STUDIES ON SILICON CARBIDE:
HETEROEPITAXY ON SILICON
AND TITANIUM ALLOY OHMIC CONTACTS

by

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List of Acronyms

AES  Auger electron spectroscopy
APB  antiphase boundary
AST  accelerated stress test
BF   bright field
CBED convergent beam electron diffraction
CMOS complementary metal-oxide semiconductor
CTE  coefficient of thermal expansion
CVD  chemical vapor deposition
DCA  direct chip attach
DF   dark field
EELS electron energy-loss spectrometry
EFTEM energy-filtering transmission electron microscopy
ESI  electron spectroscopic imaging
EXLO  ex-situ liftout
FIB  focused ion beam
FWHM full width at half maximum
GIF  Gatan image filter
HAADF high-angle annular dark field
HMDS hexamethyldisilane
HRTEM high-resolution transmission electron microscopy
LMIS liquid metal ion source
LP-MOCVD low pressure metal-organic chemical vapor deposition
MCP multi-channel plate
MOCVD metal-organic chemical vapor deposition
RF radio-frequency
RHEED reflection high-energy electron diffraction
ROI region of interest
RT room temperature
RTA rapid thermal anneal
SAD selected-area diffraction
SBH Schottky barrier height
SCSAM Swagelok Center for Surface Analysis of Materials
SEM scanning electron microscopy
SOI silicon-on-insulator
STEM scanning transmission electron microscopy
TCGF temperature coefficient of gauge factor
TCR temperature coefficient of resistance
TEM transmission electron microscope/microscopy
TMA trimethylaluminum
TMG trimethylgallium
UHV ultra high vacuum
XEDS X-ray energy dispersive spectroscopy
XRD X-ray diffraction
ZLP zero loss peak
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The first half of this dissertation describes the design and construction of a new low pressure MOCVD reactor. Various problems and concerns with leakage, fitting and safety were solved to make the reactor more reliable and safer.

For SiC growth on Si substrates, the so-called two-step growth procedure was adopted and a single precursor hexamethyldisilane was used. XRD results showed that the films on Si(100) were polycrystalline, while epilayers on Si(111) are single crystalline. A few GaN films were also epitaxially grown on Si(111) using a buffer layer of SiC. A possible explanation for the advantages of the two-step over the one-step growth procedure is proposed involving the interfacial energy and total energy change during nucleation.

The second half of the dissertation deals with a microstructural investigation of multi-layer Ti alloy contacts to SiC. For this purpose, numerous site-specific TEM thin foils were prepared for (Au/)TaSi$_2$/Ti ohmic contacts with different annealing histories using the Focus Ion Beam liftout technique. Subsequently, the thin foils were studied by various imaging and analytical techniques.
On either sides of the Ti layer in the TaSi$_2$/Ti/SiC multi-layer structure, two interfaces could be clearly observed. While no C or Si were detected in the Ti contact layer of the as-deposited sample, the annealed samples exhibited strong Si and C signals throughout the Ti layer. This is indicative of the formation of new phases such as silicide(s) and/or carbide(s) of titanium. Moreover, the TaSi$_2$ layer had acted as a diffusion barrier and prevented the diffusion of Ti to the surface and in-diffusion of oxygen.

In samples with four more layers (i.e. Au/Ti/TaSi$_2$/Ti in addition to TaSi$_2$/Ti/SiC, making a seven-layer contact), which were annealed from 1 to 50 hours, a thick interface had formed between the upper TaSi$_2$ layer and the top Au layer. In addition, on the surface of the contacts, cross-linked Au micro-wires had formed under which many irregular dark patches were present with high concentrations of C, O and Si.

Using the microcharacterization information, we have proposed a failure mode and mechanism for the Ti alloy contacts.
Part I

Background and Introduction
Chapter 1

Introduction

Silicon carbide (SiC) is a promising candidate for high temperature and high power electronic applications. However, single-crystalline SiC substrates are expensive and have a high density of dislocations. Similar to normal practices in silicon technology, a SiC-based device is actually fabricated on the epilayers on the substrate, be it SiC, Si, or whatever.

In chapter 2, a brief review is given on the structure and properties of SiC. The next section (§2.2) summarizes the previous work on hetero-epitaxy of SiC on Si. The principles and fabrication procedures of SiC pressure sensors are then explained, followed by their reliability issues (§2.3–§2.4). Finally in the last section (§2.5) of this chapter, the versatility of the focused ion beam (FIB) is reviewed.

Chapter 3 involves the background and experimental setup of X-ray diffraction (XRD), which was used to characterize SiC epi-films. The investigation of Ti ohmic contacts was made possible by site-specific TEM (transmission electron microscopy) specimen preparation using an FIB liftout technique from regions
susceptible to failure, e.g. metal/semiconductor junctions (§3.2). The next few sections explain the principles of various modes of TEM.

Chapter 4 describes the design, modification, and construction of our homemade low pressure metal-organic chemical vapor deposition (LP-MOCVD) reactor. In the first section of chapter 5, a simple statistical experiment, carried out to determine the major factors that control the substrate temperature, is described. Some preliminary results are followed by SiC (and GaN) epitaxially growth on Si(100) and Si(111) substrates.

The third part (chapter 6) presents the TEM investigations of Ti ohmic contacts to SiC, including scanning transmission electron microscopy (STEM), X-ray energy dispersive spectroscopy (XEDS), energy-filtering transmission electron microscopy (EFTEM), and electron energy-loss spectrometry (EELS). The findings on many different samples are compared and summarized in sections §6.2.1 and §6.6.1. The diffusion aspect is discussed in chapter 7; a failure mode and failure mechanism are also proposed in this chapter.

Finally, some conclusions about SiC epitaxy on silicon, and titanium contacts to SiC are summarized in chapter 8, followed by suggestions for future work.
Chapter 2

Literature Review

2.1 The Structure and Properties of SiC

Nearly a century ago, SiC was discovered and found out to have many different SiC structures, the so-called polytypes [10, 11]. Today, more than 250 polytypes have been discovered, which are identical in one crystallographic plane but different by the stacking sequence of these planes [24].

Structure of Silicon Carbide: Polytypes. Just as a close-packed structure (fcc or hcp) can be considered as an assembly of spheres, any SiC polytype can also be considered as an assembly of tetrahedra. Figure 2.1a is a schematic of one tetrahedron, where the c-axis or [0001] direction coincides with the vertical Si-C bond. The corners of this tetrahedron are occupied by silicon (or carbon) atoms and its centroid by C (or Si) atoms (i.e. either SiC$_4$ or CSi$_4$). The projection of

---

1See Appendix B for a brief introduction to Miller-Bravais indices.
this tetrahedron along the [1120] direction (parallel to the righthand edge of base triangle of the tetrahedron) is shown in Figure 2.1c. Note that the projection of two Si-C bonds overlap and result in a double-bond. Moreover, a 180°-rotation about $c$-axis of the tetrahedron breaks its 3-fold symmetry and produces another variant. This so-called twinned tetrahedron, and its projection along [1120] direction are shown in Figures 2.1b and 2.1d, respectively [92, 95]. The normal and twinned tetrahedra can occupy different spatial positions A, B and C (or 1, 2, 3), as shown in Figure 2.2. Each tetrahedron corresponds to a double sheet of Si and C atoms, which is denoted by a Roman (A, B, C) and a Greek ($\alpha, \beta, \gamma$) letter (or vice versa).

![Figure 2.1](image-url) Schematic of (a) a SiC tetrahedron, (b) its twinned variant, and their projections along the [1120] direction [(c) and (d) respectively] (modified from [92]).

![Figure 2.2](image-url) (a) $T_1, T_2, T_3$ are untwined tetrahedra with different spatial positions; (b) twinned tetrahedra $T'_1, T'_2, T'_3$ (modified from [92]).
There are several restrictions on assembling tetrahedra to form a crystalline structure since two tetrahedra can share one and only one corner. For example, going from bottom up, $T_1$ can only be followed by $T_2$ and $T'_3$, but not by $T_1$, $T_3$, $T'_1$ or $T'_2$. In general, $T_i$ (or $T'_i$) can only be followed by $T_{i+1}$ or by $T'_{i-1}$, where $i = 1, 2, 3$, in a cyclic fashion.ii Each different stacking sequence of tetrahedra produces a different polytype.

The tetrahedral configuration of 3C(n0), 2H(11), 4H(22) and 6H(33) SiC polytypes are shown in Figure 2.3, where the Zhdanov notation of each polytype is included in parenthesis after its Ramsdell notation. The number in Ramsdell notation equals the periodicity in the $c$-direction for a polytype; the letter shows the symmetry of the structure. If the number is even, the crystal would often be hexagonal (H).iii If the number is odd, the crystal will have rhombohedral (R) symmetry except for 3C (it has cubic symmetry). In fact, this is the only cubic polytype (also known as $\beta$-SiC) and has the zincblende structure with a space group $F\overline{4}3m$ ($T_d^2$ or No. 216 in the International Table [30]). The 3C-SiC has an fcc Bravais lattice with a basis of two atoms, i.e. Si at $(0,0,0)$ and C at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, or vice versa. The hexagonal polytype has a wurtzite structure with a space group $P\overline{6}3mc$ ($C_{60}^4$ or No. 186). Zhdanov notation often uses a set of two integers $ij$ that respectively denote the number of normal and twinned tetrahedra [37]. For example, 4H can also be denoted as 22 because it consists of two normal and two twinned variants in one period; its stacking sequence can be expressed as $\cdots T_1T_2T'_1T'_3 \cdots$, or $\cdots aA\beta B\alpha A\gamma C \cdots$. The 15R polytype can also be expressed as $(32)_3 \equiv 323232$, or $\cdots T_1T_2T_3T'_2T'_1T_2T_3T'_4T'_3T'_1T_2T'_1T'_3 \cdots$.

iiHere we should reduce $T_4 \to T_1$, $T_0 \to T_3$, $T'_4 \to T'_1$, and $T'_0 \to T'_3$.

iiiFor example, there are 2H, 4H, 6H, 8H, etc. However, 24R is one well-known exception.
Figure 2.3: Stacking sequence of several SiC polytypes: (a) 3C(n0), (b) 2H(11), (c) 4H(22), and (d) 6H(33), modified from [92].
Defects in Silicon Carbide. SiC crystals are usually defective, associated with line dislocations, stacking faults, micropipes and other imperfections. The stacking fault energy is usually low in SiC, e.g. $\gamma \simeq 3 \text{mJ/m}^2$ for 6H-SiC [33, 51], 15 mJ/m$^2$ for 4H [33], and -2 mJ/m$^2$ for 3C (calculated value after [49]) as compared with 55 mJ/m$^2$ for Si. Dislocations in these polytypes often dissociate into two widely-separated partials bounded by a ribbon of stacking fault. In cubic polytype ($\beta$-SiC), dislocations usually lie on $\{111\}$ glide planes with a Burgers vector of $\frac{1}{2}\langle\overline{1}10\rangle$. As in other crystals with an fcc lattice, the perfect dislocations dissociate according to [32]:

$$\frac{1}{2}\langle1\overline{1}0\rangle = \frac{1}{6}\langle2\overline{1}\overline{1}\rangle + \frac{1}{6}\langle1\overline{2}1\rangle. \quad (2.1)$$

Dislocations in hexagonal polytypes lie on the basal $(0001)$ plane with a Burger vector $\frac{1}{3}\langle11\overline{2}0\rangle$. These are practically always dissociated into two partials by:

$$\frac{1}{3}\langle11\overline{2}0\rangle = \frac{1}{3}\langle10\overline{1}0\rangle + \frac{1}{3}\langle01\overline{1}0\rangle. \quad (2.2)$$

There are two possibilities for the glide plane in SiC, depending as to whether it is in between the widely-spaced A$\alpha$ (or B$\beta$ or C$\gamma$) planes (this is known as the shuffle set of planes), or between the narrowly-spaced $\alpha$ and A planes (known as the glide set of planes). Consequently, there are two types of possible partial dislocations, belonging to the shuffle or glide set.

For the motion of a shuffle partial dislocation (Figure 2.4a), all atoms above the slip plane are sheared by $\frac{1}{3}[1100]$, i.e. A→B, B→C, and C→A; while atoms below remain unmoved. Note the distortion of the Si-C bonds in the shuffle
case; this results in a high energy configuration. For the motion of a glide partial dislocation (Figure 2.4b), all atoms above the slip plane are again sheared. The tetrahedra in the glide set change to their *twinned* variants after motion; there are no distortions in the bond lengths or angles. This gives a low-energy bond configuration. Considering the geometry of the dangling bonds along a dislocation line, reconstruction of the dangling bonds are very likely for the glide set but unlikely for the shuffle set. In summary, it is expected that a translation by $\frac{1}{3}\langle 10\bar{1}0 \rangle$ vector should take place in the glide rather than the shuffle set of (111) or (0001) planes, which changes the tetrahedra above the slip plane in the order of $T_i \rightarrow T_{i+1}$; the tetrahedra enclosing the glide slip plane are changed in the order of $T_i \rightarrow T'_{i+1}$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.4}
\caption{Difference between the motion of a partial dislocation of the (a) shuffle and (b) glide set (modified from [92]).}
\end{figure}

**Properties of Silicon Carbide.** The unique thermal, mechanical, and electronic properties of SiC have great potential for high frequency, high temperature, and high power devices. For instance, all SiC polytypes have a wide bandgap: 2.39 eV for 3C, 3.26 eV for 4H and 3.02 eV for 6H (compare these with 1.1 eV for Si; all values are at room temperature). SiC also has a very good thermal conductivity (see Table 2.1), which helps to dissipate heat during the operation of a device.
Unfortunately, as in all semiconductors, the performance (especially yield) of SiC devices is greatly affected by its macroscopic and microscopic defects. Many attempts have been undertaken to produce high-quality single crystal SiC wafers and epilayers. Nakamura et al. recently reported the first virtually dislocation-free SiC single crystal [66]. Intrinsic Semiconductor launched Zero-Micropipes (ZMP™) SiC substrates in 2005. Cree also pushed the size of its 4H- and 6H- SiC wafers and epitaxy to 100 mm (4 inch) diameter [1]. These materials will definitely promote the utilization of high-yield and low-cost SiC devices [15, 85].

2.2 Previous Work on SiC Heteroepitaxy on Si

Similar to the normal practices in silicon technology, a SiC-based device is actually fabricated on an epilayer grown on the substrate, be it SiC, Si or whatever. Although Si has been widely used as the substrate for SiC hetero-epitaxy, it is very hard to grow single-crystalline SiC films because of the large mismatches of lattice parameters (about 20%) and thermal expansion (about 10%, see Table 2.1).

