ABSTRACT

BIGGERSTAFF, TRINITY LEIGH. Characterization of the Origin of Mobility Loss at the SiC/SiO\textsubscript{2} Interface. (Under the direction of Dr. Gerd Duscher).

Silicon carbide (SiC) is a wide band gap semiconductor with material properties which make it ideally suited for high temperature, high frequency, and high power metal oxide semiconductor field effect transistor (MOSFET) applications. The wide scale commercial development of these devices has been hindered due to disappointing electron mobility when compared to properties of the bulk material. This mobility loss has been associated with the interface between SiC and the native oxide formed (SiO\textsubscript{2}). Many improvements in mobility have been realized, but it is currently still significantly less than that of the bulk material. The work in this dissertation is aimed at understanding the origin of this mobility loss from an atomic perspective.

Analytical electron microscopy techniques including scanning transmission electron microscopy (STEM), Z-contrast imaging, electron energy loss spectroscopy (EELS), and convergent beam electron diffraction (CBED) are used in this study to characterize the 4H-SiC/SiO\textsubscript{2} interface. The effect of aluminum implantation, nitric oxide annealing, oxidation rate, and activation annealing temperature on the interface was examined. We found a carbon rich transition layer present on the SiC side of the interface which varies in thickness depending on processing conditions. The thickness of this transition region is linearly related to the electron mobility.

We were also able to determine that this transition region occurs as a result of the oxidation process. During oxidation, carbon interstitials are emitted on both sides of the
interface, causing a carbon pileup on the SiC side of the interface, which we detect as a transition region. The rate of oxidation is also very important as oxidizing at a fast rate leads to greater carbon pileup. The extra carbon in this transition region acts as electron scattering centers, which ultimately lead to a reduced electron mobility.

This study is able to directly correlate the microstructure on an atomic scale with macro-scale properties. Using analytical electron microscopy, we are able to detect a carbon rich transition region in the SiC at the interface, determine that it is linearly related to mobility, and fundamentally establish how this transition region is detrimental to the electron mobility.
Atomic Scale Characterization of the Origin of Mobility Loss at the SiC/SiO$_2$ Interface.

by
Trinity Leigh Biggerstaff

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APPROVED BY:

________________________________  __________________________________
Dr. Gerd Duscher     Dr. Lewis Reynolds
Committee Chair

________________________________  __________________________________
Dr. Nadia El Masry     Dr. Salah Bedair
DEDICATION

To Dad, Mom, and Jessica
BIOGRAPHY

Trinity Leigh Biggerstaff was born and raised in Vale, North Carolina. She attended Fred T. Foard High School in Newton, NC. After high school, she enrolled at North Carolina State University in the college of engineering, where she ultimately went on to join the Materials Science and Engineering Department and obtain a Bachelor of Science in Materials Science and Engineering in 2005.

During her undergraduate studies, Trinity joined the research group of Dr. Gerd Duscher and this ultimately led to her decision to pursue a graduate career in this group. After completing her Bachelor of Science, she enrolled in North Carolina State University as a graduate student and her PhD research focused on using analytical electron microscopy to determine the origins of mobility loss at the SiC/SiO₂ interface. In addition to her research, during graduate school, Trinity worked in the Atomic Resolution Electron Microscopy Facility (AREMC) as a teaching assistant for 3 years. She earned a Masters of Materials Science and Engineering in May of 2007.
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CHAPTER 1: LITERATURE REVIEW

1.1 Silicon Carbide Semiconductor properties

Silicon carbide is the only compound of silicon and carbon which is currently known. The following sections review the properties of SiC as well as recent advancements in the technology. It can exist under various structures called polytypes\(^1\) with a common building block, the Si-C tetrahedron. This tetrahedron can be seen in figure 1-1 (a) (adapted from ref 1). This structure consists of one silicon atom bonded to four carbon atoms or conversely, one carbon atom bonded to four silicon atoms.

![Figure 1-1: (a) The basic structural building block of the SiC system is the Si-C tetrahedron which consists of one silicon atom which is bonded to four carbon atoms. (b) A close packed hexagonal sheet of atoms with the centers at position A. An identical sheet of atoms can be stacked on top of this sheet with centers at position B or C\(^1\).](image)

Figure 1-1: (a) The basic structural building block of the SiC system is the Si-C tetrahedron which consists of one silicon atom which is bonded to four carbon atoms. (b) A close packed hexagonal sheet of atoms with the centers at position A. An identical sheet of atoms can be stacked on top of this sheet with centers at position B or C\(^1\)
The Si-C bond length in SiC is 1.89 Å which is smaller than the 2.35 Å bond length for the Si-Si system which indicates that there is a stronger atomic interaction in the SiC system. Based on this, it is expected that SiC is a stiffer material than silicon, which is confirmed by the higher Young’s modulus. Table 1-1 indicates some critical materials values in 4-H SiC and Si.

Table 1-1: Critical materials values in 4-H SiC and Si$^{1,2,3,4}$

<table>
<thead>
<tr>
<th>Quantity</th>
<th>4H-SiC</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band-gap $E_g$ (eV)</td>
<td>3.26</td>
<td>1.12</td>
</tr>
<tr>
<td>Electron mobility $\mu_e$ (cm$^2$ V$^{-1}$s$^{-1}$)</td>
<td>1000</td>
<td>1400</td>
</tr>
<tr>
<td>$\mu_\perp/\mu_\parallel$</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>Hole mobility $\mu_h$ (cm$^2$ V$^{-1}$s$^{-1}$)</td>
<td>115</td>
<td>471</td>
</tr>
<tr>
<td>Electron effective mass $m^*/m_0$</td>
<td>0.20-0.42</td>
<td>0.26</td>
</tr>
<tr>
<td>Critical field $\xi_c$ (MV/cm)</td>
<td>2.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Dielectric constant $\epsilon_s/\epsilon_0$</td>
<td>6.5-6.7</td>
<td>11.7</td>
</tr>
<tr>
<td>Young’s modulus $Y$ (GPa)</td>
<td>100-750</td>
<td>47</td>
</tr>
<tr>
<td>Thermal conductivity $\theta$ (Wcm$^{-1}$K$^{-1}$)</td>
<td>3.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Debye temperature $T_d$ (K)</td>
<td>1300</td>
<td>640</td>
</tr>
</tbody>
</table>
In addition to the Youngs modulus, it is important to note that due to the fact that carbon is a significantly lighter atom than silicon, which promotes lattice vibrations and ultimately leads to SiC having a much higher thermal conductivity than that of silicon.

Each of the SiC polytypes is constructed by stacking a close packed planar hexagonal array of the Si-C tetrahedra joined at the corners. This can be seen in figure 1-1(b). After the addition of each tetrahedra plane, the upper tetrahedra can be aligned between the bottom ones in two different ways. In figure 1-1B, if A is used as the reference point, then B and C represent the two possible positions of the upper tetrahedra. It is also important to note that the tetrahedra can be rotated 180° along the stacking direction, leading to planes labeled \( A', B', and C' \). While there are some rules restricting the stacking of the planes, it is clear that there are many possible combinations. Over 250 SiC polytypes have been reported but the resulting crystal lattice structure can only be cubic, hexagonal, or rhombohedral. Cubic SiC is known as 3C because it is constructed with the recurring stacking sequence ABC. A good example of hexagonal SiC is 4H which is constructed with the stacking sequence ABA’C’. The preferred polytype for electronic applications is 4-H SiC because it has the widest bandgap, 3.3eV. Figure 1-2 indicates bandgaps and band offsets for some common SiC polytypes. In addition to its large bandgap, 4H SiC also has a high electron mobility which is nearly isotropic.
Figure 1-2: Bandgap and relative band offsets of several common SiC polytypes, SiO2, and Si. Information in figure is compiled from results by Afanas'ev et al.5

The hexagonal crystal unit cell is shown in figure 1-3. In device processing, the most commonly used faces are the (0001) Si-face, the (000-1) C-face, and the (11-20) a-face. Each of these faces has a different density of carbon and silicon atoms. The Si-face consists of 100% silicon atoms, the C-face consists of 100% carbon atoms, and the a-face consists of 50% carbon atoms and 50% silicon atoms. The differences in each of these faces lead to different oxidation rates and interface properties.
SiC forms a native oxide SiO$_2$, in the same manner as silicon, which makes it a good candidate for wide band-gap electronics applications because the silicon tools and technology can be transferred for its processing. The oxidation on the Si-face of SiC is up to 10 times slower than on silicon (100) and the oxidation on the C-Face of SiC is 5 times slower than silicon (100)$^{7,8}$. This SiO$_2$ growth rate is proportional with the carbon surface areal density,
thus this is not an unusual phenomenon. Oxide thicknesses obtained by dry oxidation at 1150°C on the three faces and on silicon (100) are indicated as a function of time in figure 1-4. This high temperature is required for oxides to form in a feasible time. Such distinctive kinetics can be related to the complex oxidation process which requires the ejection of carbon. A net oxidation reaction can be written as:

\[ 2 \text{SiC} + 3 \text{O}_2 \rightarrow 2 \text{SiO}_2 + 2 \text{CO} \]  

Figure 1-4: Oxide thickness over time for 3 different faces of 4H-SiC. Si is shown as reference. Values are measured by ellipsometry (filled symbols) or Rutherford Scattering (empty symbols).

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Another benefit of having a native thermal oxide is that the SiC/ SiO$_2$ interface is expected to be of a higher quality than that of a deposited dielectric. However, the complex oxidation process can lead to a variety of defects at and near the interface. Because of this complicated interface, surface conditioning, oxidation conditions, and post oxidation anneals to control the interface have become critical in the realization of SiC technology.

1.2 Physics of Silicon Carbide Devices

SiC has much potential for high power devices which can ultimately out-perform silicon devices. Silicon devices operating voltages are limited by the breakdown field of the material (~3x10$^5$ V/cm) and by the resulting maximum blocking voltage of PN junctions. An overview of these areas follows.

1.2.1 Critical Field and Blocking Voltage

The kinetic energy of carriers is proportional to the electric field to which they are subjected. In solids, they are thermalized by phonon interactions yielding a finite carrier velocity at low fields. When this field exceeds a critical bulk value $\xi_c$, then the rate at which a carrier gains energy is higher than the rate at which it can exchange this energy with the lattice. In such a case, carriers in a semiconductor can reach energies which are on the order of the band-gap energy and induce avalanche breakdown due to the multiplication of electron-hole pairs. Due to this, the energy of the phonon distribution is pivotal in
determining the critical field where the higher the phonon energy, the higher the field at which carriers can be thermalized. The phonon energy can be estimated using the Debeye temperature $T_d$. Based on this and according to the values reported in Table 1-1, the critical field is expected to be higher in SiC than in Si. Indeed, $\xi_c$ is measured to be $2.2 \times 10^6$ V/cm in SiC which is an order of magnitude higher than that of silicon. It is important to note that since SiC and silicon are indirect band-gap semiconductors, the phonons are also involved in the inter-band transitions associated with impact ionization. Both transport and breakdown mechanisms will be discussed further in subsequent sections.

The blocking voltage of PN junctions operating in reverse bias is limited by the current of minority carriers which can lead to an avalanche process in the space-charged region\textsuperscript{10,3}. This breakdown mechanism is similar to the one described for the bulk material. In the case of a junction where n doping $<<$ p doping or vice versa (known as a one-sided junction), the reverse bias leads to the depletion of carriers almost exclusively in the lower doped region. If the highly doped region is grounded and a large positive bias $V_d >> E_g/q$ is applied to a lowly n-doped region, the width of the depletion layer in the step junction can be approximated by

$$x_d = \sqrt{\frac{2\epsilon_s V_d}{qN_d}}$$

(1.2)
where $\varepsilon_s$ is the dielectric constant of the semiconductor, $q$ is the elementary charge, and $N_d$ is the density of positively charged donor atoms. The value of the electric field reaches a maximum of $\xi_{max}$ at the junction.

$$\xi_{max} = -2 \frac{V_d}{x_d} = -\sqrt{\frac{2qN_dV_d}{\varepsilon_s}}$$

(1.3)

If it is assumed that avalanche breakdown occurs when $\xi_{max}$ reaches $\xi_c$, then it can be derived from equation (1.3) that the maximum blocking voltage supported by a PN junction is given by the following.

$$V_c = \frac{\varepsilon_s\xi_c^2}{2qN_d}$$

(1.4)

Based on this, the maximum achievable blocking voltage for a given dopant concentration is predicted to be 30 times more in a SiC PN junction than in a silicon diode.

1.3 Technology Status and Challenges

SiC-based devices have the potential to outperform silicon in high power and/or high temperature applications, but their properties are still far from reaching the theoretical optimum. This is due to a variety of factors including the quality of the substrate, the oxide,
and the interface. The feasibility of high-power MOSFETs has been demonstrated and now reliability issues are attracting research interests. The most promising step being investigated currently is the role and impact of NO annealing which was implemented as a part of the device processing in 2000. This section will review properties of available substrates, the thermal gate oxide, and the SiC/ SiO₂ interface and will demonstrate that although progress has been realized, there is still room for much improvement.

