
<tr>
<td>3.06 eV</td>
<td>0.05 eV</td>
<td>donor-acceptor (distant) N-Al pairs</td>
<td></td>
<td>LT PL at 2K</td>
<td>p-type CVD</td>
<td>108</td>
</tr>
<tr>
<td>2.95 eV</td>
<td>0.05 eV</td>
<td>and their phonon replicas</td>
<td></td>
<td>LT PL at 2K</td>
<td>p-type CVD</td>
<td>108</td>
</tr>
<tr>
<td>3.0 eV</td>
<td>0.05 eV</td>
<td>no-phonon recombination of the neutral shallow boron acceptor four-particle bound exciton with B replacing Si</td>
<td>4B o</td>
<td>LT PL at 2K</td>
<td>p-type CVD</td>
<td>108</td>
</tr>
<tr>
<td>3.231 eV</td>
<td>3 meV</td>
<td>no-phonon lines of the neutral nitrogen donor four-particle bound exciton complex (4N o) substituting hexagonal</td>
<td>P o</td>
<td>LT PL at 2K</td>
<td>B-doped CVD</td>
<td>108</td>
</tr>
<tr>
<td>3.257 eV</td>
<td>1.5 meV</td>
<td>no-phonon lines of the neutral nitrogen donor four-particle bound exciton complex (4N o) substituting hexagonal</td>
<td>P o</td>
<td>LT PL at 2K</td>
<td></td>
<td>108,160</td>
</tr>
<tr>
<td>3.244 eV</td>
<td>1.5 meV</td>
<td>no-phonon lines of the neutral nitrogen donor four-particle bound exciton complex (4N o) substituting cubic sites</td>
<td>Q o</td>
<td>LT PL at 2K</td>
<td></td>
<td>108,160</td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>Width (meV)</td>
<td>Description</td>
<td>Associated with</td>
<td>Appearance</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>-------------</td>
<td>----------------</td>
<td>------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>2.902</td>
<td>&lt;1 meV</td>
<td>Associated to D1 defect</td>
<td>L1</td>
<td>LT PL at 2K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.777-2.834 (multiple peaks)</td>
<td>&lt;&lt;1 meV to 1.5 meV</td>
<td>Phonon replicas of L1 peak Show up after annealing damage at 1000 C for 10 min</td>
<td>L1</td>
<td>LT PL at 2K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.876</td>
<td>&lt;&lt;1 meV</td>
<td>not associated with D1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2295</td>
<td>0.5 meV</td>
<td>Al related 4-part complex, replicas</td>
<td>4Al</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.25, 3.15, 3.16, 3.18, 3.21 eV (from graph)</td>
<td>~2 meV</td>
<td>B related 4-part complex, replicas</td>
<td>4B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.35</td>
<td>400 meV</td>
<td>B -related</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.61</td>
<td>15 meV</td>
<td>N-B DAP transition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.64</td>
<td>10 meV</td>
<td>(FB conduction electron to neutral deep boron acceptor)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.07-2.91</td>
<td></td>
<td>DAP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td></td>
<td>Al acceptor (Ev+0.23 eV)</td>
<td>DLTS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.67</td>
<td></td>
<td>D center (Ev+0.59 eV)</td>
<td>DLTS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.265</td>
<td></td>
<td>excitonic bandgap</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.8-2.9, set of peaks</td>
<td></td>
<td>Appears after electron irradiation at room temperature (2MeV)</td>
<td>Ea</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.901</td>
<td></td>
<td>possibly due to antisite pair, L1-ground state</td>
<td>L1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E_C - 0.052 eV)</td>
<td></td>
<td>N imp on C recombination with bound exciton (Al, Ga, B)</td>
<td>V_{Si-N_C}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E_C - 0.092 eV)</td>
<td></td>
<td>N imp on Si recombining with bound exciton (Al, Ga, B)</td>
<td>N_{Si}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>Description</td>
<td>Impurity</td>
<td>Substrate</td>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>----------</td>
<td>-----------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EV + 0.23 eV)</td>
<td>Al imp on Si recombining with bound exciton Al-N DAP, CA recomb.</td>
<td>Al</td>
<td>Si</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EV + 0.29 eV)</td>
<td>B imp on Si recombining with B-N DAP</td>
<td>B</td>
<td>Si</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EV + 0.3 eV)</td>
<td>Ga imp on Si recombining with bound exciton, Ga-N DAP, CA recomb</td>
<td>Ga</td>
<td>Si</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EC – 0.12 eV)</td>
<td>Ti imp on Si recombining with bound exciton</td>
<td>Ti</td>
<td>Si</td>
<td>117</td>
<td></td>
<td></td>
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<tr>
<td>(EC – 0.16 eV)</td>
<td>Ti imp on Si recombining with bound exciton</td>
<td>Ti</td>
<td>Si</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EC – 0.15 eV)</td>
<td>Cr imp on Si recombining with bound exciton</td>
<td>Cr</td>
<td>Si</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EC – 0.18 eV)</td>
<td>Cr imp on Si recombining with bound exciton</td>
<td>Cr</td>
<td>Si</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EC – 0.74 eV)</td>
<td>Cr imp on Si recombining with bound exciton</td>
<td>Cr</td>
<td>Si</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EC – 0.97 eV)</td>
<td>V imp on Si recombining with radiative intracenter transition</td>
<td>V</td>
<td>Si</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EV + 0.24 eV)</td>
<td>V C</td>
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<td>Al implanted, α-irradiated</td>
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<tr>
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<td>B-diffused α-irradiated</td>
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<td>(EV + 0.54 eV)</td>
<td>B+V C, “Boron” EL</td>
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<td>(EC – 0.63/0.68 eV)</td>
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**Energies and Corresponding Phenomena:**

- **3.24 eV**: No-phonon line due to recombination of exciton bound to neutral Nitrogen
- **3.18 eV**: One-phonon replica
- **3.04 eV**: Two-phonon replica
- **2.14 eV**: (broad) Deep B acceptors recombining
- **2.4 eV-2.5 eV [510-520 nm]**: B-related, goes down as Al content goes up
- **2.92 eV**: N-Al DAP
- **Ec-0.7 eV**: Z defect

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REFERENCES


[69] W. Schottky, Naturwiss. 26, 843, (1938)