A real breakthrough occurred with the work of Nishino et al. who developed a two-step growth procedure [71, 72]. These authors used 0.03 mole% of propane (C$_3$H$_8$) in a H$_2$ carrier to carbonize the silicon substrate and form a SiC buffer layer. In the second step, both silane (SiH$_4$) and propane were introduced in an H$_2$ flow for homoepitaxial growth. Crack-free films were grown up to 34 µm thick and several square centimeters in size on Si(100) substrates. Crack-free films on Si(111) only have very limited thickness because of the build up of high stresses.

The buffer layer is made of both C and Si [2, 47, 72]. Addamiano and Sprague [2] duplicated the buffer layers formed on (100) Si wafers and studied...
### Table 2.1: Physical properties of SiC and related materials.\(^a\)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Materials</th>
<th>Si</th>
<th>3C-SiC</th>
<th>4H-SiC</th>
<th>6H-SiC</th>
<th>(\alpha)-AlN</th>
<th>(\alpha)-GaN</th>
<th>(\beta)-GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at RT (nm)</td>
<td></td>
<td>0.5431</td>
<td>0.4360</td>
<td>(a = 0.3073)</td>
<td>(c = 1.0053)</td>
<td>(a = 0.3081)</td>
<td>(c = 1.5117)</td>
<td>(a = 0.3111)</td>
</tr>
<tr>
<td>Density ((\times 10^3 \text{ kg/m}^3))</td>
<td></td>
<td>2.329</td>
<td>3.166</td>
<td>N/A</td>
<td>3.211</td>
<td>3.255</td>
<td>6.07</td>
<td>N/A</td>
</tr>
<tr>
<td>Thermal conductivity at RT (W/(m K))</td>
<td></td>
<td>156</td>
<td>490</td>
<td>300-380(^b)</td>
<td>420(^c)</td>
<td>320</td>
<td>130@300K</td>
<td>N/A</td>
</tr>
<tr>
<td>Thermal expansion coefficients ((\times 10^{-6}/\text{K}))</td>
<td></td>
<td>2.616</td>
<td>2.27</td>
<td>N/A</td>
<td>4.46 (\perp c)</td>
<td>4.16 (c)</td>
<td>3.17 (\perp c)</td>
<td>5.59 (c)</td>
</tr>
<tr>
<td>Band-gap energy (eV)</td>
<td></td>
<td>1.124</td>
<td>2.39</td>
<td>3.26</td>
<td>3.02</td>
<td>6.2</td>
<td>3.44</td>
<td>3.17</td>
</tr>
<tr>
<td>Rel. dielectric constant</td>
<td></td>
<td>11.9</td>
<td>9.7</td>
<td>9.7</td>
<td>9.7</td>
<td>9.1</td>
<td>5.2</td>
<td>8.90</td>
</tr>
<tr>
<td>Breakdown field ((\times 10^8 \text{ V/m}))</td>
<td></td>
<td>0.6</td>
<td>N/A</td>
<td>2.2</td>
<td>2.5</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Electron mobility ((\times 10^{-4} \text{ m}^2/(\text{Vs})))</td>
<td></td>
<td>1450</td>
<td>980</td>
<td>790 (\perp c)</td>
<td>370 (\perp c)</td>
<td>N/A</td>
<td>900@300K</td>
<td>N/A</td>
</tr>
<tr>
<td>Work function (eV)</td>
<td></td>
<td>4.2</td>
<td>5.2</td>
<td>N/A</td>
<td>4.7 ((n\text{-type});)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Electron affinity</td>
<td></td>
<td>N/A</td>
<td>4.0</td>
<td>N/A</td>
<td>4.85 ((p\text{-type});)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^{a}\) Compiled after \([37, 50, 69, 96, 108]\).
\(^{c}\) Data adapted from \([107]\).
\(^{d}\) Data for 373K.
them by reflection high-energy electron diffraction (RHEED) and scanning electron microscopy (SEM). They found that the buffer layer is stressed but single crystalline. Liaw and Davis [46, 47] adopted the same two-step approach and grew some films on (111) and (100) Si substrates. They were also able to produce single crystal epilayers, as indicated by X-ray diffraction (XRD), transmission Laue diffraction and transmission electron diffraction. However, this was not surprising since similar results have been found in the past. For example, Jackson and Howard [35] have grown a few micron thick of single crystal SiC films on Si from silicon tetrachloride (SiCl₄) and propane (C₃H₈) at 1100°C. Moreover, the idea of growing a buffer layer for heteroepitaxy had also been reported before for other growths. For example, Ohnishi and colleague [75, 114] sputtered a thin ZnO buffer layer on sapphire substrates to obtain good-quality single crystalline ZnO films. Although the mechanism of forming a single crystalline buffer layer is not well understood, this two-step process has converted an often-difficult hetero-epitaxy process into homoepitaxy on the buffer layer.

These films are far from perfect. In most SiC epilayers, as shown in a typical SEM image in Figure 2.5a, there are pits (or irregular shaped depression) and hillocks on a rough surface [2, 47, 100, 111]. Misfit dislocations (indicated by the arrow in Figure 2.5b) and threading dislocations are the most common line defects. Planar defects are also common features (see Figure 2.6a). Nutt et al. [74] found microtwins and stacking faults on {111} planes at the SiC/Si interface. They attributed these planar defects to the lattice and thermal mismatch. Pirouz et al. [93] used the convergent beam electron diffraction (CBED) technique as suggested by Taftø and Spence [118]. In the CBED patterns obtained from both
sides of an antiphase boundary (APB) as shown in Figure 2.6b, the contrast of two
Kikuchi lines 751 and 551 is reversed when an APB is crossed. The Si substrate
surfaces are assumed to be not atomically flat but contain many atomic steps. If
two neighboring islands on Si(100) have a vertical displacement of

\[ R = (2m - 1)(a_{Si} - a_{SiC})/4, \]

where \( m \) is an integer, an APB is produced at the “displacement boundary”.

Figure 2.5: (a) A typical SEM image of epitaxial \( \beta \)-SiC on Si(100), after [111]; (b) Interface between epitaxial \( \beta \)-SiC and Si(100) substrate, after [74].

Figure 2.6: (a) Plane view TEM DF image of CVD epitaxial SiC; (b) CBED patterns from both sides of an APB as indicated by an arrow in (a), after [93].
Similar results were also found in GaP films grown on Si(100) substrates [23]. Combing also results for SiC/Si(100) and GaAs/Si(100), Ernst and Pirouz argued that lattice mismatch and thermal stresses are not the reason for planar defect formation, but the low stacking fault energy is. Powell and coworkers [101] have successfully used off-axis Si(100) substrates (0.5–4° from the ⟨001⟩ axis also) and eliminated APBs; the films are also smoother than those grown on exactly on-axis Si(100) substrate. The results can be explained by Pirouz’s model of APB formation—if the steps on Si(100) consist of an even number of atomic layers, there are only “displacement boundaries” but no APBs.

Many more precursors have been used in the past in order to reduce the reaction temperature, to adopt less H₂ containing carrier gas, and so on. Avigal et al. [6] used various alkyl-sliced compounds, such as tetramethylsilane (TMS), diethylsilane (DES), and tripropylsilane (TPS), to epitaxially grow SiC. The films on Si(111) were single crystalline, but those on (100) were not. Powell and Will [102] used methyltrichlorosilane (MTS) to grow 6H-SiC on 6H-SiC(1120) substrates. Takhashi et al. [119] reported hexamethyldisilane (HMDS) as a single source for Si and C for SiC epitaxy on Si(111) substrates. However, a buffer layer is vital to grow single crystal SiC on Si(100), which is done by the so-called “carbonization step” using propane (C₃H₈). In all these practices, pure H₂ was used as the carrier gas, which is highly flammable and hazardous.

Nordell et al. [73] also used HMDS as a single-source precursor to grow SiC on Si(111), Si(100) and SiC(0001) substrates. Note that they used pure Ar or 4% H₂ in Ar mixture as carrier gas, both of which are nonflammable. In fact, Chaudhry and colleague [17] have grown crystals of reasonable quality in
a mixture carrier gas of 50% Ar+50% H\(_2\). The growth rate is higher in a pure Ar ambient than that in a Ar:H\(_2\) mixture [3]. However, the mixture carrier gas improves the film quality even though all are polycrystalline. Later, Wu et al. [132] grew some 3C-SiC films on Si(111) at atmospheric pressure by using a single precursor HMDS and a mixture of 8% H\(_2\)+Ar as the carrier gas. The higher concentration of H\(_2\) seems to help the removal of the excess carbon species, which is inevitable in HMDS and one reason for the poor epitaxy quality [120]. The two-step process was also proven to improve the film quality. During the initial step for buffer layer growth, a lower temperature around 1200°C is more desirable to maintain a high nucleation rate. However, in the second step of homoepitaxy, a “low nucleation rate and high growth rate” is more favorable and requires a higher growth temperature (usually above 1300°C).

In the second part of this dissertation, I will describe the design, modification, and construction of our home-made LP-MOCVD reactor, followed by some preliminary results are followed by SiC (and GaN) epitaxially growth on Si(100) and Si(111) substrates.

### 2.3 Principles of SiC Pressure Sensors

Conventional silicon devices do not perform well at high temperature because of the narrow band gap of this material, and related contact and packaging technologies. However, SiC pressure sensors, which can be operated up to 600°C, have been successfully fabricated by our collaborator Dr. Robert S. Okojie at NASA Glenn Research Center [79].
2.3. Principles of SiC Pressure Sensors

Fabrication of SiC Pressure Sensors. The starting material of these sensors is (0001)-oriented, 3.5° off-axis, high resistivity p-type 6H-SiC substrate with a 0.5 μm thick n-type epilayer \((N_d - N_a = 2 \times 10^{19}/\text{cm}^3)\) from Cree Inc. The backside of the wafer was covered with a circular mask and a cavity was created by electrochemical etching by dark current, resulting in a circular diaphragm \([82]\).

Oxidation and etching processes were followed to create contact holes in the front side \([115]\). An in situ dehydration process in vacuum at 300°C for 1h was then carried out in a three-gun sputtering system, followed by in-vacuo sequential deposition of Pt/TaSi\(_2\)/Ti metal contacts (Table 2.2) \([81, 84]\). The piezoresistive mesas as shown in Figure 2.7 were configured as a Wheatstone bridge circuit.

**Table 2.2:** Deposition parameters for Pt/TaSi\(_2\)/Ti contacts.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Thickness (nm)</th>
<th>Pressure (mTorr)</th>
<th>Power (W)</th>
<th>Gas Flow (sccm)</th>
<th>Sputtering Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>100</td>
<td>6</td>
<td>200 RF</td>
<td>50 Ar</td>
<td>16.5</td>
</tr>
<tr>
<td>TaSi(_2)</td>
<td>200</td>
<td>6</td>
<td>100 RF</td>
<td>50 Ar</td>
<td>33.3</td>
</tr>
<tr>
<td>Pt</td>
<td>300</td>
<td>9</td>
<td>75 AC</td>
<td>50 Ar</td>
<td>6.3</td>
</tr>
</tbody>
</table>

![Figure 2.7](image)  
(a) SEM top view image, after \([106]\), and (b) equivalent circuit of a SiC pressure sensor.
Chapter 2. Literature Review

Principle of SiC Pressure Sensors. In a Wheatstone bridge circuit as shown in Figure 2.7b, the pressure offset voltage is given by.

\[
V_{oz} = V_{in} \left( \frac{R_4}{R_3 + R_4} - \frac{R_1}{R_1 + R_2} \right), \quad (2.3)
\]

where \( V_{in} \) is the input voltage, and \( R_1, R_2, R_3 \) and \( R_4 \) are bridge resistor elements.

The resistance will change due to residual and applied strain according to:

\[
\Delta R = R(\epsilon + \epsilon_\delta)G, \quad (2.4)
\]
\[
\epsilon_\delta = (\alpha_{\text{glass}} - \alpha_{\text{SiC}})(T_\delta - T). \quad (2.5)
\]

\( \epsilon \) is the strain due to the applied pressure; \( \epsilon_\delta \) is the residual strain due to the coefficient of thermal expansion (CTE) mismatch of the package glass and SiC; \( T_\delta \) is the glass cure temperature 750°C [83].

In general, the gauge factor \( G \) (strain sensitivity) of a resistor is defined as \( G \equiv \Delta R / (R\epsilon) \) [70, chapter 72]. Consider a metal bar with length \( l \), width \( w \), thickness \( t \) (cross-section area \( A = wt \)) and resistivity \( \rho \), we have

\[
R = \rho l / A, \quad (2.6)
\]
\[
\frac{\Delta R}{R} = \frac{\Delta l}{l} + \frac{\Delta \rho}{\rho} - \frac{\Delta A}{A} = \epsilon(1 + P_z + 2\nu), \quad (2.7)
\]
\[
G = 1 + 2\nu + P_z, \quad (2.8)
\]

\(^{iv}\)The equation as given in the literature is [83, 106]

\[
V_{oz} = V_{in} \times \frac{1}{2} \left( \frac{R_2 - R_1}{R_1 + R_2} + \frac{R_4 - R_3}{R_3 + R_4} \right).
\]

\(^v\)\( \Delta A / A = \Delta t / t + \Delta w / w \approx 2\Delta t / t \) is used here.
where $\epsilon \equiv \Delta l / l$ again is the strain due to the applied pressure $P$; Poisson’s ratio is given by $\nu \equiv -\Delta t / \Delta l / l$; $P_z = \Delta p / \rho$ is the measure of piezo-resistive effect. It can be shown that the gauge factor is temperature dependent according to:

$$G_T = G_0 (1 + \gamma \Delta T),$$

(2.9)

where $\gamma$ is the temperature coefficient of gauge factor (TCGF); $G_T$ and $G_0$ stand for the gauge factor at $T$ and reference temperature (usually room temperature, $RT=25^\circ C$ in this case), respectively; $\Delta T = T - 25^\circ C$.

Moreover, the resistance $R$ itself is also temperature dependent

$$R_T = R_0 (1 + \beta \Delta T),$$

(2.10)

where $\beta$ stands for the temperature coefficient of resistance (TCR); $R_T$ and $R_0$ are the resistance at temperatures $T$ and $RT$, respectively.