1.3.1 SiC Wafer Quality

Silicon carbide wafers have been commercially available since the 1990s. In the past 15 years, notable progress has been achieved in both the wafer size and quality. The wafer diameter has increased from 1 inch to four inches, drastically reducing the material cost.

There are two growing steps involved in the synthesis of electronic grade single crystalline silicon carbide. First, a SiC boule is formed using physical vapor transport (PVT) of silicon and carbon from a heated polycrystalline seed source onto a seed crystal¹¹. Wafers are then created by slicing the SiC boule. Due to the high hardness of the material, polishing is done using chemical-mechanical polishing (CMP)¹². It is important to note that residual stress can cause the wafer to bow, which causes problems for other processing steps such as lithography¹³. For electronic applications, a high quality epitaxialtaxial layer (usually tens of microns) is then grown on top of the substrate by high temperature chemical vapor deposition (CVD) using silane (SiH₄) and propane (C₃H₈)¹⁴. Implementation of equipment such as hot
wall reactors has enabled good uniformity of the epitaxial layer over large wafers and acceptable growth rates on the order of 50µm/hour.

In order to minimize the number of stacking faults, crystals are commonly grown along the <0001> c-axis\textsuperscript{15}. This practice leads to another huge issue, that of micropipes. Micropipe is the industry name for hollow-core dislocations which extend throughout the substrate and act as “killer” defects limiting the yield of operating devices. Fortunately there have been improvements in growth techniques which have led to their reduction from over 1000/cm\textsuperscript{2} in the early 1990s to approximately zero in commercially available wafers today. Polytype inclusions have also been limited by off-axis growth (typically 8° for 4H SiC) which yields surface steps where homoepitaxy can occur. Unfortunately, this also leads to surface roughness and step bunching during high temperature implant annealing, both of which negatively affect channel mobility and oxide reliability. These effects can be minimized by using a carbon cap during activation anneals or subsequently polishing the surface. Recent advances in CVD SiC growth have enabled the development of high quality on axis crystals which could one day suppress the need for surface steps\textsuperscript{16}.

There are other structural defects which still strongly affect device properties. Plane dislocations can reduce the achievable blocking voltages and there are indications that stacking faults limit the long-term reliability of SiC diode, and these stacking faults can also propagate during operation\textsuperscript{13}. Additionally, point defects such as vacancies can potentially
play a significant role in limiting carrier lifetime which is very closely related to bulk mobility\textsuperscript{17,18}. It is worthwhile to note that the mobility is an order of magnitude lower in p-type as opposed to n-type SiC; therefore currently n-channel MOSFETs are the preferred device. However, in order to continue fruitful development of SiC technology, progress toward fabrication of CMOS (complementary n- and p-channel MOSFETs) should be made.

\subsection*{1.3.2 Gate Oxide}

There is very little evidence which suggests that the properties of the bulk thermal oxide grown on SiC are different from the bulk thermal oxide grown on silicon. Raynaud\textsuperscript{19} suggested that SiC oxidation yields a stoichiometric SiO\textsubscript{2} whose density, refractive index, dielectric constant, and breakdown strength are very similar to those of Si thermal oxides.

Even though the SiO\textsubscript{2} is similar in Si and SiC, the growth kinetics are quite different. The thermal budget required to form a gate oxide of specific given thickness is ten times higher in SiC than in Si. Because of this, it is possible to deposit CVD oxides, but a thermally grown SiO\textsubscript{2} layer is still necessary to ensure the quality of the SiC/ SiO\textsubscript{2} interface.

During oxide-based device operation, charge buildup in SiO\textsubscript{2} can occur as a result of carrier injection. This leads to threshold voltage instability, mobility degradation, and eventually oxide breakdown, i.e. failure of the device. For these reasons, it is important to
understand and recognize in which conditions charge buildup can occur and how it affects the properties of the device.

When a MOSFET is in the OFF state, an electric field is present in the gate oxide and this field can limit the achievable blocking voltages. This is directly related to the breakdown field of SiO₂ (~10MV/cm) as well as to gate leakage currents which can occur via tunneling or emission of carrier from the gate contact. Additionally, even if the oxide field is negligible above the base region, tunneling of the majority carrier can occur and this can cause a trap in the dielectric within a few angstroms of the interface.

In the ON state, a bias voltage is applied to the gate which forms an inversion layer in the base region. When high fields are present, this can lead to minority carrier injection from the semiconductor into the oxide via Fowler-Nordheim tunneling. The distance \( x_t \) that a carrier has to tunnel in order to leak through the gate dielectric can be approximated by \( \frac{\phi_{bo}}{\xi_{ox}} \), where \( \phi_{bo} \) is the appropriate band-offset (Volts) between the semiconductor and SiO₂. The tunneling probability is dependent exponentially on \( x_t \). Figure 1-2 illustrates that the band-offsets of 4H-SiC relative to SiO₂ are smaller than those of Si⁵. For a given oxide field, this yields a leakage current in SiO₂ on 4H-SiC which is always larger than SiO₂ on Si. This raises significant concerns, particularly for n-channel devices as the offset between the conduction bands of 4H-SiC and SiO₂ is only ~2.7 eV, thus promoting electron tunneling from the semiconductor toward the positively biased gate contact.
Injection of carriers in both the ON and OFF state of device operation leads to charge trapping in the oxide, Coulomb scattering, and interface degradation. The density of electron and hole traps is therefore a critical parameter in determining device reliability and stability. Understanding the SiC/ SiO$_2$ interface is therefore critical in improving predictability and reliability of these devices.

1.4 The SiC/SiO$_2$ Interface

In contrast to the properties of bulk SiO$_2$, those properties of the interface between the oxide and the semiconductor depend strongly on the substrate and its orientation. The quality of the interface is a critical parameter for devices and it is believed to be directly reflected in the channel mobility of MOSFETs.

1.4.1 Scattering Mechanisms

Hall Mobility can be expressed as

$$\mu = \frac{q\tau}{m^*}$$

(1.5)

where $\tau$ is the mean scattering time responsible for the finite speed $\bar{v}=\mu\xi$ of the carrier in a solid. Because various processes can induce scattering, $\tau$ can be decomposed into
The contributing processes being considered here are respectively carrier-phonon interactions, Coulomb scattering by charged centers, carrier trapping or recombination, and surface-roughness induced scattering. Combining equation (1.5) and (1.6) leads to the result that the true mobility can also be written as

\[
\frac{1}{\tau} = \sum_i \frac{1}{\tau_i} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_{Cb}} + \frac{1}{\tau_{lt}} + \frac{1}{\tau_{rg}} + \ldots
\]

(1.6)

It is generally possible to determine the dominate scattering mechanism by examining the dependence of mobility on temperature and the electric field³.

At the interface between an oxide and a semiconductor, defects and surface-induced states can ultimately lead to localized energy levels within the band-gap. For n-channel devices, an electron inversion layer is formed when the amplitude of the gate bias is large enough for the Fermi level to be close to the semiconductor conduction band edge at the interface. In that region, most levels lying within the band-gap are filled with electrons which reduce the density of free carriers and yields negatively charged centers. This ultimately leads to a reduced carrier lifetime and to enhanced Coulomb scattering. These
factors cause the mobility in the channel be expected to be lower than in bulk (e.g. the drift region). In the case of as-grown SiO₂ on 6H- and 4H-SiC, \( \mu_{ch} \) is indeed a fraction of \( \mu_{dr} \); about 25 and 1% respectively\(^{20} \).

**1.4.2 Interface Defects**

Historically, the poor electrical quality of the as-grown SiO₂/SiC interface has two origins: the wide SiC band-gap and the presence of carbon. The large band-gap of SiC makes it more susceptible to a wider range of defects than silicon. At SiO₂/Si interfaces, the presence of several electrically active defects including silicon (Si-) dangling bonds on the substrate side\(^{21,22} \) and oxygen vacancies in the transition region of the oxide (Si-Si suboxide bonds)\(^{23} \) have been reported. The Si- dangling bonds can be passivated by hydrogen\(^{24,25} \). Additionally, a large density of levels located approximately 2.8eV below the SiO₂ conduction band edge has been observed\(^{26,27} \), but due to their location within the Si conduction band, these levels do not affect the channel mobility of the SiO₂/Si interface. In SiC, electron spin resonance (ESR) measurements have not yet been able to identify Si-dangling bonds at the interface\(^{28} \). In addition, studies suggest that hydrogen passivation alone is ineffective\(^{29,30,31,32} \), however at this point, this cannot completely be ruled out. On the contrary, suboxide bonds can contribute to the density of levels with are electrically active. The bonding-antibonding splitting is strongly dependent on the length of the Si-Si bonds. Only those bonds which are longer than 2.35 Å, which is the normal length in a
silicon crystal, can contribute to levels within the silicon band-gap. These levels are effectively passivated with hydrogen. Silicon carbide is different in that even the short bonds lead to active interface states due to the relative position of the band edges as shown in Figure 1-5. Theory also suggests that these short bonds cannot be readily passivated by hydrogen\textsuperscript{29}. 

![Figure 1-5: Schematic of the density of traps at the oxide/semiconductor interface. The relative positions of the conduction band (Ec) and valence band (Ev) edges are indicated. 4H-SiC is sensitive to a larger amount of states than 6H-SiC and silicon. This illustration is modified from a publication by Schorner et al\textsuperscript{33}](image)

Comparably, the fact that the n-channel mobility in 4H-SiC devices ($\leq 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) is lower than in 6H-SiC devices ($100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) can be attributed to levels located above the 6H-SiC conduction band edge and below the 4H-SiC conduction band edge, as these levels will trap carriers only at the SiO$_2$/4H-SiC interface. This corresponds nicely to Hall mobility.
measurements which indicate a much larger reduction (~90%) of the free electron density at SiO$_2$/4H-SiC interfaces as compared to SiO$_2$/6H-SiC interfaces (~10%)\textsuperscript{20}. These results also imply that the density of states is largest close to the 4H-SiC conduction band, giving rise to the qualitative picture for the distribution of levels illustrated in Figure 1-5. Capacitance-voltage (CV) and conductance measurements, which have the ability to resolve the energy distribution of the traps, indicate that the density of interface states ($D_{it}$) is in fact rising in the upper part of the SiC band-gap and is an order of magnitude higher close to the conduction band edge of 4H-SiC ($\sim10^{13}$ cm$^{-2}$eV$^{-1}$) as compared to 6H-SiC ($\sim10^{12}$ cm$^{-2}$eV$^{-1}$) for as grown oxides (see figure 1-6). It is also important to note that the 4H-SiC n-channel mobility is found to increase with temperature (from 200 to 475K), therefore it can be inferred that the main mechanism limiting charge transport is Coulomb scattering of the remaining free carriers induced by the negatively charged centers. Conversely, the 6H-SiC n-channel mobility decreases as temperature rises (from 200 to 500K), indicating a phonon limited transport which is less affected by interface traps. This high density of states located between the 4H- and 6H-SiC conduction bands has not been attributed to a particular defect. Even though it is not clear where these states should be attributed, it is clear that they correspond to the levels which were previously observed at Si interfaces located 2.8 eV below the SiO$_2$ conduction band edge which is 0.1 eV below the 4H-SiC conduction band edge and therefore within the band-gap of that polytype. These defects are generally assumed to be due to near-interface defects within the oxide due to their slow response time.
and wide energy distribution\textsuperscript{34,35,36,37}. If these defects are related to SiO\textsubscript{2}, it would provide an explanation for their presence in both Si and SiC. Even though 4H-SiC is generally the preferred polytype of SiC over 6H-SiC for electronic applications because of its greater bulk mobility, the high density of states corresponding to slow border traps only fall within its band-gap which leads to a lower inversion mobility and higher channel resistance for its as-grown oxide interfaces.

Figure 1-6: $D_{it}$ obtained by CV (shown above as triangles) and conductance (shown above as circles) measurements as a function of the energy within the band-gap of 6H-SiC (filled symbols) and 4-H SiC (empty symbols). The Dit at oxide interface formed on the Si-face of the two polytypes are similar throughout the gap and rises sharply between their conduction band edges\textsuperscript{36}. 

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Another reason for the high defect density associated with the as-grown SiO$_2$/SiC interface is the complex oxidation process (described in equation 1-1) which necessitates the release of carbon. Previous studies have suggested that although the oxide should theoretically have no carbon, it is not ideally removed from the interface during oxidation. Several techniques have found carbon in the oxide within 1 nm of the interface including Rutherford backscattering (RBS)$^{39,40,41,42}$, X-ray photo-electron spectroscopy (XPS)$^{43,44,45,46,47}$, transmission electron microscopy (TEM) with electron energy loss spectroscopy (EELS)$^{48,49,50}$, and spectroscopic ellipsometry$^{51}$. As a result, it is expected that some of these carbon related defects contribute to $D_{it}$. ESR has led to the detection of unsaturated, three-fold coordinated carbon, which could be referred to as carbon dangling bonds$^{28}$, and XPS suggests the presence of both C-C and Si-O-C bonds.