In conclusion, the resistance change due to temperature difference and strains can be expressed as

$$\Delta R = R_0 G_0 (1 + (\beta + \gamma) \Delta T + \beta \gamma (\Delta T)^2)(\epsilon + \epsilon_\delta).$$

(2.11)

**Direct Chip Attach (DCA).** The pressure sensor was packaged by a novel MEMS-DCA (microelectromechanical system direct chip attach) technique (see Figure 2.8), which eliminates wire bonding and related failure mechanisms [79]. AlN was selected as the packaging material because it has a coefficient of thermal expansion

---

This method is actually similar to the traditional flip-chip packaging technology.
(CTE) of $4.1 \times 10^{-6}/K$, which is very close to that of SiC ($4.2 \times 10^{-6}/K$) and it can minimize the thermal stress for the packaging. Moreover, $\alpha$-AlN has a good thermal conductivity ($3.2 \text{ W/cm K}$, see Table 2.1 in page 11), which helps to dissipate heat. The SiC sensor was placed on the circular cavity of the AlN receptacle and sealed with specialized sealing glass which also has a CTE ($4.7 \times 10^{-6}/K$) close to that of SiC [107]. The bond pads align perfectly with wire holes, which enables immediate contact when wires are inserted. Only the diaphragm of the sensor is free to deflect and it is this deflection that gives rise to the desired signal.

![Figure 2.8](image)

**Figure 2.8:** Top and cross-sectional views of a SiC pressure sensor with MEMS-DCA package, after [83].

**Accelerated Stress Test (AST).** An simple AST protocol, as shown in Figure 2.9, was developed to evaluate the reliability of SiC pressure sensors from $25^\circ C$ to $T_{\text{unstable}}$, the temperature at which $V_{oz}$ fluctuates so much that the measurements are no longer reliable [83].
In step 1—“Sensitivity and Maximum Operating Pressure (MOP) Test”, 20 cycles of 0 psi → $P_{\text{max}}$ → 0 psi applied pressure were performed with intervals of 10\%$P_{\text{max}}$ and held for 10 seconds each at 25°C. The sensors passing this test were then heated from 25°C to 100°C with 20 cycles of applied pressure between 0 psi and 100 psi (i.e. $P_{\text{max}}$).\(^\text{vii}\) These 20 cycles were repeated with a temperature interval of 100°C and held for a one-hour stabilization up to $T_{\text{unstable}}$. From these results one could determine the maximum stable temperature $T_{\text{max}}$.

Figure 2.9: A simple AST protocol to evaluate SiC pressure sensors, after [83].

Only sensors with $T_{\text{max}} \geq 300^\circ\text{C}$ proceeded to step 3, where the offset voltage was tested and recorded at 25°C and $T_{\text{max}}$ for each heating and cooling cycle of 25°C → $T_{\text{max}}$ → 25°C. Prior to step 3, reference offset voltages ($V_{oz,\text{ref}}$) were obtained by a non-linear finite element analysis (FEA) [106].
determined at 25°C and $T_{\text{max}}$. Finally, step 2 was repeated on passing sensors to rate their stability and pressure sensitivity $S$, which is given by

$$S(T) = \frac{V_{oz,\text{net}}}{V_{\text{in}} \times P} \equiv \frac{V_{oz}(P=100 \text{ psi}, T) - V_{oz}(P=0, T)}{V_{\text{in}} \times P}. \quad (2.12)$$

Figure 2.10a shows $V_{oz}(P=100 \text{ psi}, T)$ and $V_{oz}(P=0, T)$ with an input voltage of $V_{\text{in}} = 5 \text{ V}$. The net output offset voltage $V_{oz,\text{net}}$ under other applied pressures is shown in Figure 2.10b. Note that it increases with increasing applied pressure, but decreases with increasing temperature. The resulting operating sensitivity (given by Equation 2.12), as shown in Figure 2.10c, is a good indicator of the thermal stability of these sensors under applied pressure.

(a) Zero offset voltage of one sensor at 0 psi or 100 psi and different temperatures.

**Figure 2.10:** Some typical results after step 3 of AST, after [83] (continued).
2.3. Principles of SiC Pressure Sensors

![Graph showing net bridge output voltage at different pressures and temperatures.](image)

(b) Net output voltage at different temperatures and applied pressures.

![Graph showing sensitivity vs. temperature.](image)

(c) Operating sensitivity determined by AST.

Figure 2.10: Some typical results after step 3 of AST, after [83].
2.4 Metal-SiC Contacts and Reliability Issues

Many metals have been investigated as contacts to SiC. Some metals like Ag and Au do not react with SiC; some can form silicides and/or carbides (eg. Co, Cr, Fe, Ni, Pd, Pt, W); some can form ternary phases such as Mo, Ta, Ti and Zr [44]. The nature (Schottky or ohmic) and properties of a metal-SiC contact are very complex, which largely depend on the SiC polytype (mainly 3C, 4H and 6H), n-type or p-type doping and levels, SiC surface treatment, metal selection and growth parameters, and so on [20, 96, 108, 122].

One important physical property of the contact is Schottky barrier height (SBH) \( \Phi_B \). Mott-Schottky theory gives that

\[
\phi_B = \phi_m - \chi_s, \quad \text{for } n\text{-type semiconductor (see Figure 2.11b)}; \quad (2.13a)
\]

\[
= E_g - (\phi_m - \chi_s), \quad \text{for } p\text{-type semiconductor (see Figure 2.11d)}; \quad (2.13b)
\]

where \( \phi_m \) is the work function of the metal, and \( \chi_s \) is the electron affinity of the semiconductor [104, 125]. The work function of the semiconductor is given as \( \phi_s = \chi_s + \xi \equiv \chi_s + (E_C - E_F) \). One can use the Mott equation—which constitutes one limit—only under ideal conditions where there are no surface states. It can be easily shown that an ohmic contact forms when \( \phi_m < \phi_s \) for n-type semiconductor or \( \phi_m > \phi_s \) for p-type.

The other limit is stated in the Bardeen model [7], where localized states are formed at the free semiconductor surfaces. For a high density of states (DOS),

\[ viii \text{Strictly speaking, one can call } \phi_B \text{ the Schottky barrier height only if the contact is rectifying (} \phi_B > 0). \text{ For ohmic contacts, } \phi_B \text{ is negative and small; the barrier is often referred as the dipole surface charge barrier (DSCB) [108].} \]
Figure 2.11: Band diagrams of a metal and $n$-type semiconductor (a) before and (b) after contact. The case for $p$-type is shown in (c) and (d), from [20].

Figure 2.12: Band diagrams of a metal and $n$-type semiconductor (a) before and (b) after contact with interface states, after [19].
the energy level $\Phi_0$ of the surface states, measured from the top of valence band, approaches the surface Fermi level ($E_F$) and the barrier height is given as (see Figure 2.12, [19, 108]):

\[
\Phi_B = E_g - \Phi_0, \quad \text{for } n\text{-type semiconductor; (2.14a)}
\]

\[
\Phi_B = \Phi_0, \quad \text{for } p\text{-type semiconductor. (2.14b)}
\]

In other words, the Fermi level is pinned in the middle of band gap and $\Phi_B$ is independent of $\Phi_m$.

Figure 2.13: SBH vs $\Phi_m$ for some metal contacts to (a) $n$-type and (b) $p$-type 6H-SiC, after [128, 129].

The real $\Phi_B$ of a metal-SiC contact falls between these two limits. Waldrop et al. [128, 129] have reported SBH for several metal Schottky contacts to $n$-type (Figure 2.13a) and $p$-type (Figure 2.13b) 6H-SiC. SBH increases with increasing $\Phi_m$ for $n$-type SiC and decreases with $\Phi_m$ for $p$-type, as predicted by Equation 2.13.
However, the slope $S$ of the $\Phi_B$ vs. $\Phi_m$ curve is much smaller than unity for metal/$n$-type SiC contacts (or larger than $-1$ for $p$-type). The small slope $S$ in the results obtained by Porter et al. [96, 97, 98, 99], as shown in Figure 2.14, also suggests a strong Fermi level pinning.

![Figure 2.14: SBH vs $\Phi_m$ for metal/$n$-type 6H-SiC contacts, after [96].](image)

A reliable ohmic contact is vital for any device as a bridge between input and output signals, which requires a small specific contact resistance:

$$r_c \equiv \lim_{V \to 0} \left( \frac{dJ}{dV} \right)^{-1}, \quad (2.15a)$$

$$r_c \propto \exp\left(\frac{\Phi_B}{\sqrt{N}}\right), \quad (2.15b)$$

where $V$ is the applied voltage, $J$ is current density, and $N$ is carrier (doping) concentration [117]. The relation given in Equation (2.15b),\textsuperscript{x} was confirmed for

\textsuperscript{x}It holds when current transport is dominated by tunneling. See also reviews on the physics ([20]) and recent advances ([122]) of metal/SiC.
metal/SiC contacts by Crofton et al. for Al-Ti ([20]) and Uemoto for Ni [126]. One needs to lower SBH and/or increase doping in order to reach a useful small $r_c$. It is extremely difficult to reduce SBH for $p$-type SiC because of its large bandgap and work function. As a result, an ohmic contact to $p$-type SiC usually requires high temperature annealing, a known process as used in metal/Si contacts to promote silicide formation. A substrate with a heavily-doped epilayer is a more suitable choice (see also Figure 2.15).

![Figure 2.15](image)

**Figure 2.15:** $r_c$ as a function of doping of $n$-type 6H-SiC, after [20, 126].

A multi-layer Pt/TaSi$_2$/Ti contact to SiC was employed in our SiC pressure sensor, and it has been proven to be a good solution. As mentioned before, wire bonding is a pitfall for SiC sensors, which can be eliminated or at least minimized by the DCA packaging technique (see page 18). However, under the target high temperature and high pressure, contacts usually suffer from diffusional and
chemical reactions; this often limits the maximum operation temperature of SiC devices. Previous results suggest that under long term annealing around 600°C, there might be reactions at Pt/TaSi$_2$ and Ti/SiC interfaces [80, 81, 84]:

\[
\begin{align*}
6 \text{Pt} + \text{TaSi}_2 & \rightarrow 2 \text{Pt}_3\text{Si} + \text{Ta}, \\
6 \text{Ti} + 3 \text{SiC} & \rightarrow \text{Ti}_5\text{Si}_3 + \text{TiC} + 2 \text{C}.
\end{align*}
\] (2.16a)

(2.16b)

The formation of Ti$_5$Si$_3$ was demonstrated by HRTEM, which was also documented by Porter et al. [98]. In addition, they reported formation of TiC$_{1-x}$ carbides at the Ti/SiC interface. Makhtari and colleague [52] were able to find TiC and Ti$_5$Si$_3$ after annealing the contact at 900°C. An additional unstable phase Ti$_3$SiC$_2$ was found after 950°C annealing. Although the existence of Pt$_3$Si phase is not very certain, Auger electron spectroscopy (AES) results of some specimens clearly show Ti migration to the surface and O penetration in the SiC substrate [81]. These are detrimental to the device since the diffusion barrier TaSi$_2$ has lost its function.

In the third part of this dissertation, I will present the investigations on (Au/)TaSi$_2$/Ti contacts to SiC by FIB and TEM.

### 2.5 The Indispensable Role of FIB

So, why do we need focused ion beam (FIB)? For this project, it is simply because the samples are small and limited in quantity. FIB is the best choice to make site-specific TEM specimens so far. In fact, FIB found its strength in the semiconductor industry such as microfabrication early on after the introduction...
of the instrument [60, 86, 109]. It has now become a versatile tool for milling (sputtering or enhanced etching with gas), imaging (SIM: scanning ion microscope), implantation, and deposition. For better understanding of these aspects, one should consider the details of the ion-solid interaction (see Appendix C). The stopping power $S$, as shown in Equations C.1, C.7 and C.10, can be calculated by many computer programs with an error less than 10% [134]. Table 2.3 summarizes the typical implantation depth and sputtering yield, obtained by SRIM simulation,\(^x\) of Ga\(^+\) ions into Si, SiO\(_2\) and Al at normal incidence [103].

**Table 2.3:** Typical implantation depth and sputtering yield of Ga\(^+\), after [103].

<table>
<thead>
<tr>
<th>Ga(^+) energy (keV)</th>
<th>Implantation depth (nm)</th>
<th>Sputtering yield (atoms/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>SiO(_2)</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----</td>
<td>-----------</td>
</tr>
<tr>
<td>10</td>
<td>13 ± 5</td>
<td>12 ± 4</td>
</tr>
<tr>
<td>20</td>
<td>20 ± 7</td>
<td>19 ± 6</td>
</tr>
<tr>
<td>30</td>
<td>27 ± 9</td>
<td>25 ± 8</td>
</tr>
<tr>
<td>40</td>
<td>33 ± 11</td>
<td>31 ± 10</td>
</tr>
<tr>
<td>50</td>
<td>39 ± 14</td>
<td>38 ± 11</td>
</tr>
</tbody>
</table>

**FIB Instrument.** The FIB system consists primarily of a vacuum chamber with a sample stage, a liquid metal ion source (LMIS) and ion column, detectors, gas injector, and a computer frontend. The FEI Nova 200 NanoLab DualBeam\(^\text{TM}\) system at the Swagelok Center for Surface Analysis of Materials (SCSAM), combines an ion beam and an electron column (Figure 2.16). It is equipped with several detectors, including Thru-the-Lens detector (TLD), Everhart Thornley detector (ETD) and Infrared (IR)-CCD. The resolution of the e-beam and ion-beam can be as good as 1.1 nm and 7.0 nm, respectively.

\(^x\)See also srim.org, the official website of SRIM, which is a collection of software packages to calculate many features of the transport of ions in matter.
2.5. The Indispensable Role of FIB

Figure 2.16: A snapshot of the (a) exterior and (b) interior (taken by an infrared camera), of an FEI Nova 200 NanoLab DualBeam™ system.

Figure 2.17: (a) A schematic diagram of a FIB ion column, after [103]. (b) A snapshot (after [34]) and schematic (after [27]) of the LMIS.
Chapter 2. Literature Review

The major breakthrough of the modern FIB system is the LMIS, which was first developed in 1975 [43]. It consists primarily of a tungsten needle attached to a metal reservoir (Figure 2.17). The ceramic insulator has a diameter about 1 cm. Ga-LMIS is the most popular because Ga has a melting point around RT, relatively large atomic number, low vapor pressure and thus a long lifetime (500–1500 hours). It also has good wetting capability to the W tip, is very pure and highly vacuum compatible. The ion beam with an typical energy of 10–50 keV and current of 1 pA–10 nA goes through a set of apertures and lenses before reaching the target. Nowadays, a LMIS is able to deliver a resolution at 5 nm or better and it makes FIB a very useful tool for many academic and industrial applications.

![Figure 2.18: Schematic of the most important applications for FIB: (a) imaging, (b) milling, and (c) deposition, after [103].](image)

**Applications of FIB.** Figure 2.18 demonstrates the principle of the most important applications of FIB: for imaging (SIM), for milling, and for deposition [103]. A multi-channel plate (MCP) is often used to collect secondary particles for imaging. As compared to SEM, the main difference of the SIM is channeling effect and Ga$^+$-ion damage. To etch the sample, a beam current of 100 pA–7 nA is often used. As shown in Table 2.3, the implantation depth and sputtering yield are
controlled by the ion energy, density and atomic number of the target, incident angle, scanning mode, etc.

FIB deposition is usually made possible by (ion-beam assisted) chemical vapor deposition. The most useful Pt precursor is C₉H₁₆Pt (Figure 2.19),¹ methyl-cyclo-pentadienyl-trimethyl-platinum (IV) [123], which has an operating temperature of 38–42°C and renders a tough and chemically resistant Pt deposition. Tungsten (W) can be deposited by injection of W(CO)₆ (tungsten hexa-carbonyl) [40]. SiO₂ is also often deposited by using C₄H₁₆O₄Si₄ (TMCTS: tetramethylcyclo-trasiloxane) and oxygen (O₂) or water vapor (H₂O) [103].

![Molecule views of (a) C₉H₁₆Pt, (b) W(CO)₆, and (c) C₄H₁₆O₄Si₄ produced by the open-source program jmol at jmol.sourceforge.net.](image)

Figure 2.19: Molecule views of (a) C₉H₁₆Pt, (b) W(CO)₆, and (c) C₄H₁₆O₄Si₄, produced by the open-source program jmol at jmol.sourceforge.net.

In the next example, the FIB was used to diagnose a defective design and then repair it [110]. A complementary metal-oxide semiconductor (CMOS) programmable logic array (PLA) was found to be not functional due to a design error. FIB images showed that the input of the PLA, the vertical metal lines as shown in Figure 2.20a, were shorted to another bus (see horizontal lines). The instrument was then used to sputter away the shorted metallization and the device was successfully salvaged (Figure 2.20b).

¹Cyclo-pentadienyl-trimethyl-platinum (IV),Pt(CH₃)₃C₅H₅, is also an often-used Pt precursor.
Using a phenanthrene (C_{14}H_{12}) precursor, Morita et al. have made many 3D structures, such as diamond-like-carbon (DLC) free-space-wirings of parallel resistances (Figure 2.21), with a wiring width of 80 nm grown in 2.8 min [62].

Field emitters and arrays have also been fabricated using a dual-beam system [121]. The gate opening was made by FIB etching, which was followed by wet-etching by buffered HF. The emitter was then deposited using electron beam (Figure 2.22).

One often overlooked application of FIB is ion implantation. With a finely focused ion beam, maskless doping of semiconductors, such as B and As in Si, and
2.5. The Indispensable Role of FIB

Figure 2.22: (a) Fabrication procedures; (b) top and (c) cross-sectional SEM views of a Au-gated Pt emitter, after [121].

even FIB lithography have been achieved [58]. Many FET (field effect transistor) and bipolar devices have been fabricated by this technique [60].

FIB is also the indispensable tool to prepare site-specific TEM specimens (see section §3.2 for details), which are the basis for the second half of this text.
Chapter 3

Experimental Details

3.1 XRD: X-ray Diffraction

X-ray diffraction (XRD) was done with a Scintag XGEN-4000 Advanced Diffraction System. The instrument has a Scintag X-1 diffractometer, a high-purity Ge solid state detector, and a monochromatic Cu K$_\alpha$ X-ray source ($\lambda = 0.154056$ nm for Cu K$_{\alpha1}$; refer to §3.4 for more details). A tube voltage of 45 kV and current of 40 mA were set as standards during this work. A normal $\theta$-2$\theta$ scan ($2\theta = 20 – 80^\circ$) was controlled by a program called DMSNT and JCPDS (Joint Committee for Powder Diffraction Standards)$^i$ database was used for data analysis.

The value of $2\theta$ at the “reflecting” (hkl) planes can be calculated by Bragg’s law [14]:

$$2d_{hkl} \sin \theta = \lambda,$$

(3.1)

$^i$JCPDS changed its name to International Center for Diffraction Data (ICDD) in 1977 [39].
Table 3.1: Computed $2\theta$ values for some major XRD peaks.

<table>
<thead>
<tr>
<th>hkl</th>
<th>111</th>
<th>200</th>
<th>220</th>
<th>311</th>
<th>222</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>28.442</td>
<td>32.959</td>
<td>47.304</td>
<td>56.121</td>
<td>58.854</td>
<td>69.130</td>
</tr>
<tr>
<td>$\beta$-SiC</td>
<td>35.597</td>
<td>41.385</td>
<td>59.979</td>
<td>71.777</td>
<td>75.494</td>
<td>90.007</td>
</tr>
<tr>
<td>$\beta$-GaN</td>
<td>35.634</td>
<td>41.380</td>
<td>59.954</td>
<td>71.732</td>
<td>75.461</td>
<td>89.921</td>
</tr>
</tbody>
</table>

where $d_{hkl}$ is the spacing between two neighboring (hkl) planes in real space. Note that Si(200) and (222) are rarely detected since the structure factor is 0 in the diamond cubic structure according to

$$F_{hkl} = \sum_j f_j \exp \left( 2\pi i (hx_j + ky_j + lz_j) \right).$$

The summation is over the whole unit cell, where the $j$-th atom at $(x_j, y_j, z_j)$ has an atomic scattering factor of $f_j$. This factor depends on the atomic number $Z$, $\lambda$, and scattering angle $\theta$; to be precise, $|f|^2$ equals to the differential scattering cross section (see Equation 3.3 later on).

Figure 3.1: Schematic ray path to prove Bragg’s law, after [14].
3.2 TEM Specimen Preparation by FIB Liftout

In the FIB, one can view a sample (especially its cross-sectional area) while it is being milled by the ion beam. Hence, it is a powerful instrument for site-specific TEM specimen preparation, another important application of FIB in materials science. There are three popular methods to prepare a site-specific TEM specimen using FIB: H-bar (or trench technique), \textit{ex situ} and \textit{in situ} liftout.

**H-bar Method (Trench Technique).** Since its first introduction in 1989 by Kirk \textit{et al.} \cite{Kirk1989}, the H-bar method has been adopted by many researchers \cite{9, 28}. The region of interest (ROI) is first located and cut from its surroundings, which is then hand-polished (or by means of a tripod) to less than 50 µm thick. After being mounted to a half-grid, it is milled e-beam transparency in the FIB, as shown in Figure 3.2. Because the region around this membrane is quite thick, specimen-tilt in TEM is limited and this method was soon surpassed by the liftout technique.

![Figure 3.2: Schematic of the FIB H-bar method, after \cite{28}.](image)
3.2. TEM Specimen Preparation by FIB Liftout

**Ex situ Liftout (EXLO).** The first liftout attempt was published by Overwijk et al. in 1993, which is also an *ex situ* liftout [87]. The procedures for EXLO are straightforward [28, 65, 91]:

1) The region of interest (ROI) is selected via SEM/SIM of the FIB (Figure 3.3a);
2) The ROI is then protected by a thin coating of Pt (or W). Two “X” marks can be milled for auto-detection of this ROI by the AutoTEM scripts. The stage tilt of these steps is usually 52°, which is also the angle at which the ion-beam is perpendicular to the sample surface;

3) Two initial trenches are cut from the front and back portion of the specimen; this leaves a membrane about 1 µm thick (Figure 3.3b). These steps can also be automated;

4) A “U”-shape undercut is then milled under stage tilt of 7° (Figure 3.3c);

5) After final manual polishing to e-beam transparency, the membrane is cut free from its surrounding and ready for EXLO (Figure 3.3d);

6) EXLO is usually done under an optical microscope and by a micromanipulator, which is essentially a glass/metal probe with very fine tip (about 1 µm in diameter). Once the specimen is in contact with the probe, the latter can lift it up by attractive electrostatic force. The specimen is then transferred to a carbon-coated copper TEM grid.

### 3.2.1 In situ Liftout (INLO)

In this case, the membrane is transferred to a TEM grid inside the FIB before final thinning. The first three steps are the same as EXLO (see also Figure 3.4a).

4) A micromanipulator (or probe) is moved right on top of the membrane and
Chapter 3. Experimental Details

(a) Select ROI by SEM/SIM in the FIB.

(b) Two trenches have been cut.

(c) A “U”-shape undercut is made.

(d) It is cut free and ready for EXLO.

Figure 3.3: Straightforward procedures to prepare an EXLO TEM specimen.
attached to it by Pt deposition under a stage tilt of 7°. The membrane is then cut free from its surrounding and lifted out (Figure 3.4b); 5) The TEM specimen is carefully moved very close to the grid and attached to it by Pt deposition at 0° stage tilt. The probe can be cut loose (Figure 3.4c); 6) After further polishing, the thin foil is ready for TEM examination (Figure 3.4d).

**Figure 3.4:** Procedures to prepare an INLO TEM specimen via FIB.
3.3 Imaging: STEM, EFTEM and beyond

All TEM investigations were performed on a Tecnai F30 S-TWIN (Figure 3.5), a 300 kV field-emission gun (FEG), energy-filtering analytical scanning transmission electron microscope. It combines “high performance in all TEM, EFTEM, . . . , STEM and EDX/EELS spectrum imaging modes”, as claimed by FEI.ii EFTEM, STEM, EDX (i.e. XEDS), EELS are acronyms for energy-filtering transmission electron microscopy, scanning transmission electron microscopy, X-ray energy-dispersive spectroscopy, and electron energy-loss spectroscopy, respectively.

---

An electron will be scattered either elastically or inelastically when it encounters a TEM thin foil. If the electrons are scattered elastically, they will not lose any energy. They will only change their directions and become diffracted beams or simply transmit through as the direct beam. The positions and intensities of the interfered beams give rise to a diffraction pattern. Moreover, they are often used to produce images, such as bright field (BF) images of the thin foil. On the other hand, electrons will lose energy in an inelastic scattering process and this will produce many different signals that one can use in an analytical electron microscope.

The contrast of a TEM image closely depends on how the image is formed.

As shown in Figure 3.6, one can use the objective aperture to select either the direct beam or the scattered electrons to form a BF or a dark field (DF) image, respectively. The contrast of these BF and DF images (see Figure 2.6a for example) are mostly due to the intensities of the transmitted and diffracted beams [26]. When diffraction contrast does not dominate and the scattering angle is small, mass-thickness contrast may predominate. This alternative of the amplitude contrast is due to the incoherency of the elastically scattered electrons.
Taking screening and relativity effects into account, the Rutherford (differential) cross section for atoms with atomic number \(Z\) and atomic weight \(W\) can be written as [63]

\[
\frac{d\sigma(\theta)}{d\Omega} = \frac{\lambda_R^4 Z^2}{64\pi^4 a_0^2 \left(\sin^2(\theta/2) + (\theta_0/2)^2\right)^2},
\]

(3.3)

where \(\lambda_R\) is the relativistically corrected wavelength for electrons (0.00197 nm for a 300 keV electron). The well-known Bohr radius \(a_0\) has a value of 0.0529 nm. \(\theta\) is the scattering angle, while \(\theta_0\) is the Born scattering angle. The probability of scattering from atoms in the TEM specimen foil with thickness \(t\) (and density \(\rho\)) is given by [130]

\[
Q_T t = t\rho N_A \sigma_T / W \propto t Z^2,
\]

(3.4)

where \(N_A\) is the Avogadro number \((6.022 \times 10^{23} \text{ particles/mole})\), \(\sigma_T\) is the total scattering cross section and \(Q_T\) is the total cross section from the specimen.

Now considering a BF image schematically shown in Figure 3.7, the regions in the specimen with higher mass-thickness will have a larger scattering cross section. Hence, they appear darker in the BF image.

Almost all the scattered (predominately elastically) electrons are selected by a high-angle annular dark field (HAADF) detector in the STEM mode, as shown schematically in Figure 3.8. It is not just a normal DF image, which is obtained by selecting a particular diffraction beam. The mass-thickness contrast often predominates in STEM images. The partial scattering cross section from scattering

[^ii]: The angles in all the ray diagrams are highly exaggerated. The real semiangles are on the order of tens of milliradians (10 mrad = 0.57°).
angle $\theta_1$ to $\theta_2$ was obtained by Pennycook et al. [89]

$$
\sigma_{\theta_1, \theta_2} = \left( \frac{m}{m_0} \right)^2 \frac{Z^2 \lambda^4}{4\pi^2 a_0^2} \left( \frac{1}{\theta_1^2 + \theta_0^2} - \frac{1}{\theta_2^2 + \theta_0^2} \right)
$$

(3.5)

where $m$ and $m_0$ are the mass and rest mass of electron with a wavelength $\lambda$. For the TEM thin foil, its thickness also affects the scattering intensity $I_s$ in a similar fashion as written in Equation (3.4), $I_s \propto tZ^2$.

Figure 3.7: Mass-thickness contrast for a BF image, after [130, §22.3].

Figure 3.8: Schematic of STEM-HAADF image mode, after [113].
The STEM-HAADF image is often called *Z contrast image* because the effect of different atomic numbers dominates the image contrast. However, one needs to exclude the “diffraction contrast” due to low-order Bragg reflections. By using HAADF detector and collecting only scattered electrons at higher angles, the intensity of Bragg reflection can also be reduced [89].

When more than two beams are selected by using a larger objective aperture (see Figure 3.6c), the observed image will exhibit a **phase contrast** since it arises due to the different phases of the scattered electron waves. The most important examples are high-resolution TEM images as well as any image with “fringes”.

### 3.4 XEDS: X-ray Energy Dispersive Spectroscopy

The models in the previous section only deals with the cross section of elastically scattered electrons. However, there are also many ways in which an electron can be scattered inelastically and produce phonons, electron excitation or X-ray emission. When the incoming electron (eg. 300 keV for our Tecnai F30) displaces a K shell electron as shown in Figure 3.9, the target atom is ionized. The atom has to rearrange its electrons and return to a lower energy state. In this example, when an $L_3$ electron fills the K-shell hole, a characteristic $K_{\alpha_1}$ X-ray is generated with an energy of $\Delta E = E_{L_3} - E_K$. However, not every transition is allowed. Only those excitations are permitted that follow the three selection rules: $\Delta n \geq 1$, $\Delta l = 1$, and $\Delta J = 0$ or 1 [39]. Here $n, l, s$ are the principle-, angular- and spin- quantum number, respectively. The total angular momentum is given by $J = |l + s| = |l \pm 1/2|$.