Several theoretical works have predicted defects and their respective energy levels within the 4H-SiC band-gap. Some of these configurations are illustrated in Figure 1-7, and more complete defects can be found in publications by Deák$^{52,53,54}$ and Pantelides$^{55,56,29}$. It is found that carbon is energetically stable in a variety of configurations at the interface. For example, a single carbon can be inserted into a Si-O-Si configuration in two ways, by forming a Si-O-C-Si with carbon weakly linked to a silicon atom on a neighboring ring or it can form a Si-C-Si with an oxygen protrusion. These defects are stable in the negatively charged and neutral states respectively. It is also possible for split carbon interstitials sharing
a silicon site on the substrate to occur, yielding a carbon cluster with a maximum of six atoms. This is not unreasonable because DFT calculations have demonstrated that large aggregates are not stable at the interface and simulations of the oxidation process have suggested that their size is limited by carbon removal during oxidation$^{57}$.

Figure 1-7: Defects which can occur at the SiC/SiO2 interface and their respective energy levels in the 4H-SiC band-gap. From Pantelides et al$^{28}$

1.4.3 Interface Passivation

It is well understood that both oxidation and post-oxidation conditions can affect the $D_\alpha$ distribution within the 4H-SiC band-gap. Studies conducted with argon anneals at growth temperature$^{58}$ and at lower temperatures (900°C) as part of a re-oxidation$^{59}$ lead to a modest
reduction of deep states. This reduction has been attributed to removal of some excess carbon without additional oxide growth, therefore without generation of additional carbon defects. Additionally, wet oxidations can lead to a lower $D_{it}$ toward the center of the gap when compared with dry O$_2$, but this still does not remove the critical slow near-interface states which contribute to the poor 4H-SiC device properties.

The effects which have been observed with water correlate with results from hydrogen post-oxidation anneal (POA) which were performed either before or after gate contact deposition. As mentioned earlier, hydrogen is very effective in passivating Si-dangling bonds at the SiO$_2$/Si interface, leading to the reduction of the $D_{it}$ from approximately $10^{11}$ to $10^{10}$ cm$^{-2}$eV$^{-1}$ in the middle of the silicon band-gap. This allows silicon to achieve a high channel mobility, nearly half the value of the bulk mobility. In SiC, hydrogen only has a limited effect and it is confined to deep interface states which are only reduced to $10^{11}$ cm$^{-2}$eV$^{-1}$, even in the presence of a catalyst cracking H$_2$ into very reactive radicals as seen in figure (1-8)$^{29,30,31,32}$. Hydrogen annealing does not have an effect on the slow, near-interface states. This again highlights differences in the SiO$_2$/Si and SiO$_2$/Si interfaces. Due to the fact that Si-dangling bonds and long Si-Si bonds do not dominate the $D_{it}$ at the SiC interfaces, hydrogen POA is not as effective for SiC. Following H$_2$ exposure at 400°C, C-H bonds were detected by ESR at the SiO$_2$/SiC interface$^{60}$, which correlates with
theoretical predictions\textsuperscript{20}, and also suggests that H\textsubscript{2} could bind to a minority of carbon related defects, explaining the small but noticeably beneficial effect on the $D_{it}$.

Figure 1-8: Interface trap densities in the upper half of the 4H-SiC band-gap obtained after different post-oxidation anneals. Discontinuities near $E_c-E\sim0.6\text{eV}$ are the result of CV measurements taken at 23$^\circ$C and 300$^\circ$C, to extract $D_{it}$ below and above 0.6ev from the conduction band edge respectively\textsuperscript{20}.
One of the biggest accomplishments in the improvement of the SiC/ SiO$_2$ interface has been the incorporation of high temperature NO annealing into the processing procedures. In 1997, the S. Dimitrijev’s group at Griffith University in Australia demonstrated that high temperature (1100°C) NO annealing effectively reduces the $D_{it}$ at the SiO2/6H-SiC interface. After this, in 2000 Chung et al. published results on the effects of NO at the SiO$_2$/4H-SiC interface indicating that not only did the anneal remove deep states, it also very efficiently reduced the density of slow states (by a factor of ten), as shown in Figure 1-8, and ultimately led to an increase in the channel mobility an order of magnitude to 50 cm$^2$V$^{-1}$s$^{-1}$, as shown in Figure 1-9. This discovery was the result of a joint effort between Auburn University and Vanderbilt University and ultimately led to the incorporation of the NO...
process by both scientific and industrial communities\textsuperscript{9} because it enables the fabrication of high quality oxide based SiC power devices. Due to the fact that this is a relatively new technology, the understanding of the NO POA benefits is not understood and is the subject of active research within government laboratories, research universities, and companies worldwide.

The positive impact of NO annealing has been largely attributed to the bonding of nitrogen at the interface. Indeed, medium energy ion scattering (MEIS)\textsuperscript{6}, nuclear reaction analysis (NRA)\textsuperscript{62}, secondary ion mass spectroscopy (SIMS)\textsuperscript{63}, and EELS\textsuperscript{50} have indicated that NO POA leads to a nitrogen profile located at the SiO2/SiC interface and extending 1.5 nm into the oxide. The length is comparable to that of the transition layer observed in the oxide after oxidation. The density of the incorporated nitrogen is between $10^{14}$ and $10^{15}$ atoms/cm$^2$. Nitrogen has also been introduced to the system in other ways including plasma nitridation\textsuperscript{64} and NH$_3$ or N$_2$O POA\textsuperscript{61,65,62,66}. Plasma nitridation has led to similar improvements in the channel mobility but incorporates nitrogen throughout the oxide which causes problems with reliability. Similarly, ammonia (NH$_3$) also shows benefits but incorporates unnecessary hydrogen and nitrogen in the oxide. Nitrous oxide (N$_2$O) is successful in localizing nitrogen to the interface but does not work as efficiently as nitric oxide (NO). In both cases, this is because the nitrogen incorporation is related to the cracking of NO molecules. N$_2$O quickly decomposes into a small fraction NO and larger
fractions of N$_2$ and O$_2$ yielding a re-oxidation process and therefore negating the positive effects of the nitrogen$^{63}$.

After NO exposure at high temperatures, the amount of excess carbon in the oxide near the SiO$_2$/SiC interface is reduced. Specifically, AFM images reveal a smoother surface after the etching of an oxide which has been NO-annealed$^{67}$, and XPS measurements suggest a reduction of the carbon related compounds at the interface and the formation of Si-N and C-N bonds$^{43}$. There are two possible origins for the benefits of NO annealing: N binding at defect sites and/or the removal of three fold coordinated atoms following N substitution. The binding of N at unsaturated C- and potential Si- sites can result in the formation of strong bonds, therefore eliminating defect levels from the gap. Substitution of three-fold carbon or silicon by nitrogen could drastically transform a given atomic configuration and therefore affect its corresponding energy levels as well. Theoretical studies of nitrogen affinity at defect sites located near the SiO$_2$/SiC interface have indicated that nitrogen could in face substitute for both silicon and carbon atoms$^{29}$. One key difference between nitrogen and hydrogen is that nitrogen is predicted to be efficient at passivating short Si-Si suboxide bonds and C-C pairs of correlated carbons, both of which are defects that are most likely responsible for the high $D_s$ and the poor mobility at as-grown interfaces. NO annealing is very efficient in the upper part of the 4H-SiC band-gap but does not lead to clear improvement close to the valence band. This could be because each substitutional nitrogen
atom brings an extra valence electron to the system. A nitrogen which is three-fold coordinated has a lone pair of electrons in its outer shell. When this three fold coordinated nitrogen replaces Si or C, it removes the dangling bonds in the upper part of the 4H-SiC band-gap but also to induce a donor level associated with the lone pair close to the valence band of the semiconductor. Even though NO annealing does not improve band states in the lower part of the 4H-SiC band-gap, this is apparently less critical for the mobility of n-channel devices whose value is mostly dependent on the reduction of the density of levels close to the 4H-SiC conduction band.

It is also important to note that different forms of POA can also reduce the $D_{it}$ at interfaces formed on the a-face and the C-face of 4H-SiC, also yielding higher channel mobilities$^{68}$ as seen in Figure 1-9. Of particular interest is the a-face, which showed improvement to $100\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in some instances$^{69,70}$, which is extremely notable because it is twice the mobility obtained on the Si-face after NO annealing. This is an indication that even though the Si-face has been the preferred face for device fabrication, the introduction of NO and other POAs have changed the outlook and other faces in the material will likely be the focus of upcoming research. An example of this is UMOSFETs, dismissed early but depend on the a-face channel mobility$^{71}$, and present several advantages worth considering with the advent of successful POAs. It is also worthwhile to note an additional advantage of the a-
face is that it typically does not have a miscut as the Si-face does, yielding a more limited surface roughening during annealing, and therefore a reduced carrier scattering.

1.5 Process optimization

In this section, three fabrication steps of oxide-based SiC devices will be discussed. They are mentioned and described briefly in terms of their impact on device quality and reliability.

1.5.1 Channel implantation

In MOSFET design, a double implant is required to form base and source regions. Because of this, a high temperature activation anneal (at least 1500°C) is required. There are several problems associated with this implantation are ion-induced defects in the channel region and surface roughening during annealing. Due to the low diffusion coefficients of the dopant atoms in SiC, the doping cannot be achieved by driving in the dopants. A proposed method to avoid this problem is to implement a UMOSFET design in which source and base regions are formed by successive CVD epitaxial-growths, but this design has other problems such as field crowding in sharp corners of the trench oxide. High temperature annealing in implanted devices has also been attributed to the problem of surface roughening due to Si-emission and step bunching (as mentioned earlier, step bunching is a result of steps at the surface as a result of off axis growth to limit polytype inclusions).
1.5.2 Gate Oxide Growth

Gate oxide formation conditions are critical because the conditions at which the gate oxide is formed greatly affect the quality of the SiO₂/SiC interface. It has been reported that placing alumina in the vicinity of SiC during the oxidation process leads to growth rates which are up to 10 times faster than without the presence of alumina. The interface formed with this process can also have a lower $D_t$ and higher channel mobility. Additionally, work at Vanderbilt University has been conducted with good results exploring high pressure growth of oxides of SiC with reduced thermal budgets.

1.5.3 NO Annealing

The introduction of nitrogen at the SiO₂/SiC interface with POA leads to a reduced ON resistance in the channel in oxide based devices. Figure 1.10 shows data indicating that SiC power devices can out-perform silicon devices for operating voltages down to several hundred volts.
Figure 1-10: Achievable specific ON resistance as a function of the designed blocking voltage for Si and 4H-SiC devices. Continuous lines indicate the theoretical limits set by the drift resistance alone. Dotted lines indicate the impact of the channel resistance on the total resistance for a poor (as-oxidized) and a better (NO-annealed) interface. The symbols correspond to values extracted from actual SiC MOSFETs fabricated before\textsuperscript{75,71,76} (shown above as triangles) and after\textsuperscript{77,78,79,80} (shown above as squares) 2001. Note, figure adapted from Rozen\textsuperscript{9}.

NO annealing also facilitates faster and sharper turn-on characteristics which is important for the realization of high frequency devices\textsuperscript{81}. Since the benefits of the NO POA have been
established, the emphasis has now shifted to the importance of optimizing the nitridation process to avoid excess nitrogen at the interface. The impact of nitrogen on the stability of device properties and device reliability is a focus in current SiC research because the small band-offsets between SiC and SiO₂ are a cause for concern about gate leakage upon operation.

1.6 MOSFET Introduction

Due to the importance of MOSFET devices as potential applications for SiC, a brief introduction to MOSFETs follows. A diagram of an n-channel DIMOSFET (DI = double implanted) is shown in Fig. 1-11. The source and p-well regions are formed by high dose nitrogen and low dose aluminum implants, respectively (N > 10⁹ cm⁻³, Al ~ 10¹⁶ cm⁻³). In the absence of a positive gate voltage (right side of figure), no current flows in the device, and the device blocks the voltage VSD applied between the source and drain. A positive gate voltage inverts the p-well surface at the oxide-semiconductor interface (left side of figure) to form an n-conducting channel. A large current I_SD flows between the source and drain, and the voltage drop across the device is small, resulting only from the internal resistances of various portions of the device. Two of the important internal resistances (R_CH = channel resistance and R_D = drift layer resistance) are labeled in Fig. 1-11. The “on-resistance” R_ON represents the total resistance of the MOSFET to current flow and is the sum of the various internal resistances, including R_CH and R_D. The on-resistance determines the internal power loss in the device.
Figure 1-11: Vertical DIMOSFET. Left: n-inversion channel formed by the application of a positive gate voltage $V_G$. Right: conducting inversion channel does not form when $V_G$ is removed. Inset: Interfacial defects arising from Si-Si bonds, C-C bonds, Si dangling bonds and missing O atoms.

A convenient parameter for evaluating the performance of vertical MOSFETs is the “specific on-resistance” or “resistance-area product” of the drift region:

$$R_{SP} \sim \frac{V_B^2}{\mu_N \varepsilon_S E_C^2}$$

$V_B$ is the voltage blocked by the MOSFET, $\mu_N$ is the bulk electron mobility in a direction perpendicular to the oxide-semiconductor interface, $\varepsilon_S$ is the permittivity of SiC and $E_C$ is the critical field. This parameter represents the “ideal” on-resistance, neglecting any other
resistances in the device. The great promise of SiC can be seen in the expression for \( R_{SP} \), where \( E_C \) is approximately seven times larger for SiC than for Si. Lower on-resistance by a factor of more than 300 should be possible with SiC. Significant improvements in performance can be realized compared to Si MOSFETs for devices that operate near this theoretical performance limit \(^{82}\). 4H-SiC MOSFETs have been fabricated with blocking voltages above 10kV \(^{83}\). These devices have thick drift layers (~150µm), and the resistance of the drift region \( R_D \) dominates the on-resistance. The channel resistance is small in comparison and does not contribute significantly to \( R_{ON} \). However, SiC MOSFETs have their greatest commercial potential for applications at voltages \( \leq 3kV \), and for these voltages, the channel resistance can be the most important component of the on-resistance.

The low field channel resistance \( R_{CH} \) is given by

\[
R_{CH} = \frac{L}{WQ_N\mu_{CH}}
\]

where \( L \) and \( W \) are the length and width of the channel, respectively, \( Q_N \) is the inversion layer charge available for current conduction and \( \mu_{CH} \) is the mobility of the electrons in the inversion channel. The quality of the SiO2/SiC interface determines \( \mu_{CH} \) and \( Q_N \), which in turn determine \( R_{CH} \). Clearly \( Q_N \) and \( \mu_{CH} \) should be as high as possible so that \( R_{CH} \ll R_D \). A large interface defect density limits \( Q_N \) by trapping \(^{84,85}\) and \( \mu_{CH} \) by coulomb scattering. The introduction of nitrogen at the SiO2/4H-SiC interface significantly reduces this defect density, thereby increasing both \( Q_N \) and \( \mu_{CH} \).
CHAPTER 2: RESEARCH METHODOLOGY

In this chapter, research methodologies used to conduct atomic analysis of the 4H-SiC/SiO2 interface will be discussed. These methods include Z-contrast imaging, electron energy loss spectroscopy, and convergent beam electron diffraction.

2.1 Z-Contrast Imaging with a Scanning Transmission Electron Microscope (STEM)

Z-contrast images are images in which the intensity in the image is directly related to the square of the atomic number of the species being imaged. These images are unique because they contain both structural and chemical information. In addition, the images can be directly interpreted in a manner which is much more straightforward than the conventional high resolution transmission electron microscopy (HRTEM). These images are also known as high-angle annular dark field images and are formed by scanning a highly focused electron beam (convergence angle $\alpha \approx 15-35$ mrad) across the surface of the sample material and collecting those electrons which are scattered to high angles (40-100 mrad at 200kV in the JEOL 2010F) on a high-angle annular dark field detector. This setup can be seen in (figure 2-1).
By using high angles and integrating over a large angular range, coherence effects between near neighbors can be minimized\textsuperscript{91,92}. Based on this, in the approximation of large collection angles, each atom can now be considered an independent scattering source with a scattering cross-section of approximately $Z^2$, where $Z$ is the atomic number. The object function is effectively formed by this cross-section in a manner such that the object function is maximized at the atom sites. This means that for specimens thin enough such that the dynamical diffraction effects can be neglected, the detected intensity is a convolution of this object function with the probe intensity profile (figure 1)\textsuperscript{93,94}. Due to the small width of the object function (~0.01nm), the spatial resolution is limited only by the size of the probe in the
microscope, which has been shown to be as small as 0.6 Å for a spherical aberration corrected (Cs corrected) STEM at 300 kV. In crystalline materials in a zone-axis orientation, the atomic spacing is greater than the probe size therefore the columns are illuminated sequentially as the probe is scanned over the specimen and an atomic resolution compositional map is subsequently generated.

The same is also true for thicker specimens. It has been noted that for specimens in zone-axis orientation, the STEM probe forms narrow spikes around each atomic column as it propagates through the material. This effect is known to be caused by the coherent nature and large angular spread of the STEM probe, leading to the tightly bound s-type Bloch states adding constructively and the less localized states interfering destructively. This effect is increased for scattering processes localized at atomic cores, such as high-angle thermal diffuse scattering (TDS), causing a great reduction in beam broadening. With only one dominant Bloch state, dynamical diffraction effects are largely removed and are manifested only as a columnar channeling effect, thus maintaining the thin specimen description described above.

Finally, Z-contrast imaging is highly desirable because the phase problem which is associated with the interpretation of HRTEM images is eliminated. In thin specimens, the dominant contribution to the intensity of the image is always its composition, and the effect of changing focus is understandable as the focus control alters the probe intensity profile on
the surface of the specimen. For any defocus away from the optimum Scherzer condition, the probe broadens, lowering resolution such that the individual atomic columns cannot be resolved. The optimum focus is realized when the maximum intensity is present in a narrow probe profile without the presence of significant probe, thus assuring the localization of the image information. This is also the optimum probe for microanalysis. The other important advantage of Z-contrast imaging is that simultaneous with the image chemical analysis through electron, energy-loss spectroscopy is also possible.

2.2 Atomic Resolution Electron Energy Loss Spectroscopy (EELS)

Figure 2-1 illustrates the experimental setup for data collection within the TEM. It is clear based on this figure that the annular detector which is used for Z-contrast imaging does not interfere with the low-angle scattering used for EELS. This means that the Z-contrast image can be used to position the electron probe over a specific structural feature for the acquisition of a spectrum. This simultaneous analysis allows for direct chemical analysis of extremely localized structures.
The basic physical principle behind EELS relates to the interaction of fast electrons with the sample to cause either collective excitations of electrons in the conduction band, or discrete transitions between atomic energy levels, e.g. $1s \rightarrow 2p$ transitions. The ability to observe discrete atomic transitions allows compositional analysis to be performed by EELS due to the fact that the transitions occur at characteristic energy losses for a given element. Additionally, the transitions to unoccupied states above the Fermi level allows the degree of hybridization between atomic orbitals to be determined, that is, information on local electronic structure (bonding) changes can be established. Figure 2-2 shows a typical EELS spectra and its components.
In order to accurately analyze the chemical content of the samples, a new method called "QuantiFit,” developed by our research group headed by Dr. Gerd Duscher, is used. In order to extract bonding information of the atoms, we analyze the shape of the element specific ionization edges known as the electron near edge structure (ELNES)\textsuperscript{103,104}. Based on these two techniques we develop a clearer understanding of the atoms present and their bonding configuration.

A very important aspect of this study is the necessity to be able to correlate the EELS spectrum with a particular location on the sample. This requires that the spectra have the same spatial resolution as the Z-contrast image. In order to achieve this resolution, the range over which an electron can cause an excitation event must be less that the inter-atomic spacing\textsuperscript{105}. Hydrogenic models\textsuperscript{106} indicate that for the majority of the edges which are accessible through conventional energy-loss spectrometers (\(\Delta E < 2\text{keV}\)) the object functions are localized within 0.1nm of the atom cores\textsuperscript{107,108}. In other words, the object function is localized at the atom cores in the same way as the Z-contrast image and an experimental probe of atomic dimensions. An important aspect of this experimental approach is that the probe channeling effect discussed for Z-contrast imaging also preserves the spatial resolution of the spectrum, thereby allowing atomic resolution analysis of the electronic structure to be achieved.
2.2.1 Qualitative Compositional Analysis

A core loss in EELS occurs when the incident electron beam excites a core level (K,L,M,N,O) electron in a material and therefore loses energy (see figure 2-2 to identify core loss region of EELS spectrum). This excitation process (also known as inner-shell ionization process) contains elemental information, therefore it plays an important role for compositional analysis.

In the EELS spectrum, this process is reflected as an ionization edge of triangular or saw-toothed shape. Its start energy is defined by the minimum energy loss (ionization threshold or critical ionization energy $E_c$) which is required to overcome the nuclear electron binding energy. Based on this, the critical ionization energy is specific for each element and can thus be used for elemental identification in EELS. In general, the intensity in the core-loss region on the EELS spectrum is maximum at $E_c$ because this is the point with the highest scattering probability (cross section). For energy losses greater than $E_c$, the atomic electron can still be ionized, but the probability is less than at $E_c$, therefore the intensity in the EELS spectrum drops sharply.

In addition to elemental identification, bonding information such as coordination number and charge state can also be revealed by shifts in the ionization edge. For example, in silicon, for the L$_{2,3}$ edge, Lopatin$^{109}$ reported that there is roughly a 6eV shift between silicon (99.8eV) and silicon oxide (106eV) (see figure 2-3).
Figure 2-3 EELS linescan across the Si/ SiO₂ interface indicating a 6 eV shift in the L₃,₂ edge onset\textsuperscript{109}

Inner shell ionization usually occurs at high energies (>50eV). Additionally, $E_c$ increases for K shell ionization as the atomic number increases, therefore L and M edges are more practical for elements with a large atomic number. One negative effect of using L and M edges is that their ionization is often edge overlapping, especially at low energies. There are several examples of this which will not be discussed because they are not part of this thesis. The primary core edges studied in this work are the Si L₃,₂ edge, the C K edge, and the O K edge.
2.2.2 Quantitative Compositional Analysis

Integration of ionization edges in EELS can yield quantitative information. After subtraction of the background, the ratio of elements present can be determined following this relation $N_A$

$$\frac{N_A}{N_B} = \frac{I_A(\beta, \Delta_A)}{I_B(\beta, \Delta_B)} \cdot \frac{\sigma_B(\beta, \Delta_B)}{\sigma_A(\beta, \Delta_A)}$$

where $I_A$ and $I_B$ are the integrated intensities of element “A” and “B” and $\sigma_A$ and $\sigma_B$ cross sections of element “A” and “B”.

It is important to note that in reality, the ionization edges in an EELS spectrum are much more complex than a simple Gaussian peak. Ionization edges are always superimposed on the Plasmon peak. The Plasmon peak is due to the low loss interaction between the incident electron beam and out-shell weakly bonded electron, and it occurs at energies $<50\text{eV}$. These interactions are particularly important for our study because some of our EELS spectra show interaction between the Si L$_{2,3}$ edge and the Plasmon peak. The second complication with ionization edges is that it is very unusual to get a sample which is thin enough for the ideal single scattering. Instead, electrons from the incident beam can undergo multiple scattering events. This plural scattering takes place not only in the Plasmon region, but also 15-20eV above the ionization edge. Finally, the fine structure information is contained within the first 50eV of the edge onset, and can complicate quantitative analysis.
Conventional quantification methods have been developed to remove the background and fit the edges. There are two main methods used, each with sources of error. The first method utilizes a power law background fit of the form $A x^{E^{-r}}$ where $A$ and $r$ are fixed parameters and $E$ is the energy loss. This method is based on the theory of the Plasmon resonance decay of a free electron gas. This method ignores the variation of $r$ observed in real experiments and thus does not accurately model the background of a real EELS spectrum. The second method is described by Verbeeck and Aert\textsuperscript{110} and features edges which only account for the free electron state. More recent \textit{ab initio} calculations\textsuperscript{111,112} prove the existence of solid state effects within the first 50 eV after the edge onset, complicating edge fitting and causing errors within Verveeck and Aert’s method.

Due to the problems described in the preceding paragraph, Dr. Duscher’s group developed a new quantification method, QuantiFit. QuantiFit follows the same physical principles as Verbeecks and Aerts method but also adds two modifications. (1) A linearly combined power law and polynomial fitting for the background (instead of the power law alone), and the addition of a polynomial fit. The polynomial fits act like a variation of the parameter $r$ and higher orders (3\textsuperscript{rd} and 4\textsuperscript{th} order) to produce a change in the curvature allowing for more degrees of freedom and ultimately a better fit. The interference of solid state effects is successfully avoided by starting the fit at least 50eV after the edge onset,
which is believed to be dominated by free electrons. QuantiFit operates within a spreadsheet environment and has been very effective for EELS analysis within Dr. Duscher’s group.

2.2.3 Energy-loss near-edge fine structure (ELNES)

There is pronounced fine structure information within 50ev of the ionization threshold for each ionization edge, and this information termed energy-loss near-edge fine structure (ELNES). ELNES is closely related to the available excited states which are dependent on local bonding environments\textsuperscript{111}, and usually interpreted by density of states (DOS). According to DOS, a single scattering intensity of an ionization edge $J^l_k$ is correlated to the density of final states $N(E)$ and an atomic transition matrix $M(E)$\textsuperscript{102}:

$$J^l_k(J^l_k (E) \propto |M(M (E)|^2 \cdot N(N (E))$$

$M(M (E)$ is described as a transition probability between the core state and the final state. It represents the general saw-tooth shape of the edge. $N(N (E)$ is different as it reveals chemical and crystallographic information of the excited atom. Due to the extremely localized nature of core-loss scattering, $N(E)$ is different even for elements in the same sample but with different symmetry, coordination, or chemical composition.

Recent studies have suggested that DOS theory alone is not enough to explain experimental observations in semiconductors, even though it works nicely for metals. Work by Duscher and Buczko in 2000 and 2001 suggests that a core-hold effect\textsuperscript{111,112} needs to be
taken into account. In semiconductors, core electrons can be excited into the vacuum, leaving one hole at the core-level, referred to as a core-hole. This process leaves the atom in an excited state and therefore alters the band structures causing band-shifts. When the effect of core holes is considered in the DOS calculations, there is an obvious improvement in fit between experimental and simulated curves, not only with the steepness of edge onset, but also with intensity. See figure 2-4 for a schematic illustration to compare “experiment” and “core hole” curves.
Figure 2-4: Experimental and theoretical X-ray absorption spectra of the Si-L\textsubscript{2,3} edge. There is a close match between the two thick black curves which are from “experiment” (top) and “core-hole”—full calculation including electron-hole interactions (bottom). The two thin black curves are from “Z+1” model (left) and “Z”—calculation without electron-hole interactions (right)\textsuperscript{111}.