---

[iv]IUPAC (the International Union of Pure and Applied Chemistry) recommends to use the notation KL3, after [38]
3.4. **XEDS: X-ray Energy Dispersive Spectroscopy**

Our Tecnai (Figure 3.5) is equipped with a high sensitivity HAADF detector (Fischione Instruments Model 3000), which enable us to raster the beam in STEM mode. The XEDS spectrum of a point, a line or even an area defined in a STEM image, can be collected for microanalysis by a Si-Li detector through an ultra-thin polymer window (Moxtek Inc.), which has a resolution of 129.9 eV at Mn-K$_{\alpha 1}$.

![Atomic energy levels](image)

**Figure 3.9:** Schematic of the ionization process when a high-energy electron interacts with inner-shell electrons, after [130, §4.2].

After careful identification of every peak in the spectrum, a quantitative analysis can also be performed. The peak intensity $I_i$ and the weight percentage $C_i$ of each element $i$ (eg. A and B) are related by the Cliff-Lorimer equation [18]:

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B},$$

(3.6)

where $k_{AB}$ is not a constant but a sensitivity factor ($k$ factor), which can be calculated from first principles. The X-ray intensity generated from elements A and B
have a relationship given by

\[
\frac{I_A}{I_B} = \frac{(CQ\omega a/W)_A}{(CQ\omega a/W)_B} \int_0^t \phi_A(\rho t) e^{-\chi \rho t} (1 + \delta_A) d(\rho t) = \frac{C_A}{C_B} (Z^* A^* F^*),
\]

(3.7)

where \(Z^*, A^*, F^*\) are correction factors due to atomic-number, absorption and fluorescence, respectively. The \(e^{-\chi \rho t}\) term accounts for absorption, and the \((1 + \delta)\) term accounts for fluorescence. \(Q\) is the ionization cross section, \(\omega\) is fluorescence yield, \(a\) is the relative transition probability defined by \(a = I(K_\alpha)/I(K_\alpha + K_\beta)\), and \(\phi(\rho t)\) is the X-ray depth distribution. For a well-prepared TEM thin foil, one can often neglect \(A^*\) and \(F^*\). By comparing Equations (3.6) with (3.7), we have

\[
k_{AB} = \frac{1}{(Z^* A^* F^*)} = \frac{1}{Z^*} = \frac{(Q\omega a/W)_B}{(Q\omega a/W)_A}
\]

(3.8)

### 3.5 EELS: Electron Energy Loss Spectrometry

EELS analysis in Tecnai is made possible by a post-column, imaging energy filter (Gatan GIF 2002, see Figure 3.10a). The magnetic prism can disperse and focus electrons in the plane of the spectrometer. Rather than using a photodiode array to gather the spectrum simultaneously as in the traditional PEELS (parallel-acquisition EELS, see Figure 3.10b), Gatan image filter (GIF) uses a slow-scan CCD (charge-coupled device) array. The quadrupoles after the (energy-selecting) slit can project the electron energy-loss spectrum of the illuminated area onto the CCD, which is essentially a standard PEELS. They can also compensate energy dispersion and project a magnified image of the specimen to the CCD.
The energy-loss electrons also carry valuable information of the TEM foil. A typical PEELS spectrum is obviously the intensity versus energy loss diagram, as
shown in Figure 3.11 for NiO. It contains three major regions: the zero-loss peak, low-loss region and high-loss region.

![EELS spectrum of NiO](image)

**Figure 3.11:** A typical EELS spectrum of NiO, after [130, Figure 38.9].

**Zero-Loss Peak:** Zero loss peak (ZLP) contains not only electrons with the beam energy $E_0$ (zero loss), but also some with very small energy loss. ZLP has very high intensity and its main use is for EELS alignment and zero-loss imaging.

**Low-Loss Region:** Low loss describes energy-losses up to 50 eV. In this region, plasmon peaks\(^V\) are common features especially for elements with free-electrons, such as Li and Al. The so called “single electron interactions“, when a core electron changes its orbital state, are also possible with energy-

\[ E_P = h\omega_P = \hbar \sqrt{n_e^2/\varepsilon_0 m_e}, \]  

(3.9)

with typical values of 5–25 eV.
losses up to about 25 eV. The plasmon peak for NiO has an energy level of conduction/valence band.

**High-Loss Region:** In a similar process as X-ray emission, the decay of an ionized atom may also produce an Auger electron. This inner-shell ionization electron energy loss is also characteristic of each element, which is the foundation for a useful EELS analysis. A characteristic minimum energy $E_C$, so-called “critical ionization energy”, is required to activate an atom. For $E > E_C$, the probability of ionization decreases with increasing energy loss. Hence, ionization loss usually gives rise to saw-tooth shape edge peaks. The Ni L$_{2,3}$ edge corresponds to an energy-loss of 855 eV, which is the minimum energy required to ionize a 2$p$ electron; while the 530 eV energy-loss corresponds to oxygen K edge.

When the slit aperture is positioned such that only electrons with zero-loss can pass, a zero-loss (or elastic) image can be recorded. In a similar fashion, GIF has the ability to admit electrons with a certain range of energy-loss (eg. element A) and record the resultant image, which is also called electron spectroscopic imaging (ESI). The region will appear bright in the elemental map of A, where there is a high concentration of A. Three energy-filtered images are usually recorded for a region of interest (ROI), which are then Color Mixed by the Gatan DigitalMicrograph program, and produce a useful R(ed)-G(reen)-B(lue) map for these elements. In principle, one can repeat the same procedure for some other elements and gain better knowledge of this ROI.
Part II

SiC Heteroepitaxy on Si by

LP-MOCVD
Chapter 4

Home-Made MOCVD Reactor

![Diagram of CVD reactor classification]

**Figure 4.1**: Classification of CVD reactors, after [131].

### 4.1 General Considerations

Chemical Vapor Deposition (CVD) is defined as “a process in which reactants are transported in the vapor phase to the substrate surface, where they react to form a film” [16]. CVD can be classified by the heating methods, operating pressure, reactants, and so on (see Figure 4.1).
Manasevit introduced metal-organic chemical vapor deposition (MOCVD) in the late 1960’s, which is also called organometallic CVD (OMCVD), or metal organic vapor phase epitaxy (MOVPE) [53, 54, 55, 56, 57]. In terms of geometry, there are two types of MOCVD reactors, either vertical or horizontal. Using atmospheric pressure (AP-) MOCVD reactors, such as the one developed by Nakamura (Figure 4.2), people has fabricated some very high-quality GaN films. However, AP-MOCVD is not suitable for large-scale production. On the other hand, LP-MOCVD is a mature technology for large-scale productions of III-As and III-P materials. A necessary modification is to increase the NH$_3$ flow rate as ammonia has a relatively low cracking efficiency.

![Figure 4.2: A typical vertical MOCVD system, after [68].](image-url)

$^{1}$An emphasis toward III–N is obviously given in this section. Please check section §2.2 for a short review on SiC heteroepitaxy on silicon substrates.
The basic reactions during MOCVD III–N growth are considered as a pyrolysis reaction:

\[ R_3M(g) + NH_3(g) \rightarrow M-N(s) + 3R-H(g), \quad (4.1) \]

where \( M \) stands for Al, Ga or In; \( R \) is an organic radical, usually \( \text{CH}_3 \) or \( \text{C}_2\text{H}_5 \). However, the specific thermodynamics and kinetics of the real reaction depend on the chemicals (precursors, carrier gases), substrates, growth pressure and temperature, flow rates, reactor geometry, and so on.

### 4.1.1 Precursors

In our work, a single precursor, hexamethyldisilane (HMDS), was adopted for SiC epitaxy. For growth of GaN on SiC, Ga-alkyl (methyl and ethyl derivative) is often chosen as the Ga source, i.e. \( R_3\text{Ga} \), where the organic radical \( R \) is usually \( \text{CH}_3 \) (our choice) or \( \text{C}_2\text{H}_5 \) (see Table 4.1).

The data on phase diagrams of AlN, GaN and InN are limited and contradict each other since these materials have high melting temperatures and very high nitrogen dissociation pressures \( P_{\text{N}_2}^{\text{dis}} \) \([41, 90, 105]\). The latter is defined as the nitrogen pressure at which the following reaction is in thermal equilibrium:

\[ \text{III–N}(s) = \text{III}(l) + \frac{1}{2}\text{N}_2(g), \quad (4.2) \]

where \( \text{III} \) stands for Al, Ga or In. In the case of GaN, we have

\[ \frac{1}{2}RT\ln(vP_{\text{N}_2}^{\text{dis}}) = \Delta G_{f,\text{GaN}}^* = \Delta H_{f,\text{GaN}}^* - T\Delta S_{f,\text{GaN}}^* \quad (4.3) \]
Table 4.1: Common precursors for MOCVD growth of SiC and III-nitrides.\(^a\)

<table>
<thead>
<tr>
<th>Metalorganic Compound</th>
<th>Formula</th>
<th>Vapor Pressure(^b)</th>
<th>(T_m) (°C)</th>
<th>(T_b) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyldimethylamine Alane (EDMAA)</td>
<td>((\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{NaAlH}_3)</td>
<td>(B = 6.17, A = 1550)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylaluminum (TEAl)</td>
<td>((\text{C}_2\text{H}_5)_3\text{Al})</td>
<td>(B = 8.999, A = 2361.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethylaluminum (TMA)</td>
<td>((\text{CH}_3)_3\text{Al})</td>
<td>(B = 8.224, A = 2134.86)</td>
<td>15.4</td>
<td>127</td>
</tr>
<tr>
<td>Trimethylamine Alane (TMAA)</td>
<td>((\text{CH}_3)_3\text{NaAlH}_3)</td>
<td>(P = 0.13) Torr at 303K</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ga</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylgallium (TEGa)</td>
<td>((\text{C}_2\text{H}_5)_3\text{Ga})</td>
<td>(B = 8.083, A = 2162)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethylgallium (TMG)</td>
<td>((\text{CH}_3)_3\text{Ga})</td>
<td>(B = 8.07, A = 1703)</td>
<td>-15.8</td>
<td>55.7</td>
</tr>
<tr>
<td>Triisobutylgallium</td>
<td>((\text{C}_4\text{H}_9)_3\text{Ga})</td>
<td>(B = 4.769, A = 1718)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mg</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bis(methylcyclopentadienyl) magnesium</td>
<td>((\text{CH}_3\text{C}_5\text{H}_4)_2\text{Mg})</td>
<td>(B = 7.302, A = 2358)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bis(cyclopentadienyl) magnesium (Cp2Mg)</td>
<td>((\text{C}_5\text{H}_5)_2\text{Mg})</td>
<td>(P = 0.07) Torr at 303K</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>N</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-butylamine (TBN)</td>
<td>((\text{C}_4\text{H}_9)_3\text{CNH}_2)</td>
<td>(B = 7.61, A = 1509.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylhydrazine (PhHy)</td>
<td>(\text{C}_6\text{H}_5\text{NHNH}_2)</td>
<td>(B = 8.749, A = 3014)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethylhydrazine (DMHy)</td>
<td>((\text{CH}_3)_2\text{NHNH}_2)</td>
<td>(B = 7.61, A = 1509.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>(\text{NH}_3)</td>
<td>(P = 66.7) kPa at 27°C</td>
<td>-33.4</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>(\text{N}_2)</td>
<td>(-209.9)</td>
<td>-195.8</td>
<td></td>
</tr>
<tr>
<td><strong>Si</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silane</td>
<td>(\text{SiH}_4)</td>
<td>(P = 1250) psi at 293K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disilane</td>
<td>(\text{Si}_2\text{H}_6)</td>
<td>(P = 33) psi at 293K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexamethyldisilane (HMDS)</td>
<td>((\text{CH}_3)_3\text{Si}−\text{Si}(\text{CH}_3)_3)</td>
<td>(B = -8.011, A = 1935.12)</td>
<td>14–14</td>
<td>112–113</td>
</tr>
<tr>
<td><strong>Zn</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethylzinc (DEZn)</td>
<td>((\text{C}_2\text{H}_5)_2\text{Zn})</td>
<td>(B = 8.28, A = 2109)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethylzinc (DMZn)</td>
<td>((\text{CH}_3)_2\text{Zn})</td>
<td>(B = 7.802, A = 1560)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Compiled from [21], MSDS data sheets, product catalogs, and other sources. The unit of pressure is Torr unless it is written otherwise.

\(^b\) \(\log P = B - A/T\). Note that 1 psi = 1 pound/square inch = 6892.7 Pa and 1 Torr = 133.33 Pa.
where $\nu$ is the fugacity coefficient of $N_2$ that is unity for an ideal gas. The gas constant $R$ equals 8.31 J/(mole K). The terms $\Delta G^*_{f,GaN}$, $\Delta H^*_{f,GaN}$ and $\Delta S^*_{f,GaN}$ are the standard free energy, heat, and entropy of formation for GaN, respectively.

The reported values of the nitrogen dissociation pressure show large discrepancies (Figure 4.3). In most cases, however, there is a very high nitrogen dissociation pressure at elevated temperatures. In the case of solution growth from Ga and $N_2$, a high temperature is required to increase nitrogen solubility in liquid gallium. Hence, a very high nitrogen pressure is needed for GaN growth, which is not so applicable. On the other hand, by using NH$_3$ as the N source, single crystalline GaN were successfully grown on sapphire at 900–1100°C under 0.1–1 atm. We used NH$_3$ instead of $N_2$ as the nitrogen source.

![Figure 4.3: Nitrogen dissociation pressure of GaN, after [105].](image-url)
4.1.2 Carrier Gases

The widely-used carrier gases are H\textsubscript{2}, H\textsubscript{2}/Ar mixture or N\textsubscript{2}.

Yoshida et al. studied the decomposition of trimethylgallium (TMG) and Et\textsubscript{3}Ga (TEGa) in hydrogen and nitrogen atmospheres by a quadrupole mass analyzer [133]. The decomposition reactions of TMG in H\textsubscript{2} or N\textsubscript{2} and of TEGa in H\textsubscript{2} or N\textsubscript{2} take place at 370–460, 450–570, 220–330, and 270–380°C, respectively. Hence, H\textsubscript{2} can reduce the reaction temperature (Figure 4.4).

![Figure 4.4: The decomposition reactions of TMG and TEGa in H\textsubscript{2} and N\textsubscript{2}, after [133].](image)

Ambacher et al. studied the role of hydrogen as transportation gas for MOCVD growth of GaN on c-plane sapphire substrates without a buffer layer [4]. The flux rate of Et\textsubscript{3}Ga was fixed at 1.15µmol/min, which caused a partial pressure of \(1.1 \times 10^{-3}\) mbar at the substrate surface. Et\textsubscript{3}Ga reacted with ammonia in the presence of nitrogen and/or hydrogen. Figure 4.5 shows the topography of as-grown GaN films at a substrate temperature of 950°C. Without hydrogen as transport
gas, a mosaic structure of hexagonal GaN crystals with sizes of 3 mm was identified. Using hydrogen as transport gas, the deposition rate was reduced from 2 to 1 mm/h and the crystal shape changed to circular with sizes of 3–5 mm.