2.2.4 Dept Profiling

There are two main methods for calculation localized elemental ratios using EELS and Z-contrast imaging, spot mode and linescan mode. Both are used in this study to
determine the ratios between silicon, carbon, and oxygen. Spot mode is time consuming and is used to measure specific, extremely localized areas, such as to measure the gradual concentration change across an interface. Line scan mode is used more commonly in this study, and it is conducted by the electron beam raster-scanning the area of interest, pixel by pixel, from left to right, top to bottom for a given amount of tie. A series of EELS spectra (for example 20) are collected simultaneously with the image with an integration time corresponding to 1/20th of the total time it takes the Z-contrast image to raster. Based on this, it is possible to determine how elemental ratios change across an interface, which is a critical part of this study.

2.3 Theory of Convergent Beam Electron Diffraction (CBED)

CBED is a very powerful method for the determination of the crystal structure of a material in TEM. The CBED technique was first used by Kossel & Mollenstedt\textsuperscript{113}. CBED became more widely used as STEM units with fine probes and large convergence angles were developed and utilized. This technique has become even more powerful with the development of more coherent electron sources such as LaB\textsubscript{6}, field emission, and field ion guns\textsuperscript{114}, the improved quality of lens systems which have less aberrations, and imaging using energy filtering devices\textsuperscript{115}

2.3.1 Introduction to CBED

A common way to introduce CBED is to compare it to the more conventionally used and well-known technique, selected area diffraction (SAD). In SAD, the electron beam
which is incident on the specimen is parallel with a beam diameter typically on the order of 1-10 µm (figure 2-5(a)). The resulting transmitted information is in the form of a spot pattern. CBED is different because instead of parallel illumination from the incident beam, the beam is focused to a converged point, typically from sub-nanometer to a few nanometers in diameter (figure 2-5(b)). The resulting transmitted diffraction pattern is in the form of overlapping discs. These overlapping discs are the result of a wide range of incident beams corresponding to various k-vectors producing useful crystallographic information.

Figure 2-5 Ray diagrams indicate (a) parallel illumination forms a spot pattern in the selected area diffraction setup; (b) converged illumination forms a disc pattern in convergent beam electron diffraction setup
The area of the sample from which the diffraction information is collected in SAD is selected by introducing a mechanical aperture into the image plane of the TEM. The image of the demagnified aperture on the specimen plane allows for the direct selection of the area of interest. The smallest area which can be selected for SAD is limited by the size of the aperture and the spherical aberration present in the lenses of the microscope, and is approximately 500nm in the JEOL 2010f. In CBED, the area of the sample from which diffraction information is collected is selected differently. This area is chosen by focusing the beam to a very fine spot (<1nm) directly on the region of interest on the sample. The convergence angle can be controlled by varying the size of the condenser aperture. Controlling the convergence aperture determines the type of CBED pattern obtained by controlling the amount of overlap in the discs. Observation of figure 2-5 elucidates that SAD patterns and CBED patterns are formed by interchanging the nature of the incident and diffracted beams. In SAD, the incident beam is parallel, or a disc of electron beams incident on the sample, and the resulting diffracted beams are spots. In CBED, the incident beam is a converged spot on the surface of the thin sample, and due to the nature of the converged beam introduced; the resulting diffracted beams are discs.

2.4 Transmission Electron Microscopy (TEM) Sample Preparation

Sample preparation is critical for any TEM or STEM investigation. In order to perform TEM or STEM analysis, samples must be thinned to electron transparency. The
requirements for samples which undergo EELS analysis are more stringent than conventional TEM, STEM, or HRTEM because the samples should ideally be between 0.3 and 0.7 times the mean free path of an electron in the sample material\textsuperscript{102}.

Techniques for the preparation of TEM cross-sectional samples are well documented\textsuperscript{116} and include electro-chemical polishing, cleaving, focused ion beam, and the sandwich/ion mill (often referred to as “conventional) method. The latter two methods mentioned are used in this study.

\textbf{2.4.1 Conventional Sandwich/Ion Milling Sample Preparation}

The sandwich/ion mill method involves creating a sandwich of material which is then mechanically thinned, dimpled, and then ion milled to form an electron transparent region. This method has been used for a long time and was first described by Abrahams et al in 1974\textsuperscript{117}. Sample preparation conducted in this study utilized the method described by Abrahams in combination with optical microscopy based thickness measurement applicable to certain materials which are transparent to visible light, documented in the PhD dissertation of Dr. E.A. Preble\textsuperscript{118}.

SiC is a particularly difficult sample to prepare using conventional sample preparation methods because the high bond strength of SiC results in ion milling times which are much longer than other materials of the same thickness. Additionally, the film, which has
a notably lower bond strength than the SiC substrate can be destroyed during ion milling if it is not properly shielded or if the milling is started when the sample is still too thick. These problems can be minimized if ion milling is only performed when the sample is less than 10 microns thick, which necessitates the use of Preble’s thickness determination method. In this method, using a Nomarski enhanced, interference contrast based optical microscopy technique specifically for the measurement of thickness in dimpled and ion milled cross-sectional TEM samples of thin film/SiC substrate assemblies. When viewed with a Nomarski microscope, it is possible to directly correlate the thickness of the sample to the number and color of Nomarski rings present. Figure 2-6\textsuperscript{118} indicates the Nomarski image of the sample after dimpling. The multi-colored rings are Nomarski fringes. Figure 2-7\textsuperscript{118} is the correlation between Nomarski fringe and sample thickness for SiC. Preble’s technique was useful because it allowed for accurate thickness determination. Samples were ion milled after they were determined to be less than 4 microns thick.

Figure 2-6 Nomarski images of SiC sample after dimpling. The multi colored fringes are Nomarsky fringes.
2.4.2 Focused Ion Beam (FIB) Sample Preparation

Another method of TEM sample preparation which is being widely utilized today is focused ion beam (FIB) sample preparation. In this method, a focused beam of gallium ions is used to thin an area of interest on the specimen to electron transparency\textsuperscript{119}. The sample can then be lifted out using a needle and loaded onto a TEM specimen grid. All FIB samples used in this study were prepared using the FEI Quanta 3D located in the Analytical Instrumentation Facility at North Carolina State University. This FIB is known as a dual beam FIB which is also equipped with an electron column allowing form imaging of the surface in addition to the FIB.
There are several advantages to using FIB sample preparation as opposed to conventional sample preparation. FIB sample preparation is preferred for samples which have a specific and limited area of interest because the dual beam allows for imaging of the sample for direct selection of the area of the sample from which the TEM sample will come. Another advantage is that FIB allows for large electron transparent regions which are completely flat with no bending (typically 5-20 square microns) which is significantly higher than conventional samples. The disadvantage of FIB is that the sample is generally not as thin as a conventional sample, with typical thicknesses between 65-100nm. In this study, FIB was used for preparation of fully fabricated device samples which necessitated the site specific abilities of FIB, while blanket wafers were prepared using conventional methods.
CHAPTER 3: RESULTS AND DISCUSSION

In this chapter, results collected from samples received from both the Army Research Laboratory and Cree, Inc will be presented. Based on these results, a discussion of possible atomic scale mechanisms contributing to the mobility loss associated with the 4H-SiC/SiO$_2$ interface will be discussed.

3.1 Effect of Processing Conditions on Microstructure

To investigate the influence of processing parameters on the microstructure, we will focus on a series of 4 samples received from the Army Research Laboratory. The processing conditions are given in table 3-1. In this table, sample name gives the name by which these samples will be referred to in the subsequent text. “Implanted” refers to aluminum implantation which was at $5 \times 10^{13}$ /cm$^2$ at 200kv. It is found that each of these four layers has a carbon rich transition region which is directly related to the mobility.
Table 3-1: Processing conditions and descriptions of samples received from Army Research Laboratory

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Oxide Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>NO Anneal and Plain Epitaxial</td>
</tr>
<tr>
<td>9B</td>
<td>NO Anneal and Implanted Epitaxial</td>
</tr>
<tr>
<td>21</td>
<td>As-Grown Thermal and Plain Epitaxial</td>
</tr>
<tr>
<td>21B</td>
<td>As-Grown Thermal and Implanted Epitaxial</td>
</tr>
</tbody>
</table>

3.1.1 Carbon Rich Transition Region

Examination of the samples described in table 1-1 led to the discovery of a carbon rich transition region on the SiC side of the interface. This region varied from sample to sample and its nature will be discussed in subsequent sections.

3.1.1.2 Sample 21

Sample 21 has an as-grown thermal oxide and was not subjected to NO annealing or aluminum implantation. In Z-contrast images, as described in Chapter 2, the intensity in the image is proportional to the atomic number squared of the elements present as well as the density of the materials being imaged. In these images, the crystalline SiC is significantly denser than the amorphous SiO₂, therefore the SiC has significantly more intensity in the Z-
contrast image. All subsequent images in this thesis will follow this contrast relationship. Z-contrast images indicate that this sample has a transition region of approximately 21 nm on the silicon carbide side of the interface. In Z-contrast images, this transition layer has a lower intensity than the bulk SiC. The transition region is crystalline as proven by the CBED but is tilted (see chapter 3.3 for more details on tilt), this might account for the decreased intensity. Figure 3-1 indicates the transition region and accompanying intensity profile as obtained using Digital Micrograph Imaging Software which was used to quantify the width of the transition region. In order to quantify the width of the region, we use the intensity scan of the Z-contrast image, which is possible because Z-contrast images are easily interpreted. Using the intensity profile, the thickness of the transition region is measured by calculating the distance between the full width at half maximum of the onset and the area where the bulk SiC begins. This method is used to measure all transition regions described in this thesis.

EELS linescans of the transition region indicate that this region is carbon rich. Figure 3-2 shows atomic ratios calculated based on EELS results corresponding to the area in the vicinity of the interface of sample 21. In the transition region, the carbon to silicon ratio is slightly less than 1.2:1, which is notably higher than the 1:1 for stoichiometric SiC. The near edge structure of the ionization edges in the EELS spectra do not indicate anomalous activity in the oxygen or silicon peaks. In figure 3-2, the spectra labeled 13-20 are from bulk SiC. There is some slight variation in the atomic ratios in these regions, and this slight variation
can be considered our error bar. This variation is less than 2 percent, and the excess carbon observed is much higher than this, so the amount of carbon is significant. While 20% more carbon is an extremely high amount of extra carbon, previous work by Feldman’s group at Vanderbilt\textsuperscript{50} indicated the presence of excess carbon on the order of 20%, but the techniques used in Feldman’s study lacked the resolution necessary to determine the location of the excess carbon.
Figure 3-1 Z-Contrast image and corresponding intensity profile (inset) from indicated area from sample 21.
Figure 3-2 Atomic Ratios calculated with EELS data corresponding to the indicated areas of sample 21. The ratios indicate a carbon rich transition region on the SiC side of the interface.

3.1.1.3 Sample 21B

Sample 21B has undergone thermal oxidation followed by aluminum implantation with a dose of $5 \times 10^{13} / \text{cm}^2$ at 200kv. HRTEM images of this sample indicate a crystalline interface, followed by a region of disturbed crystallinity, followed by a return to the
traditional crystalline lattice of SiC. This sort of microstructure is consistent with expectations for a buried transition layer. The total transition region is 25 nm, with 5 nm at the interface being crystalline followed by a 20 nm disturbed crystalline region. The disruption in the crystallinity is determined by lattice imaging in both HRTEM and Z-contrast imaging. Figure 3-3 is a HRTEM image detailing this effect. The total width of the transition region is approximately 25 nm. CBED results also indicate that this entire transition region is tilted (see section 3.3 for discussion of tilt) and this could account for the decreased intensity. Figure 3-4 shows a Z-contrast image of the interface region with corresponding intensity profile from the selected region which was used to quantify the width of the total transition region.

EELS results indicate that the transition region in this sample is also carbon rich. Additionally, the near edge structure of the ionization peaks indicate that there is no anomalous activity occurring in the oxygen or silicon peaks. There does not appear to be a difference in the carbon concentration directly at the interface as opposed to the region of disturbed crystallinity. Figure 3-5 shows the atomic ratios as calculated from EELS linescan data. In the transition region, the carbon to silicon ratio is roughly 1.18:1 instead of the 1 from stoichiometric SiC. As described for the previous sample, the error bar is less than 2%, therefore this increase in carbon in the interface region is significant. This result is
noteworthy because the transition region is both tilted and has a significantly higher amount of carbon than the bulk SiC, and it is similar to the sample previously described.

Figure 3-3 HRTEM image of sample 21B indicating microstructure consistent with a buried implantation layer.
Figure 3-4 Z-contrast image and corresponding intensity profile of sample 21B used for quantitative measurement of 25nm total transition layer width.
3.1.1.4 Sample 9

Sample 9 was thermally oxidized followed by a standard NO anneal. This sample did not undergo aluminum implantation. Sample was found to have a transition region very similar to the previous samples. CBED data indicated that this transition region is tilted (see section 3.3 for discussion of tilt). This transition region is the smallest transition region, with the region documented in Z-contrast imaging only being 6 nm. Figure 3-6 is a Z-contrast image of this region with corresponding intensity profile quantifying the transition region.
Like the other samples, EELS results indicated that this region is carbon rich. The near edge structure of the ionization edges indicated that there was no unexpected activity in the oxygen or silicon peaks. Figure 3-7 shows the atomic ratios calculated from EELS data corresponding to local areas in the vicinity of the interface. The carbon to silicon ratio is approximately 1.15:1 in the transition region. The error bar in the EELS calculations (as described in previous sections) is less than 2%, therefore the increased amount of carbon in the transition region is significant and outside of our error. The presence of this transition region is very important because of its similarities to the transition regions observed in the previous samples.
Figure 3-6 Z-contrast image and corresponding intensity profile of indicated area used to quantitatively measure width of the 6nm transition region in sample 9.
Figure 3-7 Atomic ratios calculated from EELS spectra corresponding to interface region of sample 9 indicating a carbon rich transition region
3.1.1.5 Sample 9B

Sample 9 was thermally oxidized followed by a standard NO anneal and aluminum implantation with a dose of $5 \times 10^{13}$ /cm$^2$ at 200kv. Z-contrast imaging of this sample indicates a transition region as all the other samples, with a thickness of 11 nm. As in the previous samples, CBED results indicate that this transition region is tilted (see section 3.3 for discussion of tilt). Figure 3-8 is a Z-contrast image with corresponding intensity profile which was used to quantify the width of the transition region.

EELS results from this transition region indicate that it is carbon rich. As with the previous samples, the near edge structure of the ionization edges indicate that there is no anomalous activity in the silicon or oxygen edges. Figure 3-9 shows atomic ratios calculated based on EELS results indicating that the carbon to silicon ratio is 1.17 in the transition region. As discussed previously, our error bar in the atomic ratio calculations is less than 2%, therefore the excess carbon is significant. This transition region is similar in stoichiometry and microstructure to the transition regions observed in the above samples.
Figure 3-8 Z-contrast image and corresponding intensity profile of indicated area used to quantitatively measure width of the 11 nm transition region in sample 9B.
Figure 3-9 Atomic ratios calculated from EELS spectra corresponding to interface region of sample 9B indicating a carbon rich transition region

3.1.1.6 Standard Oxide

The final sample in this series analyzed with a transition region is a standard oxide sample received from Cree. This sample was grown under proprietary conditions and then
subjected to an NO anneal. This reference sample was necessary to ensure that the transition layer is not just a feature of bad sample preparation but inherent in state of the art material. This sample had a carbon rich transition region 8 nm in width, with the carbon to silicon ratio equal to 1.16. As in the previous samples, CBED results indicated that this transition region is tilted (see section 3.3 for discussion of tilt). Figure 3-10 shows a Z-contrast image and corresponding intensity profile used to quantify the thickness of this region.

In the same manner as the previous samples, the near edge structure of the ionization edges indicates that there is no unusual activity associated with the oxygen and silicon edges. Figure 3-11 shows the atomic ratios corresponding to selected regions in the vicinity of the interface calculated from EELS data. The error bar associated with the atomic ratios is less than 5%, therefore the excess carbon is significant. This sample is extremely important because it is from a completely different source and was processed at a different place. Based on this, we can conclude that the tilted, carbon rich transition region is inherent to the material, and not a result of a specific set of samples or conditions.
Figure 3-10 Z-contrast image and corresponding intensity profile of indicated area used to quantitatively measure width of the 8 nm transition region in Cree’s standard oxide sample.
3.1.1.7 Qualitative Estimation of Oxidation Rate

Based on the processing conditions, it is possible to qualitatively estimate the relative oxidation rate of each sample. Those samples which were subjected to NO annealing have a slower oxidation rate than those samples which were not. This is because NO annealing
environment has 50% less oxygen than annealing in an ambient environment, making less oxygen available for the oxidation process.

Another effect of processing conditions on oxidation rate is that of Aluminum implantation. Aluminum implantation introduces point defects into the lattice. Lattice damage in the form of these point defects speeds up the oxidation rate, therefore it is expected that those samples which were implanted will have a significantly higher oxidation rate. This will be discussed further in subsequent sections.

3.1.1.8 Summary of Processing Conditions

The findings discussed in the previous sections are significant. We found that a transition region is present in all 5 samples on the SiC side of the 4H-SiC/SiO₂ interface. No previous studies have found this transition region. The transition region in each of the samples was found to be tilted and carbon rich in each of the samples, and varying in width between the samples.

The excess carbon measured with EELS in these samples is present in extremely high amounts. While the amounts measured seem very high, these amounts are on the order of a previous study⁵⁰. It is important to note that this previous studie detected the excess carbon but the technique did not have the resolution to determine the exact location of carbon. Our study confirms the presence of this excess carbon and we are able to directly observe the transition region where it is located. In addition to this, we are able to estimate the error
present in our atomic ratio calculations based on EELS results. This error is estimated by observing the variation in atomic ratio in the bulk SiC region, outside of the transition region. In each of the samples, the error is less than 2%, so while it is likely that there is some error associated with our calculation of excess carbon, the amount of excess carbon is still significant, even when considering our potential error.

In the next sections, this transition layer and how it relates to properties will be discussed. The structure property relationship between the transition layer and mobility will be evaluated. Other parameters such as carbon concentration as related to scattering length, tilt, and oxidation will also be discussed.

### 3.2 Linear Relationship

Peak mobility data as measured by ARL and Cree were provided for comparison to our microstructural analysis. Table 3-2 lists peak mobility data for each sample in cm$^2$V$^{-1}$s$^{-1}$. This table also contains the transition layer widths in nanometers as discussed in preceding sections. There is no mobility data listed for sample 21B. This is because the mobility was so poor on this sample that it was not possible to get an accurate measurement. Based on this data, it is found that there is a linear relationship between the width of the carbon-rich transition region and the peak mobility measured from the fully fabricated device. Figure 3-12 is a plot of the mobility versus the transition layer thickness. Note that although we do not have a measurement for the mobility of sample 21B, we know that it is very low, and this
fits nicely into the linear relationship. It is also very important to note that the standard oxide sample from Cree is from a completely different sample set, was fabricated at a completely different place, and still fits nicely into the linear relationship, indicating that the results are indicating that the results are consistent with a common underlying physical basis for the relevance of the transition layer on the measured device mobility.

Table 3-2 Transition layer width and mobility data for samples studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transition Layer (nm)</th>
<th>Peak Mobility (cm²/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 (NO Anneal)</td>
<td>6</td>
<td>29</td>
</tr>
<tr>
<td>9B (NO Anneal + Al Implantation)</td>
<td>11</td>
<td>24</td>
</tr>
<tr>
<td>21 (As-Grown)</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>21B (Al Implantation)</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Standard Oxide</td>
<td>8</td>
<td>26</td>
</tr>
</tbody>
</table>

Peak Mobility vs. Transition Layer Width

\[ y = -1.3529x + 37.471 \]
Figure 3-12 Plot of the transition layer thickness versus mobility indicating linear relationship.

3.3 Tilt

A unique characteristic of this transition layer, which was observed in every sample, is that the transition layer is physically tilted. This tilt was observed using convergent beam electron diffraction (CBED). Figure 3-13(a) shows a CBED pattern collected from bulk SiC in the $[\bar{1}1\bar{2}0]$ zone axis. It is important to note that this pattern is not a typical CBED pattern used for collecting data, instead it is a pattern collected while the TEM was optimized for STEM mode. The red rectangle in Figure 3-13 (a) represents the center of the pattern. Figure 3-13(b) is a CBED pattern which was collected from the transition region of sample B. The red rectangle in this image also corresponds to the center of the pattern. It is clear, based on the differences in the CBED patterns that the transition region has a different crystallographic orientation than the bulk SiC. In fact, in sample 9 (CBED patterns shown in Figure 3-14), the transition layer is tilted $0.5^\circ$ away from the bulk SiC. Indexing of the CBED pattern using JEMS software lead to the conclusion that the tilt is occurring within the $[0001]$ plane.
Figure 3-13 Convergent beam electron diffraction (CBED) patterns of sample 9 taken from (a) bulk SiC and (b) transition region. The red rectangle represents the center of the pattern to illustrate the clear tilt associated with the transition region.

All of the transition layers which we observed were tilted in the same direction. The amount of tilt in the layers varied slightly but was always less than 1°. Figure 3-14 shows CBED patterns collected from both the bulk and transition region of each of the previously discussed samples. It is clear from these images that the tilt always occurs in the [0001] direction and is noticeable, but not very large (less than 1°). Another interesting fact about the tilt observed in the transition layer of each of these samples is that the tilt does not occur gradually over a gradient, but instead occurs abruptly as the beginning of the transition region. It is not possible that this tilt is a result of an artifact from the sample preparation because the samples were prepared with FIB. FIB samples generally are not subject to tilt,
warping, drastic thickness variations, or any other effect which could simulate this tilted transition layer.

The tilt of each transition region relative to the bulk SiC varies slightly between samples, but is always less than 1°. It is possible to approximate the tilt angle based on the CBED image. The CBED image (like all other electron diffraction images) is in reciprocal space. In reciprocal space, linear distances in images can be represented as angles. It is possible to estimate the tilt angle between the transition region and the bulk SiC by measuring the change in the center of the CBED pattern between the bulk SiC and the transition region. Since we know that the radius of the aperture in the image is 10 mrad, it is possible based on this to determine the tilt between the two patterns. Table 3-3 gives the tilt angle for each of the samples as well as the carbon : silicon ratio. There does not appear to be a correlation between tilt angle and mobility. It is intuitive to think that there should be a correlation between the amount of excess carbon and the tilt angle, however, we do not observe any relationship.

This could be because of the lack of formation of stacking faults. In order for stacking faults to form, there must be both carbon and silicon interstitials, but in the case of our transition region, there are only carbon interstitials, suggesting that the lack of silicon interstitials could be the limiting factor.
Table 3-3  Tilt in degrees between the transition layer and bulk SiC for each sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tilt (Degrees)</th>
<th>Carbon : Silicon Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.9</td>
<td>1.15</td>
</tr>
<tr>
<td>9B</td>
<td>0.8</td>
<td>1.17</td>
</tr>
<tr>
<td>21</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>21B</td>
<td>0.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Standard Oxide</td>
<td>0.3</td>
<td>1.16</td>
</tr>
</tbody>
</table>

(a) (b)
Figure 3-14 (Continued on page 81)
Figure 3-14 (continued from page 80) CBED data collected from (a) sample 21B bulk SiC; (b) sample 21B transition layer; (c) sample 9B bulk SiC; (d) sample 9B transition layer; (e) sample 21 bulk SiC; (f) sample 21 transition layer; (g) Cree standard oxide sample bulk SiC; (h) Cree standard oxide transition layer. The red rectangle on each CBED pattern indicates the center of the pattern to illustrate the tilt.
3.3.2 Low Angle Grain Boundary

The fact that the transition region is crystallographically different from the bulk SiC and the stoichiometry is different suggests that the transition region can be considered a separate “grain” from the bulk. The presence of extra carbon in the transition region indicates the presence of defects in this region. Because the angle between the two “grains” has been measured to be very small, and we have evidence which suggests that there are many defects present, it is possible that the defects aligned to form a low angle grain boundary. It is possible that there are stacking faults with partial dislocations at the end of the sample. Figure 3-15 is a schematic showing how such a structure would appear in three dimensions.
3.4 Scattering Length and Physical Parameters Affecting Mobility

Given the mobility data, it is possible to calculate the scattering length in these transition layers. All device measurements were conducted at the Army Research Laboratory, and the scientists performing electrical measurements provided the deduced electron velocity calculated based on their experiments. Equation 3-1 represents the relationship between mobility and scattering time where $\tau$ is the mean free time between electron scattering events, $\mu$ is electron mobility, $e$ is the electronic charge ($1.602 \times 10^{19}$ Coulombs), and $m^*$ is the effective mass of an electron in a crystal. After $\tau$ is calculated, it is
possible to get the average scattering length if the velocity is known, based on the simple relationship in equation 3-2 where \( l \) is the scattering length, and \( v \) is the electron velocity. Table 3-4 shows the calculated \( \tau \) and \( l \) values for those samples with measureable mobility data.

\[
\mu = \frac{e\tau}{m^*}
\]

Equation 3-1 Equation representing electron mobility

\[
l = v\tau
\]

Equation 3-2 Relationship between scattering length, velocity, and scattering time

Table 3-4 calculated \( \tau \) and \( l \) values from samples with measurable mobility data

<table>
<thead>
<tr>
<th>sample</th>
<th>mobility (cm²/V·s)</th>
<th>( \tau ) (seconds)</th>
<th>( l ) (angstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>29</td>
<td>6.3E-15</td>
<td>6.47</td>
</tr>
<tr>
<td>9B</td>
<td>24</td>
<td>5.2E-15</td>
<td>5.35</td>
</tr>
<tr>
<td>21</td>
<td>10</td>
<td>2.2E-15</td>
<td>2.23</td>
</tr>
<tr>
<td>Standard Oxide</td>
<td>26</td>
<td>5.7E-15</td>
<td>5.80</td>
</tr>
</tbody>
</table>

The average scattering length \( l \) can also be interpreted as the length between scattering sites. Our EELS results indicate excess carbon in the transition region. Because we know the theoretical density of SiC, it is possible to determine the number of atoms per
cubic centimeter in SiC, and using our EELS data, determine the number of extra carbon atoms in the transition region. Table 3-5 shows the extra number of carbon atoms per cubic centimeter in each of the transition regions, compared to the scattering length. Taking the inverse cube root of the extra number of carbon atoms leads to the average distance between the excess carbon, assuming that the average extra carbon atom in the transition region is not clustered. Figure 3-16 is a plot which shows that the distance between the excess carbon atoms is reasonably correlated with the scattering length calculated from the mobility measurements. This correlation suggests that the decreasing carbon concentration increases the distance between the scattering centers, which is confirmed by the scattering length calculated from mobility data. While the distance between extra carbon atoms in the lattice (presumed scattering centers) is not perfect, the data matches nicely.