![Figure 4.5: Surface micrograph of GaN grown by MOCVD (a) without, and (b) using hydrogen as carrier gas, after [4].](image)

The purities of all these precursors and carrier gases are important for the growth of high-quality epitaxial films or devices. Much effort have been made to reduce the Si and O incorporation or contamination. In our case, H₂/Ar mixture was purchased from Matheson Tri-Gas, which is 12.00% UHP (ultra high purity, 99.9999%) hydrogen in UHP argon (balance). Cylinders of Ar and NH₃ with a purity of 99.9995% were purchased from Praxair, Inc. The HMDS (bubbler) was purchased from Gelest, Inc; while the TMG (bubbler) and TMA (bubbler) were purchased from Epichem Inc. The impurity specifications are listed in Table 4.2.

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**ii** URL: [http://www.matheson-trigas.com](http://www.matheson-trigas.com)
**iii** URL: [http://www.praxair.com](http://www.praxair.com)
**iv** URL: [http://www.gelest.com](http://www.gelest.com)
**v** URL: [http://www.epichem](http://www.epichem)
Table 4.2: Specifications of the precursors and carrier gases used in our work.

<table>
<thead>
<tr>
<th>Gases</th>
<th>Purity</th>
<th>CH$_4$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>H$_2$</th>
<th>H$_2$O</th>
<th>N$_2$</th>
<th>O$_2$</th>
<th>THC$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ Ar</td>
<td>99.9999%</td>
<td>—</td>
<td>1ppm</td>
<td>1ppm</td>
<td>&lt; 3ppm</td>
<td>5ppm</td>
<td>7ppm</td>
<td>2ppm</td>
<td>0.5 ppm</td>
</tr>
<tr>
<td>Ar</td>
<td>99.9995%</td>
<td>0.5 ppm</td>
<td>0.1 ppm</td>
<td>0.5 ppm</td>
<td>0.5 ppm</td>
<td>0.5 ppm</td>
<td>2ppm</td>
<td>1ppm</td>
<td>0.5 ppm</td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bubbler</td>
<td>Grade</td>
<td>Be</td>
<td>Cd</td>
<td>Cu</td>
<td>Ge</td>
<td>I</td>
<td>Mg</td>
<td>Pb</td>
<td>Si</td>
</tr>
<tr>
<td>HMDS</td>
<td>N/A</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TMA</td>
<td>Low-O</td>
<td>0.02 ppm</td>
<td>0.02 ppm</td>
<td>0.1 ppm</td>
<td>0.5 ppm</td>
<td>0.1 ppm</td>
<td>0.02 ppm</td>
<td>0.1 ppm</td>
<td>0.3 ppm</td>
</tr>
<tr>
<td>TMG</td>
<td>Grade</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>Air$^c$</td>
<td>Ar</td>
<td>H$_2$</td>
<td>(12%H$_2$+88%Ar)</td>
<td>NH$_3$</td>
<td>N$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.38</td>
<td>0.07</td>
<td>1.22</td>
<td>0.59</td>
<td>0.97</td>
<td>—</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ THC: total hydrocarbons.
$^b$ To save space, the less than sign (<) is omitted for all the rest impurity levels in this table.
4.1.3 Gas Flow

Gas flow dynamics is a complex problem although there are many softwares available to perform possible simulations. During a typical MOCVD growth, with the gas flow in a constant-diameter and isothermal quartz tube with a low velocity, one can assume the flow is laminar. In other words, the flow velocity $\vec{v}$ has a direction parallel to the tube wall, and its magnitude is a function of the radial position ($v = 0$ at the walls).

An empirical Reynolds number is often used, which is defined as

$$N_{Re} = \nu \rho d / \mu,$$  \hspace{1cm} (4.4)

where $\rho$ is the density of the fluid (gas in our case), $d$ is the tube diameter, and $\mu$ is the absolute viscosity. For a typical CVD reactor, the Reynolds number is below 100, which indicates a laminar flow regime. If the number goes above 2000–3000, the flow would be turbulent.

The boundary layer theory is often used in the mass-transfer region. The boundary layer is defined as the transition region between the solid surface (ie. susceptor/substrate in our case where the gas velocity $v = 0$) and the free gas steam where $v = \nu$, the velocity of the flow field. The boundary layer thickness $\delta(x)$ is defined as the distance from the substrate to the point where the parallel component of gas velocity satisfies $v_\parallel = 0.99\nu$. For the gas flow over a semi-infinite plate, $x \gg \delta(x)$, we have

$$\delta(x) = 4.99 \times \sqrt{\mu x / \rho \nu}$$  \hspace{1cm} (4.5)
where \( x \) is the distance from the leading edge of the susceptor/substrate. One can clearly see that the thickness increases with the distance \( x \) but decreases with increasing gas velocity \( v \) [116].

### 4.1.4 Problems with the Old Reactor

Our system is a horizontal, cold wall, LP-MOCVD reactor, as shown schematically in Figure 4.6, which has become out of date. There are several major drawbacks. To name a few: (i) the quartz tube is so small that reaction gases will not distribute well; (ii) several valves and some fittings leak so that strong oxygen contamination occur in the epilayers; and (iii) certain flow meters are worn out so that it is impossible to control the flow rates.

![Figure 4.6: A schematic of the old LP-MOCVD reactor. The right angle means the two tubes are connected by an elbow, a tee or a cross.](image-url)
4.2 A Modified Horizontal LP-MOCVD Reactor

The focuses of modification and construction of the new reactor were as follows (see Figures 4.7 and 4.8): (i) to make sure that every valve, fitting and flowmeter was leak-free; (ii) keep the reactor simple (reduce the number of valves and fittings); and (iii) keep the reactor open for any further modification.\textsuperscript{vi}

![Diagram of the modified LP-MOCVD reactor](image)

**Figure 4.7:** A schematic of the modified LP-MOCVD reactor. The open dot in the middle of a cross means that two tubes are not connected but just overlapping.

4.2.1 Valves, Fittings and Flowmeters

A leak-detection system, which contains a quadrupole mass analyzer under ultra high vacuum (UHV), was used to check all the old valves, fittings and

\textsuperscript{vi}Richard Miller helped me to cut some heavy metal scaffolds, which were irreplaceable building blocks for the stand of the RF generator.
Figure 4.8: Photographs of the modified LP-MOCVD reactor: (a) front view, (b) side view on the left, and (c) side view on the right.
flowmeters.\textsuperscript{vii} For instance, to test a valve (X3), we connected one end of the valve to a Helium source (via a leak-prove valve X2 and a regulator X1) and the other end to the leak-detecting system (via a leak-prove valve X4), as shown in Figure 4.9. After closing the He regulator (X1) and opening X2, X3 and X4, the leak-detection system was pumped to below $10^{-7}$ Torr. Then after X4 and X3 were closed, X1 was opened slowly. Valve X4 was opened later on, while X3 was still closed. If we can not detect any He signal, valve X3 is leak-prove; otherwise, it is leaking.

![Figure 4.9: Schematic setup of the leak detection system.](image)

Most valves and fittings for our $\frac{1}{4}$ inch tubing were regular Swagelok\textsuperscript{viii} ball valves (Model S-43S4) and tube fittings (unions, union-elbows, tees, crosses, ferrules and nuts), respectively. Some pneumatic valves (4, 5, 11 and 16 in Figure 4.7) were also used, which were further controlled by in-line solenoid valves (Figure 4.10). A small circuit was built to control the power and gas input of these solenoid valves.

\textsuperscript{vii}I am grateful to Professor John C. Angus’ research group, at the Department of Chemical Engineering, for lending me this leak-detection system.

\textsuperscript{viii}www.swagelok.com
As shown schematically in Figure 4.11, pneumatic valve #1 (MDC\textsuperscript{ix} IV-150-P in-line angle valve) connects the mechanical pump and the reactor via a flexible hose. This valve is normally closed and controlled further by another solenoid valve. Moreover, if there is a leak at the downside, valve #1 will be automatically closed so that no air can backfill into the reactor.

Valve #2 was an MKS\textsuperscript{x} throttle control valve. Its downside is connected to the flexible hose, while its upside to an MKS 627A Baraton\textsuperscript{TM} gauge. An MKS 651C controller is used to control this gauge and valve #2. While it is set to “adaptive mode” and a set point button of the controller, say set point $A$ (preset to 100 Torr), is pressed, valve #2 will open further if the “growth pressure” (pressure of the reaction chamber) is larger than 100 Torr. On the other hand, it will move toward closing position if the growth pressure is lower than 100 Torr. This is a very sensitive mode so that we can maintain the growth pressure almost constant ($99.9 \pm 0.1$ Torr for set-point $A$).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_10.png}
\caption{(a) Photograph of a pneumatic valve, (b) porting diagram, and (c) schematics of the controlling circuit.}
\end{figure}

\textsuperscript{ix}URL: www.mdc-vacuum.com
\textsuperscript{x}www.mksinst.com
4.2. A Modified Horizontal LP-MOCVD Reactor

Figure 4.11: Pump side of the reactor.

Valve #3 was a manual in-line angle valve that separates the reactor chamber and a turbo pump. Once a while, this pump is turned on to get a better base pressure, typically on the order of $10^{-5}$ Torr.

All flowmeters were Brooks Instrument\textsuperscript{xi} purge rotameters (Model: Sho-Rate\textsuperscript{TM} 1355). O-rings were employed to seal these flowmeters, while the flow rate was adjusted by needles valves. It turned out that the leak problem was due to worn-out needle valves or O-rings. A typical setup for the gas flow controlling line is shown in Figure 4.12. Two valves are usually included at the inlet and outlet side of the flow meter. Moreover, a bypass line (including another valve) is also preferred in order to protect the flow meter and to purge the system quickly.

\textsuperscript{xi}www.emersonprocess.com/brooks/index.html
The actual flow rate depends on specific gravity of the gas, the pressure difference between inlet and outlet sides, and temperature of operation. The corrected flow value is related to the meter value by

\[ \nu_{fr} = \nu_{ae} \cdot CF, \quad (4.6) \]

\[ CF = \sqrt{\frac{\rho_{sg} \times (T + 460)}{36 \times (P + 14.0)}}, \quad (4.7) \]

where \( \nu_{fr} \) stands for the desired flow value (real value), \( \nu_{ae} \) is the value read from the flow meter (usually calibrated for a certain gas at 70°F and 14.7 psia), and \( \rho_{sg} \) denotes the gas specific gravity (see Table 4.2). Note that the temperature \( T \) and pressure \( P \) have the units of °F and psig, respectively.

The old \( \frac{1}{4} \) inch Swagelok tubing could not be recycled because the bends and length were not right. A few hundreds feet of new tubes were cut, bent, and swaged with ferrules or valves. Many other Swagelok fitting were also used to connect the different parts together, including unions, elbows, tees and crosses. They were also checked with the leak-detection system.
4.2.2 A Larger Quartz Tube for the New CVD System

To adopt the larger quartz tube, more flanges were acquired and installed. As a matter of fact, if one examine Figure 4.11 closely, there are many MDC ISO LF Large-Flange™ and Kiwi-Flange™ in use; the size can be NW80, NW63, NW40, NW25 and NW16. For example, the ISO NW80 cross has an inner diameter (I.D.) of 80 mm; while the quartz tube (2.5 inch or 63 mm) needs an NW63 flange. A nipple reducer from NW80 to NW63 is required to connect these two flanges.

A ball socket and adjustable clamp were used to seal the right side of the tube (Figures 4.13 and 4.15a). Even though the flat side of the quartz tube fits inside a simple NW60, it is very hard to clamp them together. A whole assembly, as shown in Figure 4.14, was used to connect the NW80 cross and the left side of the quartz tube. O-rings and clamps were used to make the connection leak free.

![Photographs of the ball socket.](a) ![Photographs of the ball socket.](b)

**Figure 4.13:** Photographs of the ball socket.

---

xii To reduce the total cost of the modification of our reactor, we used some spare parts from Professor Augus’ lab. Thanks again.

xiii For the record, the old quartz tube had an inner diameter of 30 mm.
Figure 4.14: Photographs of (a) the nipper reducer and fittings, (b) the fittings between the reducer and the tube, (c) left and (d) right side of a thin flange, (e) left and (f) right side of the flange to the tube.

Figure 4.15: (a) The quartz tube, (b) susceptor, and (c) heating coil.
4.2.3 Heating and Temperature Measurement

Our reaction chamber is made of a quartz tube, inside of which the substrate sits on top of a SiC-coated graphite susceptor (Figure 4.15). It is heated by a radio-frequency (RF) induction furnace which is operated at 450 kHz and 12.7 kW (Lepel™ Model 7-5-3-KC-BW, see Figure 4.16). An electromagnetic field will build up when an electric current passes through the copper coil. There is consequently an eddy current $I$ in the graphite that gives rise to $I^2R$ heating of the susceptor, which will then conduct heat to the substrate and raise its temperature. The heating capacity depends on the number of turns, separation between neighboring turns, and the shape of the home-made RF coil.

![Figure 4.16: The control panel of our Lepel™ RF induction furnace.](image)

One can only manipulate the grid and power knobs of the RF source from 0 to 100. There are also three Ampere meters for recording the input current (IC), grid current (GC) and plate current (PC). However, one can not control these currents directly because they will change automatically as different values of grid and power are set. One can also change the susceptor, position of the susceptor in the coil, and even the coil itself.
An infrared pyrometer (Omega™ Model OS1200) was used to measure the substrate temperature by focusing at the hole within the susceptor from one side of the quartz tube (see Figures 4.8a and 4.15b). There is a difference of about 5°C in the temperature measured at different parts of the substrate. Since substrate temperature is a very important parameter in MOCVD, some correlations between the substrate temperature and all the above variables will be given later (see section §5.1).

### 4.3 Safety Precautions

Although the system is supposed to be leak-free, some further safety measures were taken. First, the big gas cylinders were secured in a cabinet and its exhaust was connected to a chemical hood (see Figure 4.8c). Second, since HMDS, TMA and TMG are liquid at room temperature, bubblers were used, as shown in Figure 4.17a. Swagelok VCR™ valves (#31 and #32) were used for the inlet and outlet of each bubbler. Another set of valves (#25 or #26) were added at the inlet and outlet for safety purposes.