The samples with a decent mobility show that the average distance of random carbon atoms are in the same order of magnitude as the average scattering length. The Z-contrast images show the Si lattice almost undisturbed as does the CBED patterns. This means that there can only be configurations with a few carbon atoms such as 3C-Si or 2C-Si to allow for the electron scattering at interface states. Only where additional point defects are generated, is the mobility lower than the one expected from the C incorporation.
Table 3-5 Calculations based on mobility and EELS data

<table>
<thead>
<tr>
<th></th>
<th>C: Si ratio in transition region</th>
<th>additional carbon atoms per cm-3</th>
<th>Scattering Length (From Mobility)</th>
<th>Distance between extra carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample 9</td>
<td>1.15</td>
<td>7.2E+21</td>
<td>6.47</td>
<td>5.2</td>
</tr>
<tr>
<td>sample 9b</td>
<td>1.17</td>
<td>8.2E+21</td>
<td>5.35</td>
<td>4.9</td>
</tr>
<tr>
<td>sample 21</td>
<td>1.2</td>
<td>9.6E+21</td>
<td>2.23</td>
<td>4.7</td>
</tr>
<tr>
<td>sample 21b</td>
<td>1.2</td>
<td>9.6E+21</td>
<td>not known: no mobility data</td>
<td>4.7</td>
</tr>
<tr>
<td>standard oxide</td>
<td>1.16</td>
<td>7.7E+21</td>
<td>5.80</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Figure 3-16 Plot showing linear relationship between distance between excess carbon and mobility scattering length
On the basis of Figs. 3-12 and 3-16, it is clear that this carbon rich transition region plays a crucial role in the mobility degradation associated with the SiC/SiO2 interface. Subsequent discussions will focus on the origin of this excess carbon.

3.5 The “Snowplow” Effect

The next step in the interface analysis process of this thesis was to examine an industrially standard fully fabricated SiC device wafer. This sample was fabricated on a N-doped n-type 4H-SiC wafer with a 5μm Si-face terminated homoepitaxialtaxial layer, doped at approximately mid 10^{15} cm^{-3}. The oxidation was performed at 1200°C in pure oxygen, followed by an Ar annealing at 1100°C and a 950°C wet re-oxidation anneal^{120,121}. It is important to note that the processing conditions in the sample are from older fabrication methods, and are not currently used. These conditions lead to a rapid oxidation which is followed by NO annealing. The sample was prepared for STEM investigation using conventional sample preparation methods. Z-contrast images were collected simultaneously with EELS spectra to obtain localized chemical information using the line scan method as described in Chapter 2. Figure 3-17 is the Z-contrast image, divided into regions corresponding to EELS spectra and the corresponding atomic ratios as determined based on EELS analysis. The atomic ratios were determined using QuantiFit as described in Chapter
2. Each scan region is approximately 0.5nm x 5 nm. The rectangular nature of the scan region allows for localized data in the direction normal to the interface without destruction of the sample due to overexposure to the 200kev electron beam.

Figure 3-17: Z-Contrast image of conventional sample with corresponding atomic ratios as calculated from EELS results
Based on the information presented in figure 3-17, it is possible to see that there is carbon on both sides of the SiC/SiO₂ interface. As discussed in chapter 1, many previous studies have suggested that carbon is present on the oxide side of the interface in some form. In addition to the carbon on the oxygen side, there is a pileup of carbon approximately 1-2 nanometers below the interface on the SiC side, with the maximum carbon pileup located 1 nm below the interface. At the maximum point in this pileup, the carbon to silicon ratio is 20% higher than the expected 1:1 which we observe in the bulk. The oxygen behaves as expected, with the oxygen to silicon ratio changing from 2:1 in the SiO₂ to 0 in the SiC. This is similar to results collected from samples discussed in previous samples, however the previous samples in this study do not exhibit as much carbon on the oxide side of the interface, and the carbon pileup in this sample is slightly higher than that observed in previous samples.

Based on direct observations made of this result, it is possible to draw conclusions about the nature of carbon in the oxidation process. We considered the shape of the C/Si ratio plot to be a concentration profile, with the interface moving at a velocity \( v_g \) upon oxidation, therefore it is possible to determine the change in carbon concentration in terms of the moving interface and time. It was assumed that this system was in steady state. If the velocity of the moving interface is considered to be a change in position with time (equation
3-3), then the change in concentration can then be considered in terms of position and time as in equation 3-4.

$$\Delta x = v_g \Delta t$$

Equation 3-3: The relationship between the velocity of the moving interface upon oxidation, time, and position

$$\frac{\partial C}{\partial x} = \frac{C(x + \Delta x, t) - C(x, t)}{\Delta x} = \frac{C(x, t - \Delta t) - C(x, t)}{v_g \Delta t} = \frac{1}{v_g} \frac{\partial C}{\partial t}$$

Equation 3-4: The change in concentration in terms of time and position

When equation 3-4 is combined with Fick’s Second Law (Equation 3-5, 3-6), it is possible to derive an expression which represents the diffusion of carbon in SiO2 during oxidation (equation 3-7).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Equation 3-5: Fick’s 2nd law

$$\frac{\partial C}{\partial x} = \frac{D}{v_g} \frac{\partial^3 C}{\partial x^2}$$

Equation 3-6: The combination of Equations 2 and 3
Equation 3-7: The diffusion equation for carbon in SiO₂ during oxidation

\[ C(x,t) = C_0 \exp \left( -\frac{v_g}{D} (x - v_g t) \right) \]

After the diffusion equation of carbon in SiO₂ (equation 3-7) has been established, as described in the preceding discussion, even more information can be deduced based on the experimental results. It is clear based on these results that during oxidation, carbon interstitials are emitted on both sides of the interface. During this process, some carbon is released in the form of CO₅ gas, but the remaining excess carbon is evidence that not all of the excess carbon is released.

We observed the transition region, which occurs from the maximum carbon in the SiC to the minimum carbon in the oxide (as shown by the area selected in red in figure 3-18a). These points which are selected from the experimental data shown in figure 3-18a are plotted on a smaller scale in figure 3-18b. The fitted line in figure 3-18b is represented in equation 3-8. Based on this relationship, and the exponential fit equation determined from experimental results, it is possible to determine the diffusion length for carbon in SiC upon oxidation. For example, for the oxidation rate at 1250°C, the diffusion length is 7nm, which is significantly far into the SiO₂.
Figure 3-18: (a) Atomic ratios in sample calculated based on EELS data indicating the region selected for fitting and (b) the fitted region from (a)

\[
C(x) = \exp\left(-\frac{x - 2.55 \text{ nm}}{0.76 \text{ nm}}\right)
\]

Equation 3-8: The exponential fit of the experimental data as shown in figure 3-2b
Based on these calculations, it is clear that the oxidation rate in SiC is critical. For conditions that facilitate a fast oxidation rate, the diffusion length for carbon in SiO₂ is higher. Most SiC MOSFET samples are oxidized at a very high rate. This high rate is necessary for the achievement of a high quality oxide. During the oxidation process, there is ballistic emission of carbon interstitials into the SiC, which is effectively considered to be a “driving in” process. This driving in causes a “snowplow effect” where the carbon is piled up below the interface on the SiC side. The snowplow theory is now treated as an explanation for the origin of the carbon rich transition layer observed in previous samples. When the carbon is forced into the SiC during oxidation, this effectively creates a metastable material. Based on the C-Si phase diagram, it is clear that there is no stable C-Si phase other than stoichiometric SiC. The phase expected based on the carbon concentration is a combination of SiC and graphite. We do not observe graphite in the Z-contrast images and we do not expect that it is present based on our scattering length data (section 3.4), therefore the material is the transition region must be a metastable material. The transition region is the localized region of metastable material which is induced by ballistic emission of carbon into the SiC during the oxidation process.

3.6 Varying Annealing Temperature

After our work with the snowplow theory suggested that the oxidation rate in SiC is critical, the next step was to examine samples which were oxidized at a slower rate. Four
samples from Cree were examined. Each of these four samples saw the same oxidation conditions, implant activation anneals. Even though each of the samples received an implant activation anneal, none of them were implanted; the goal of this study was only to determine the effect of exposure to temperatures associated with the anneal necessary for implant activation. The ultimate objective of the analysis of these samples was to determine if there was a difference in carbon distribution with the different oxidation conditions, to determine if they behaved as expected according to our snowplow theory, and to examine how varying the implant activation temperatures effects the microstructure of the interface.

Each of these four samples will be described by a letter (A, B, C, or D) for the remainder of the discussion in this thesis. The description of these samples can be found in table 3-6. Each of the samples underwent the anneal described in the table, followed by a 2 hour 1200°C dry sacrificial oxidation (this step is typically done to oxidize away the damaged surface from implant activation). After this, each sample was subjected to Cree’s current gate oxidation process which includes a dry oxidation at 1175°C followed by a wet oxidation at 950°C, and then a final NO anneal at 1175°C for 2 hours.
### Table 3-6: Description of Sample conditions

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Annealing Time</th>
<th>Annealing Environment</th>
<th>Annealing Temperature (Celsius)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5 minutes</td>
<td>Ar</td>
<td>1200</td>
</tr>
<tr>
<td>B</td>
<td>5 minutes</td>
<td>Ar</td>
<td>1400</td>
</tr>
<tr>
<td>C</td>
<td>5 minutes</td>
<td>Ar</td>
<td>1650</td>
</tr>
<tr>
<td>D</td>
<td>5 minutes</td>
<td>Ar</td>
<td>1800</td>
</tr>
</tbody>
</table>

#### 3.6.1 Z-Contrast Images of the Interface

Z-contrast images from samples A, B, C, and D were collected. There were no noticeable differences in the 4H-SiC/SiO₂ interfaces from sample to sample. Figure 3-19 shows a typical interface, characteristic of these samples. It is clear from these images that there are steps at the interface to compensate for the miscut associated with the SiC growth as discussed in Chapter 1. Step bunching, the phenomenon where multiple steps are contained within a small area of the interface, occurs frequently in these samples and is illustrated in figure 3-19(b). Z-contrast images of each of the four samples can be seen in figure 3-20(a-d). In figure 3-20, each of the samples has a different orientation, which is due to the random orientation associated with loading the sample into the TEM, but each of them was taken in the [1120] zone axis.
Figure 3-19 Characteristic interface images from samples A, B, C, and D indicating the presence of steps at the interface and the tendency of these steps to bunch. (a) indicates an area of the interface with few steps while (b) shows many more steps in the same amount of area as (a). Both samples are oriented in the [110\bar{2}] zone axis.
Figure 3-20 Z-contrast images of sample (a) A, (b) B, (c) C, and (d) D. These images show a chemically abrupt interface with steps at the interface. There are no significant differences in the interface of the samples. All images are taken in the \([11\bar{2}0]\) zone axis.
Observation of Z-contrast images of each of the samples shows that there are no noticeable differences between each of the samples. Each of the samples has a sharp, chemically abrupt interface which has steps. Step bunching occurs in each of the samples, but there was no discernable difference in the amount of steps in each bunch or the frequency of step bunching between the samples. The only transition layer at this interface is associated with the steps at the interface. The microstructure of the interfaces in each of these samples is virtually the same.

The fact that there are no discernable differences in the interfaces of each of these samples indicates that the structure of the interface is a result of the oxidation process, rather than the high temperatures associated with the implant activation anneal. There are many processes which a sample is subjected to during the overall device fabrication process, and all were kept consistent between the samples except the implant activation anneal.

The realization that the annealing temperature has no influence has important implications. If carbon diffusion in the SiC is a factor, then temperature would have an important influence. Conversely, if there is no carbon diffusion in the SiC, then the temperature would have no influence, as we observe. This corresponds nicely with our snowplow effect data which suggests that carbon is ballistically emitted into the SiC during oxidation, which is an effect of the oxidation rate, not the temperature. The oxidation rate is
critical because more carbon is emitted with a faster oxidation rate, effectively changing more material to a metastable phase.

3.6.2 Low Angle Dark Field Imaging of the Interface

Low angle dark field (LADF) images can be acquired simultaneously with Z-contrast images due to the physical experimental setup in the JEOL 2010f in the AREMC. Figure 2-1 is a schematic of the STEM setup. It is clear that electrons which are scattered to high angles are collected with the high angle annular dark field detector (HAADF) to form Z-contrast images. In the setup shown in figure 2-1, some of the electrons which are not scattered to high angles are collected with an EELS spectrometer for EELS data. It is also possible to use a bright field detector or a low angle dark field detector to collect electrons from this region to form images. In this study, LADF images are useful because these images are sensitive to lattice distortions such as strain, where Z-contrast images are not. The two images (HADF and LADF) are complementary in that the HADF image contains chemical information and the LADF image is sensitive to strain.

Simultaneous LADF and HADF images were taken of the interface in sample B. Due to problems with the LADF detector in the AREMC, it was not possible to get LADF data from the other samples. Figure 3-21 (a-b) shows the complementary LADF and HADF images of sample B with corresponding intensity profiles. The intensity profiles are
generated digitally from the images using Digital Micrograph image processing software. Figure 3-21 (a) is the LADF image. There is a significant increase in intensity at the interface, specifically in the last two monolayers, confirmed by the intensity profile. In the HADF image, this intensity increase is not present, instead the interface appears to go from SiC directly to SiO2, also confirmed by the intensity profile. The fact that this intensity increase is present exclusively in the LADF image indicates that it is most likely a result of strain, which cannot be detected by the HADF image. This strain is not the strain that is typical of a stress-strain curve, but is instead the strain which is associated with point defects distorting the atomic columns.
Figure 3.21 (continued on Page 102)
3.6.3 Electron Energy Loss Spectroscopy Results from Samples A, B, C, and D

Localized EELS data was collected from interface region of each of these samples using the linescan method described in chapter 2. The carbon pileup which was observed in the first fully fabricated device wafer (see section 3.1) was not observed in these samples. This could potentially be attributed to the slower oxidation rate.
EELS data was collected in a manner to include the part of the core loss region of silicon, (silicon L3,2 edge with energy loss ~100eV), carbon (carbon K-edge with energy loss at 284eV), and oxygen (oxygen K-edge with energy loss at 532eV). Linescans were collected across the interface to observe changes in each of the elements near the interface. If the interface is perfect and chemically abrupt, then it is expected that the only changes in the spectra will occur on either side of the interface when the material changes from SiC to SiO2 or vice versa. In this case, where there is no transition, then the spectrum corresponding to the interface will be a linear combination of the 2 adjacent spectra (the two adjacent spectra are the spectrum directly above and directly below the interface). We modeled each of these regions mathematically using Microsoft Excel to determine if there is notable change at the interface.

We did these mathematical calculations on spectra from each sample with the same results. Results of the linear combination modeling are shown for sample B as a representative example of how the calculations are performed. Our results from each sample indicate that in both the silicon and oxygen regions, the interface spectrum is a linear combination of the two adjacent spectra. This indicates that for both silicon and oxygen, there is no anomalous activity at the interface, simply a transition from SiC to SiO2. Figure 3-22 is a plot showing the experimentally collected spectra from the interface, the adjacent SiC (directly above the interface), the adjacent SiO2 (directly below the interface), our model
of a linear combination of the two adjacent spectra, and the difference between our model and the experimental data. It is clear based on this data that our model and the experimental data match very nicely, and while there is some difference, it is small and within the range of the noise associated with collecting the data. A similar effect is observed with the oxygen edge (figure 3-23). This plot also has the interface, adjacent spectra, our model, and the difference. Like silicon, there is no significant difference in our model and the experimental data. It is worthwhile to note that these spectra in this image are noisier, which is expected due to the higher energy loss values.
Figure 3-22 Background Subtracted plots of sample B of interface and adjacent spectra, the linear combination model, and the difference between the two in the silicon region. Background subtractions were performed using QuantiFit.
Figure 3-23 Background subtracted plots of sample B of interface and adjacent spectra, the linear combination model, and the difference between the two in the oxygen region. Background subtractions were performed using QuantiFit.

The carbon edge shows a difference at the interface, which is noticed because it is not simply a linear combination of the two adjacent spectra. Based on this, we focused our attention on the carbon edge associated with the interface. Figure 3-24 is the carbon edge associated with the first few monolayers of the interface. In this figure, “interface” refers to the spectra collected from the interface, “1st monolayer” refers to the first monolayer in SiC above the interface, “2nd monolayer” refers to the second monolayer in SiC above the
interface, and “3rd monolayer” refers to the third monolayer in SiC above the interface. The second monolayer is of particular interest because it does not look like that of SiC, SiO₂, amorphous carbon, or any other known carbon edge. This edge is featureless and uncoordinated. This indicates some abnormal activity in the second monolayer associated with the carbon edge. It is also important to note that in figure 3-21(a), the LADF image of this interface indicates that there is strain or some other phenomenon occurring within the first two monolayers above the interface, and our EELS results suggest that this is related to carbon. The featureless carbon edge in the second monolayer is not confined to sample B, in fact it was seen in each of the four samples. Figure 3-25 shows the carbon peak from the second monolayer in each of the four samples. This figure also contains a characteristic carbon peak for SiC as a reference to illustrate the difference between SiC and the featureless peak observed in the 2nd monolayer. Each of the readings from the second monolayer are basically the same with the only difference being within the noise level. It is important to note that these spectra were all collected from separate samples on different days, therefore some variation in intensity is expected. These spectra have been normalized so that they are all on the same scale for ease of comparison. This normalization is possible because this result is not involving the area under the curve (quantitative chemical information), and instead we are only concerned with the shape.
Figure 3-24 Background subtracted plots of spectra collected at and adjacent to the interface in the carbon region. Background subtraction performed using QuantiFit.
Figure 3-25: Background subtracted carbon peaks from the 2\textsuperscript{nd} monolayer of each of the samples A, B, C, and D, as well as a characteristic carbon peak for SiC for comparison. The peaks from each of the four samples were basically the same with the only noticeable differences being in the noise level. Background subtractions performed using QuantiFit.

Based on our EELS data for these samples, as well as the LADF data discussed, it is possible to conclude that these samples do have a transition region which is only 2 monolayers thick. This is different from the transition regions discussed in section 3.1 which were 5-25 nm thick. The extremely thin transition region associated with these samples is a result of the snowplow effect discussed earlier limiting the amount of ballistic carbon emitted into the SiC during oxidation.
3.7 Back Side of Wafer

Our previous results and calculations suggest that the oxidation rate is critical. One way to confirm the effects of varying the oxidation rate is to examine the carbon face of a wafer. As mentioned in Chapter 1, the carbon face of a wafer has a significantly faster oxidation rate than the silicon face. We prepared a sample for TEM investigation of the backside of wafer A. The carbon face of this wafer obviously saw the same oxidation conditions as the silicon face but would oxidize faster. Figure 3-26 shows a Z-contrast image of the carbon face of wafer A. It is clear based on this image that instead of a chemically abrupt, sharp interface, there is a transition region of disturbed crystallinity. In addition to the Z-contrast image, CBED was used to confirm that the crystal structure in the transition region is disturbed. The stark differences between the front side and the back side of this wafer, combined with the known differences in oxidation rate confirm that a faster oxidation rate leads to a transition region instead of a chemically abrupt interface.
Figure 3-26  Z-contrast image of carbon face of wafer A showing a transition region which is a result of a rapid oxidation rate.

3.8 Discussion

It is clear based on the above mentioned results that there is a carbon rich transition layer present on the SiC side of the interface, which has a different crystallographic orientation from the bulk SiC. This transition layer varies in width and carbon concentration between samples. Based on mobility data combined with our experimental results, it has been possible to determine that the width of this transition region has a linear relationship
with the mobility, where a smaller transition region leads to a higher mobility. There is no obvious correlation between the amount of excess carbon and the tilt angle associated with the transition region. There is also no obvious relationship between the annealing temperature and the interface structure. These data allow us to conclude that there is no thermally activated process involved in the creation of the transition region which ultimately limits mobility. Instead, the process is a kinetic one in which ballistic carbon is emitted into the SiC during oxidation, causing this transition region.

The carbon rich nature of this interface has been attributed to rapid oxidation leading to a carbon pileup on the SiC side of the interface. Our results suggest this “snow plow” effect is completely related to the oxidation rate and not related to the implant activation annealing temperature. We have measured high amounts of carbon in this transition region. It is possible that our results overestimate the amount of carbon in this region, but even accounting for error, there is still 10%-20% more carbon in the transition region in each of the samples, which qualifies the transition region as a metastable material based on the phase diagram. The samples in which the transition region was detected were all prepared using FIB. As discussed in Chapter 2, FIB samples are often thicker than ideal for EELS analysis. These thicker samples cause multiple electron scattering results within the sample, making EELS results difficult to interpret. Even if the carbon ratios we measured are slightly higher than the actual carbon content, it is still certain that there is an excess amount of carbon in
these transition regions, and our assertions that this leads to the mobility loss remains unchanged.

The exact nature of this transition region is not fully understood. Due to its tilted nature, it is difficult to image this transition layer clearly in STEM. Our TEM samples are prepared in the cross section zone axis, and any imaging of the transition region is at an angle instead of normal to the electron beam. Our Z-contrast images were able to detect the presence of this transition region, EELS allowed for determination of stoichiometry, and CBED led to the determination of tilt, but detailed microstructural imaging of this transition region was limited because of the tilt. If the tilted transition region is a low angle grain boundary, this suggests that there is a high thermal budget in its formation because the defects were able to align themselves to form the low angle grain boundary.

The width of this transition region changes based on processing conditions. Those samples which were exposed to NO annealing had the smallest transition layers (and the best mobility). All of the four samples from ARL were oxidized under the same conditions, and had different transition regions, suggesting that the post oxidation processing conditions control the width and amount of carbon present in this.

Sample 21, which was not subjected to NO annealing, or Al implantation, can be considered a baseline. This sample had a transition region of 20 nm. Sample 21B underwent
the same processing conditions as sample 21, only it was also subjected to Al implantation, yet it had a 25% larger transition region. This Al implantation clearly increased the width of the transition region, possibly because damage introduced to the lattice as a result of the implantation resulted in defects which allowed the excess carbon to diffuse slightly further into the lattice.

Similarly, sample 9 underwent the same processing conditions as sample 21, only it was subjected to a post oxidation NO anneal, and the result is a transition region which is over 60% smaller with less carbon than sample 21. This NO anneal is clearly beneficial in reducing the width of the transition region, possibly because the NO environment passivates any carbon clusters allowing for removal of some of the excess carbon from the transition region. In any event, this NO anneal is clearly a critically needed step. Sample 9B behaves as expected with the combination of NO anneal to improve transition region and Al implantation negating some of the positive affects associated with the NO anneal. Our data suggests that the Al implantation is not beneficial to the mobility in any of the presented scenarios.

The snowplow effect discussed earlier confirms that the oxidation rate is critical and it leads to the formation of a carbon pileup on the SiC side of the interface. As mentioned earlier, most industrially prepared SiC MOSFETs undergo a fast oxidation rate because this is necessary to produce a high quality oxide. Our data suggests that by controlling this
oxidation rate (and therefore controlling the carbon pileup), and adding NO annealing, the oxidation rate can be improved even further. Figure 3-27 is a schematic suggesting the potential implications of this on the mobility.

![Figure 3-27 Schematic illustrating potential implications of combining slow oxidation rate with NO annealing.](image)

3.9 Future Prospects

Although all of our data provides microstructural atomic scale explanations for the origin of the mobility loss associated with this interface, as well as recommendations for
mobility improvement, there is still considerable potential for improvement using other avenues. Cree, Inc has seen promising mobility from structures which do not resemble the ones discussed in this thesis. Figure 3-28 shows the interface of a sample which has been subjected to Cree’s new, proprietary process. While we are not permitted to discuss the details of this process, the mobility is comparable to the best mobilities discussed in this thesis. The double nature roughness and thickness of this interface suggests that it would lead to poor mobility but Cree has been able to engineer it in a way so that its mobility is better than a standard sample. This data suggests that there is lots of room for improvement in this field via multiple avenues.
3.10 Conclusion

In this study, we studied the interface between 4H-SiC and SiO₂ using analytical electron microscopy to determine the atomic scale origin of mobility loss associated with the
SiC/SiO$_2$ interface. Z-contrast imaging, EELS, and CBED were used to discover and characterize a carbon rich transition layer present on the SiC side of the interface. After comparison with mobility data, it was found that the width of this transition region is linearly related to the mobility. NO annealing reduces the size of this transition region while aluminum implantation can increase it. The smaller transition regions also had slightly smaller amounts of carbon, which can also be a contributing factor in mobility loss as extra carbon can act as an electron scattering center.

This carbon rich transition region is a result of the snowplow effect in which carbon piles up on the SiC side of the interface during oxidation. Slower oxidation rates can minimize this snowplow effect leading to less carbon pileup. Future mobility improvements can likely result from the combination of slow oxidation rates and NO annealing. While the combination of factors discussed in this dissertation can be helpful in improving mobility, this field is not limited to these, and there is lots of potential for future improvement via other avenues.


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