Third, the TMG bubbler should be cooled before use as it has a vapor pressure of 182 Torr at room temperature. A coolant was employed to maintain a temperature of -1°C before and during GaN epitaxy. HMDS and TMA can be used at room temperature (RT) as they have a vapor pressure of 12.8 and 20 Torr. However, the temperature of all bubblers should be noted during each growth.

Finally, as most reactive gases are toxic to human beings (refer to MSDS data sheets), a cold trap (Figure 4.17b) is attached to the exhaust of our mechanical
4.4 Summary on Reactor Modification

The leak problems of the old system were examined closely, including every valve, fitting, flowmeter and even the vacuum gauge. Second, to adopt a new and bigger quartz tube, many more flanges and fittings were acquired and installed. Third, with several trials and errors, a suitable copper coil for the RF furnace was fabricated in-house with the highest heating capacity. Fourth, the gas cylinders were secured in a cabinet with an exhaust to the chemical hood. The bubblers were also secured by two sets of leak-proof valves. Last, the only exhaust of the reactor was connected to a cold trap, which also sat in the hood.
Chapter 5

SiC Epitaxy on Si Substrates by MOCVD

5.1 Factors that Control the Substrate Temperature

It is important to precisely control the substrate temperature during epitaxial growth. A simple statistical experiment was proposed with four factors (each has at least two levels) [61]. The response is of course the substrate temperature and the four factors are the susceptor, its position, grid and power settings. The levels were chosen as: A) (two different) susceptors: 0 and 1; B) position (of the susceptor): 0 and 1; C) grid (reading): 25 and 55; D) power (of the RF generator): 40 and 80. Susceptor 0 and 1 have different shapes and sizes. They can be placed in the middle (i.e. level 0) or on the right side (level 1) of the coil, but not at the left side because the temperature cannot be measured in that case. To be precise, the left end of the susceptor is aligned with the 2nd and 4th turn of the coil, which corresponds to position 0 and 1, respectively.
5.1. **Factors that Control the Substrate Temperature**

The levels for *grid* and *power* are the readings next to the knobs where the arrows pointed to. Two duplicate measurements were performed for each treatment, one during heating and one during cooling. The average temperature will be treated as the response. The objective is to find a relationship between the substrate temperature and all these factors. One can then select the right level of these factors to reach the highest temperature.

**This Is a $2^4$ Factorial Design.** By fixing the levels of A, B and C, 2 runs were performed corresponding to two different levels of D—*power*. One duplicate was noted during heating, the other during cooling. Another 2 runs were carried out with a different level of C—*grid*. The reactor was then shut down and the susceptor position was changed. Four similar runs were then performed. Finally, another 8 runs were repeated using a different susceptor. For a particular set of A, B and C, the first temperature during heating was recorded at $D = 40$. Then after 10 minutes when the substrate temperature was stabilized, the values were noted down; temperatures in other situations were recorded after 5 minutes' stabilization.

To analyze the data (D:/Changrong/Stats/tp.dat on my computer), the free software R was used.\(^1\) First, one can load the data by the following command

```
> d<-read.table("D:/Changrong/Stats/tp.dat")
```

where > indicates the prompt within a terminal when the software R is loaded, and d<-read.table... is the command. The data is displayed as

\(^1\)“R is a free software environment for statistical computing and graphics”, which is available at www.r-project.org
> d
  V1 V2 V3 V4 V5  V6  V7  V8
 1  0  0  25 40 1036 1023 1029.5 9.1923882
 2  0  0  25 80 1268 1261 1264.5 4.9497475
  ... ...
 16 1  1  25 80 1186 1187 1186.5 0.7071068

The first number (i.e. 1–16) in each line of data corresponds to the run number. Next set of columns are susceptor levels \( V_1 \) (0 or 1), followed by susceptor position \( V_2 \), \textit{grid} \( V_3 \), \textit{power} \( V_4 \), temperature reading 1 during heating (by increasing power) \( V_5 \), temperature reading 2 during cooling \( V_6 \), the average temperature of these two \( V_7 \), and the standard deviation \( \sigma \). The variables (factors A, B, C, and D) and the response \( (y) \) can be assigned by

\[
\begin{align*}
A & \leftarrow \text{factor}(d$V_1) \\
B & \leftarrow \text{factor}(d$V_2) \\
C & \leftarrow \text{factor}(d$V_3) \\
D & \leftarrow \text{factor}(d$V_4) \\
y & \leftarrow d$V_7
\end{align*}
\]

As mentioned before, the correct response should be the average of two duplicate temperature readings.

**The Main Effects.** The main effects of all the four factors (A: susceptor, B: position, C: \textit{grid}, and D: \textit{power}) can be examined by analyzing the data as if these are the only sources of variation.

\[
\begin{align*}
\text{anova}(\text{aov}(y \sim A+B+C+D))
\end{align*}
\]

\textbf{Analysis of Variance Table}
\textbf{Response: y}

\begin{tabular}{lccccc}
\hline
 & Df & Sum Sq & Mean Sq & F value & Pr(>F) \\
A & 1  & 2691 & 2691 & 2.2257 & 0.163845 \\
B & 1  & 20556 & 20556 & 17.0018 & 0.001691 ** \\
C & 1  & 44 & 44 & 0.0363 & 0.852366 \\
\hline
\end{tabular}
5.1. Factors that Control the Substrate Temperature

Because interaction effects were not taken into account, there are residuals. One might say A and C main effects are not significant. However, this conclusion turns out to be wrong when we proceed.

The Interactions. One can check the interactions between all the four factors using the full model (\textit{lm1}, see codes in the next page). However, the F-values could not be estimated in this model as there is no degree of freedom left for error. Fortunately, we can identify several outliers from the normal probability plot by \texttt{qqnorm} (Figure 5.1). In other words, this model is not normal and needs to be improved.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.1.png}
\caption{Normal probability plot for the full model \textit{lm1}.}
\end{figure}
> lm1<-aov(y~A*B*C*D)
> anova(lm1)

Analysis of Variance Table

Response: y

<table>
<thead>
<tr>
<th></th>
<th>Df</th>
<th>Sum Sq</th>
<th>Mean Sq</th>
<th>F value</th>
<th>Pr(&gt;F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>2691</td>
<td>2691</td>
<td>1</td>
<td>1.21791</td>
</tr>
<tr>
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<td>20556</td>
<td>9.30351</td>
<td>1.111e-05</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>44</td>
<td>44</td>
<td>0.1986</td>
<td>0.6676339</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>375003</td>
<td>375003</td>
<td>1697.2068</td>
<td>1.327e-10</td>
</tr>
<tr>
<td>A:D</td>
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<td>3829</td>
<td>17.3273</td>
<td>0.0031539</td>
</tr>
<tr>
<td>B:D</td>
<td>1</td>
<td>1000</td>
<td>1000</td>
<td>4.5265</td>
<td>0.0660441</td>
</tr>
<tr>
<td>C:D</td>
<td>1</td>
<td>6704</td>
<td>6704</td>
<td>30.3391</td>
<td>0.0005683</td>
</tr>
</tbody>
</table>

Residuals 8 1768 221

> e1<-lm1$effects[-1]
> e1

<table>
<thead>
<tr>
<th></th>
<th>A1</th>
<th>B1</th>
<th>C55</th>
<th>D80</th>
<th>A1:B1</th>
</tr>
</thead>
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<tr>
<td>-51.875</td>
<td>-143.375</td>
<td>-6.625</td>
<td>612.375</td>
<td>30.625</td>
<td></td>
</tr>
<tr>
<td>6.875</td>
<td>19.625</td>
<td>61.875</td>
<td>-31.625</td>
<td>81.875</td>
<td></td>
</tr>
<tr>
<td>2.125</td>
<td>-4.125</td>
<td>3.125</td>
<td>18.625</td>
<td>-4.375</td>
<td></td>
</tr>
</tbody>
</table>

> eid<-identify(qqnorm(e1))
> eid

[1] 1 2 4 8 9 10

> q1<-qqnorm(e1, plot.it=F)
> qqnorm(e1)
> text(q1$x[eid], q1$y[eid]-0.2, c("A","B","D","AD","BD","CD"))

A new model lm2 was constructed as follows. The insignificant main effect of factor C was also included as a hierarchical model. We can now see that factor A has a significant effect.

> lm2<-aov(y~A+B+C+D+A:D+B:D+C:D)
> anova(lm2)

<table>
<thead>
<tr>
<th></th>
<th>Df</th>
<th>Sum Sq</th>
<th>Mean Sq</th>
<th>F value</th>
<th>Pr(&gt;F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<td>2691</td>
<td>2691</td>
<td>12.1791</td>
<td>0.0082001</td>
</tr>
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<td>B</td>
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<td>20556</td>
<td>20556</td>
<td>93.0351</td>
<td>1.111e-05</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>44</td>
<td>44</td>
<td>0.1986</td>
<td>0.6676339</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>375003</td>
<td>375003</td>
<td>1697.2068</td>
<td>1.327e-10</td>
</tr>
<tr>
<td>A:D</td>
<td>1</td>
<td>3829</td>
<td>3829</td>
<td>17.3273</td>
<td>0.0031539</td>
</tr>
<tr>
<td>B:D</td>
<td>1</td>
<td>1000</td>
<td>1000</td>
<td>4.5265</td>
<td>0.0660441</td>
</tr>
<tr>
<td>C:D</td>
<td>1</td>
<td>6704</td>
<td>6704</td>
<td>30.3391</td>
<td>0.0005683</td>
</tr>
</tbody>
</table>

Residuals 8 1768 221
5.1. Factors that Control the Substrate Temperature

We can also drop the insignificant interaction $B:D$, which leads to a third model $lm3$. The residual plot and normal probability plot are shown in Figure 5.2. The latter looks quite linear. Hence, the assumptions of normality is valid.

![Residual and Normal Probability Plot](image)

**Figure 5.2:** (a) Residual and (b) normal probability plot for model $lm3$.

```r
> lm3 <- aov(y ~ A + B + C + D + A:D + C:D)
> anova(lm3)

Df  Sum Sq Mean Sq F value Pr(>F)
A   1 2691   2691  8.7504 0.016009 *
B   1 20556 20556 66.8436 1.86e-05 ***
C   1   44    44 0.1427 0.714347
D   1 375003 375003 1219.4054 6.40e-11 ***
A:D 1   3829  3829 12.4493 0.006431 **
C:D 1   6704  6704 21.7980 0.001171 **
Residuals 9  2768   308
> plot.lm(lm3, which = 1:2)
```

If we further examine the interaction plots generated by
From the results shown in Figures 5.3a and 5.3b, I would recommend to set \(C\) (grid) to 55, \(D\) (power) to 80, which is also confirmed by Figure 5.3d. Under these conditions, there is not much difference between the two susceptors (A=0 or A=1). However, by examining the not-so-significant interaction \(A:B\) (see Figures 5.3c and compared with interactions \(A:D\) and \(C:D\)), we would say \(A\) and \(B\) must be selected at low levels in order to reach the highest temperature. From Figure 5.3d, we can also see that simply raising the grid reading will not produce the highest temperature. For example, for a power level of \(D=40\), 25 is a better choice for the grid setting than 55. The opposite is true if the power level is set at 80.

The Results Based on This Statistical Experiment. Main factors \(A\) (susceptor), \(B\) (position of susceptor), and \(D\) (power) have significant effects on the responses (substrate temperature). Two-factor interactions \(A:D\) and \(C:D\) are also significant. Hence, the main factor \(C\) (grid) should also be included in our final model \(lm3\). To reach a higher temperature, I would recommend levels of \(C=55\) and \(D=80\); while \(A\) and \(B\) should be selected at low levels based on this statistical experiment.

Another experiment can be designed to examine the quadratic effects of \(C\) and \(D\). For example, at least 3 levels of \(C\) (grid) and 6 levels of \(D\) (power) could have been selected. We might also be able to build a regression model.

The Temperature and Power Level. Unfortunately, the RF generator stopped working before I could perform the above experiment. Hence, I could not find
5.1. Factors that Control the Substrate Temperature

Figure 5.3: Interaction plots, see text for details.
the relationship between grid and power and how this will affect the substrate temperature. However, it is always true that if all the other variables are fixed, the temperature will increase as the power level is increased (Figure 5.4). Note that the grid reading is 55, carrier gas flowmeter FL3 reading is 2 slpm (standard liter per minute), HMDS flow is 5 sccm (standard cubic centimeter/minute), and chamber pressure is 99.9 Torr, which are typical growth parameters.

Figure 5.4: Substrate temperature versus power level.
5.2 \textit{SiC Epitaxy on Si(100) Substrates}

A single precursor, \textit{HMDS}, was used for SiC epitaxy on Si substrates. The reaction is

\[(\text{CH}_3)_2\text{Si} \rightarrow \text{Si(}\text{CH}_3\text{)}_3 \longrightarrow 2\text{SiC}(s) + 4\text{CH}_4 + \text{H}_2, (5.1)\]

GaN epitaxy on SiC was employed by the following reaction in this work:

\[(\text{CH}_3)_3\text{Ga}(g) + \text{NH}_3(g) \longrightarrow \text{GaN}(s) + 3\text{CH}_4(g), (5.2)\]

Si(100) or Si(111) wafers were first cut into small pieces (roughly 1 cm by 1 cm), which were then immersed in 2\% HF acid\(^{ii}\) for about 20 minutes to remove the native oxide layers, according to the etching reaction:

\[\text{SiO}_2 + 6\text{HF} + 6\text{H}_2\text{O} \longrightarrow \text{H}_2\text{SiF}_6 + 8\text{H}_2\text{O}. (5.3)\]

The product fluosilicic acid (H\(_2\)SiF\(_6\)) is soluble in water and easily washed away [5]. Second, the wafers were cleaned ultrasonically in an acetone bath for degreasing. Last, a piece of as-cleaned Si substrate\(^{iii}\) was transferred to the reaction chamber and ready for thin film growth.

Because there are so many valves and gases in use, the MOCVD epitaxy procedures are very complicated (check the detailed manual in Appendix A). Only a few steps will be explained in the following sub-sections.

SiC epitaxy on Si (100) is quite a challenge. Based on previous results at our

\(^{ii}\)Hydrofluoric acid is just one of the many toxic chemicals in use.

\(^{iii}\)Both Si(111) and Si(100) were loaded together for comparison sometimes.
lab in the last 10 years [36, 124, 132], a two-step growth procedure was employed as shown in Figure 5.5.

The substrate was usually baked at temperature $T_0$ around 1200°C for $t_0 \approx 10$ min, while the carrier gas (a mixture of 8% $H_2$ and 92% $Ar$) was flowing. Then the substrate was ramped up to $T_1$, and HMDS was flowed for a certain time $t_1$. The chamber pressure was kept almost constant at 100 Torr by a throttle control valve (see page 65). This low temperature step is commonly used to grow a buffer layer on Si substrates. In the second step, the temperature was raised to $T_2$. HMDS flow was kept for time $t_2$ before it was closed off. The carrier gas was then switched to pure $Ar$ and the RF power shut off. The film was cooled in $Ar$ flow to room temperature before it could be taken out for examination. During
5.2. SiC Epitaxy on Si(100) Substrates

In my experiments, the flow rates of the carrier gases and HMDS were regulated by manual flowmeters FL3 and FL5, respectively (see Figure 4.7 in page 62).

There were no visible cracks in any of the films that were grown. Subsequently, the film texture was examined by X-ray diffraction (XRD). Two typical XRD results are shown in Figure 5.6. The initial time and temperature for the first step are different for these two films (1226°C and 2 min for sample #24, 1247°C and 5 min for #44). In both cases, the second step was held at 1300°C for 30 min. The flow rates are also the same for two samples—2 slpm for the carrier gas (FL3) and 5 sccm for HMDS (FL5). According to Table 3.1 in page 36, the peaks around $2\theta = 36^\circ$, $41^\circ$ and $69^\circ$ can be attributed to the reflections of SiC(111), SiC(200) and Si(400), respectively.

![Figure 5.6: Typical XRD results for SiC two-step epilayers on Si(100).](image)
Table 5.1: Two-step growth parameters for SiC epitaxy on Si substrates. The entries are run/sample serial numbers; see text for details.

<table>
<thead>
<tr>
<th>$t_1$ &amp; Si</th>
<th>1100</th>
<th>1125</th>
<th>1150</th>
<th>1175</th>
<th>1200</th>
<th>1225</th>
<th>1250</th>
<th>1275</th>
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<tbody>
<tr>
<td>2 min (100)</td>
<td>54</td>
<td>34,58</td>
<td>20</td>
<td>22</td>
<td>36,17</td>
<td>24</td>
<td>21</td>
<td>32</td>
<td>1300°C</td>
</tr>
<tr>
<td>2 min (111)</td>
<td>55</td>
<td>35,59</td>
<td>18</td>
<td>23</td>
<td>37</td>
<td>25</td>
<td>19</td>
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<td>30 min</td>
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<tr>
<td>5 min (100)</td>
<td>50</td>
<td>48</td>
<td>38</td>
<td>—</td>
<td>40</td>
<td>52</td>
<td>44,56</td>
<td>46</td>
<td>2 slpm</td>
</tr>
<tr>
<td>5 min (111)</td>
<td>51</td>
<td>49</td>
<td>39</td>
<td>—</td>
<td>41</td>
<td>53</td>
<td>45,57</td>
<td>47</td>
<td>5 sccm</td>
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<td>66,74</td>
<td>72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1300°C</td>
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<tr>
<td>2 min (111)</td>
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<td></td>
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<td></td>
<td>15 min</td>
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<tr>
<td>5 min (100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>68,73</td>
<td></td>
<td></td>
<td>2 slpm</td>
</tr>
<tr>
<td>5 min (111)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>69</td>
<td></td>
<td>10 sccm</td>
</tr>
</tbody>
</table>

Many different parameters were tested; and the run numbers (eg, #54) are listed in Table 5.1. In all these experiments, the temperature $T_1$ was varied between 1100–1275°C. To save space, column “Notes” list the four parameters $T_2$, $t_2$, FL3, and FL5. Column “$t_1$ & Si” shows the time $t_1$ and the orientation of Si substrates, ie. (100) or (111).

The XRD results of these epilayers on Si(100) are similar to what have been shown in Figure 5.6. It is clear that these films are polycrystalline with two major SiC peaks—(111) and (200). The ratios of their intensity $I_{200}/I_{111}$ for all these films on Si(100) are summarized in Figure 5.7. A larger ratio corresponds to a film with a higher-degrees of preferred orientation toward SiC(200), which is also more favorable. For a short growth time in the initial step, $t_1 = 2$ min, a lower temperature $T_1$ is more advantageous (the best is sample #34 with $T_1 = 1123$°C). However, for a longer $t_1 = 5$ min, a higher $T_1$ will produce a better epilayer.

The morphology of the epilayer is comparable to what has been published in the literature. It is rather smooth as shown in the SEM micrograph (Figure 5.8a),

---

iv The films are not bimodal since a SiC(220) peak at 60° is often detected.
where the scale bar measures 50 µm. Note there is a large bright particle on the surface. An XEDS point scan analysis (Figures 5.8c–d) shows that there are Si (58 at%), C (31 at%), and trace of O (10 at%) within this particle. The results obtained from another point (#2) from the surface are nearly the same, except that the atomic concentrations are 69% for Si, 23% for C and 7% for O. Note also there might be large errors on X-ray counts in XEDS especially for light elements. Nevertheless, the contrast is primarily due to topography.
Figure 5.8: Typical micrographs under (a) 1000x, (b) 10kx, (c) XEDS spectrum obtained from point #1 (marked in b), and (d) quantification result for sample #44.
5.3 SiC Epitaxy on Si(111) Substrates

SiC epitaxy on Si(111) is another story. In this case, except for the Si(111) peak around 28° from the substrate, only the SiC(111) peak around 36° is visible in the XRD results. Figure 5.9 shows the XRD spectra for two samples #45 and #25, where only the parameters $T_1$ and $t_1$ for the initial step are different for them. The flow rates and parameters for the second step are the same. In fact, the XRD results are very similar for all the SiC samples grown on Si (111) substrates (see the list in Table 5.1. It suggests that these films might be single crystalline.

![XRD spectra for SiC two-step epilayers on Si(111).](image)

**Figure 5.9:** Typical XRD results for SiC two-step epilayers on Si(111).

The morphology of SiC epilayer grown on Si(111) is similar to that of films grown on Si(100), as shown in Figure 5.10 for sample #45.

Moreover, similar XRD results were obtained for SiC films grown on Si(111)
Figure 5.10: Typical SEM micrographs for sample #45 at (a) 1000x, and (b) 10 kx.

with the one-step growth process. An example is given in Figure 5.11, where the major peaks are SiC(111) and Si(111) at 36° and 28°, respectively.

Note that there is a small shoulder to the left of Si(111) peak around 25.3°. This can be attributed to Cu Kβ with a wavelength of $\lambda = 0.138666 \text{ nm}$. The smaller peak around 76° belongs to SiC(222), which is parallel to SiC(111).

Some explanations on the benefits of the two step growth procedure will be discussed later in section 5.4.

5.3.1 GaN Epitaxy on Si(111) with a SiC Buffer Layer

GaN is a promising candidate for blue light emission largely due to the breakthrough of Nakamura [67, 68]. Sapphire is the most popular substrate for GaN heteroepitaxy. However, there is a large mismatch for the lattice parameters and thermal expansion coefficients between GaN and sapphire. Hence, it is very dif-
5.3. SiC Epitaxy on Si(111) Substrates

Figure 5.11: Typical XRD result for SiC epilayer on Si(111) using one-step growth.

Figure 5.12: XRD result for a typical epitaxial GaN/SiC/Si(111) multilayer #89.
ficult to grow high-quality GaN films with a smooth and crack-free surface on
sapphire. On the other hand, the mismatches between lattice parameters and
thermal expansion coefficients of SiC and GaN are much smaller and this makes
SiC a promising substrate for GaN epitaxy. Better yet, since it is possible to grow
good quality SiC films on Si, one can use high-quality and cheap Si wafers as the
substrate, grow a SiC buffer layer using the two-step procedure, and then con-
tinue GaN epitaxy. Another benefit of this approach is that one can embrace most
of the standard Si technology for GaN-based devices.

A few preliminary test runs were performed. Figure 5.12 in the preceding
page shows a typical XRD result for sample #89. Only the (111) peaks of the Si
substrate, the SiC buffer layer and the GaN epilayer are visible in this spectrum.
It indicates an epitaxial growth of GaN/SiC/Si(111) multilayer.

The initial step for SiC epitaxy was done at $T_1 = 1120^\circ\text{C}$ for $t_1 = 2\text{ min}$; while
parameters for the second step were $T_2 = 1280^\circ\text{C}$ and $t_2 = 5\text{ min}$. The flow rates
were kept the same at 2 slpm for the carrier gas (FL3) and 10 sccm for HMDS
(FL5). GaN epitaxy was preformed at 933°C with an ammonia (NH$_3$) flow of
2 slpm (FL4) and TMG ((CH$_3$)$_3$Ga) of 10 sccm (FL1). The chamber pressure was
kept at a constant 100 Torr.

5.4 Importance of the Two-Step Growth Procedure

There are two ways an epilayer can accommodate a substrate with a different
lattice parameter in heteroepitaxy, either strained or unstrained (Figure 5.13).

Consider a cubic (001) film on a cubic (001) substrate. In one case, where the
5.4. Importance of the Two-Step Growth Procedure

![Diagram showing the way an epilayer can fit a substrate lattice, after [125].](image)

**Figure 5.13:** The way an epilayer can fit a substrate lattice, after [125].

A film is said to be pseudomorphic, the unit cell of the film is elastically distorted to fit smoothly onto the lattice of the substrate. The in-plane strain is given by

\[ \epsilon_\parallel = \frac{(a_f\parallel - a_f)}{a_f}, \]  

(5.4)

where the in-plane lattice constant \( a_f\parallel \) equals the lattice constant \( a_s \) of the substrate and \( a_f \) is the lattice constant of the film (unstained). The strain perpendicular to the interface is given by \( \epsilon_\perp = \frac{(a_f\perp - a_f)}{a_f}, \) where \( a_f\perp \) is the film lattice constant perpendicular to the interface.

However, if the lattice mismatch (or mismatch parameter), \( f = \frac{|a_s - a_f|}{a_s} \), is large as in the case of SiC on Si, the epilayer is often unstrained by the introduction of misfit dislocations at the substrate/film interface right from the beginning of film deposition (since the critical thickness is about 2 nm for Si/SiC epitaxy; see also Figure 2.5b in page 13). Only the edge component of the interfacial misfit
dislocations contributes to mismatch accommodation. Sometimes these dislocations are pure edge, in which case, they are most efficient. Misfit dislocations are generally distributed uniformly along the interface with an average spacing of $S = a_f/f$. Note that in this formula, the Burgers vector is $\vec{b} = \frac{a_f}{2}\langle 110 \rangle$; again, the film and substrate are both (001)-oriented. The spacing between misfit dislocation is then 2.21 nm for $\beta$-SiC(001)/Si(001), which indicates a very high density. As a result, it is very difficult to grow high quality SiC films on Si.

The two-step growth procedure has turned out to be a good technique for growing SiC epitaxially on Si. As mentioned before, this produce can switch a much more difficult heteroepitaxy into homoepitaxial growth on the buffer layer. TEM results published in the literature have also revealed that the growth is always three-dimensional (island by island) [94].

![Figure 5.14](image)

**Figure 5.14:** (a) An STM (scanning tunneling microscopy) image of Si(100) surface, after [31]. (b) A schematic of an arbitrary surface, after [125].

To understand the nucleation stage during the initial step, one should realize that no surface is perfect; there exist terrace vacancies, kinks, and steps (Figure 5.14). The site fraction of mono-vacancies in a crystal is given by the
5.4. Importance of the Two-Step Growth Procedure

Arrhenius equation \[8, 59\]

\[
X_v \equiv \frac{n_v}{N} = \exp \left( -\frac{\Delta H_f}{kT} \right),
\] (5.5)

where \(\Delta H_f\) is the formation energy for a mono-vacancy, and \(k\) is the Boltzmann constant \((R/N_A)\). Given that \(\Delta H_f = 3.9\) eV for Si \([125]\), \(X_v = 3.1 \times 10^{-13}\) at \(T = 1300^\circ\text{C}\). Considering the atomic density on Si(001) surface, \(2/a^2 = 6.8 \times 10^{14}\) atoms/cm\(^2\), this translates to about 200 vacancies/cm\(^2\).

When an atom is deposited on the surface, it can either bind to a kink or surface diffuse. In the latter case, it is also called an adatom with a diffusivity of

\[
D_s = \lambda^2 \nu_s \exp\left( -\frac{\Delta G_s}{kT} \right),
\] (5.6)

where \(\lambda\) is the spacing between adjacent atoms, \(\nu_s\) is the vibration energy on the order of \(10^{13}\) Hz, and \(G_s\) is the activation energy for surface diffusion (0.5 eV for Si). The adatom can be desorbed (i.e. evaporated) with a mean residence time \(\tau_0\) given by

\[
1/\tau_0 = \nu_s \exp\left( -\frac{\Delta G_{\text{des}}}{kT} \right),
\] (5.7)

where \(\Delta G_{\text{des}}\) is the binding energy of the adatom (1.1 eV for Si). If a few adatoms diffuse and bond together before desorbing, they form a cluster (or nucleus) within this time frame \(\tau_0\).

In the initial step of the two-step procedure, a low growth temperature is used. The nucleation rate is thought to be high; while the growth rate is low \([94]\). One possible explanation is given as follows.
Consider the formation of a solid nucleus from the gas phase. As a result of the condensation, a certain amount of heat will be evolved (i.e. $\Delta G < 0$). At the condensation temperature $T_E$, this change of free energy should be zero at equilibrium. Since $\Delta G = \Delta H - T\Delta S$ (where $H$ and $S$ are enthalpy and entropy, respectively), one has

$$\Delta S = \Delta H / T_E.$$  (5.8)

It is obvious that the entropy change is negative, i.e. $\Delta S < 0$, for condensation; $\Delta H$ is also negative. As $\Delta H$ and $\Delta S$ do not change much with temperature, the bulk change of free energy at a lower temperature $T < T_E$ can be written as

$$\Delta G_V = \Delta H (1 - T/T_E) = \Delta H \Delta T / T_E,$$  (5.9)

where $\Delta T = T_E - T > 0$ is the degree of supercooling. Now consider the total free energy change to form a hemispherical cluster with a radius $r$ and surface energy $\gamma$ (modified from [8])

$$\Delta G_{\text{tot}} = \frac{2}{3} \pi r^3 \Delta G_V + \pi r^2 \gamma.$$  (5.10)

At the critical radius $r = r^*$, $d\Delta G_{\text{tot}}/dr = 0$; and

$$r^* = -\frac{\gamma}{\Delta G_V} = -\frac{T_E \gamma}{\Delta H \Delta T},$$

$$\Delta G^* = \frac{\pi \gamma^3}{3(\Delta G_V)^2} = \frac{\pi T_E^2 \gamma^3}{3(\Delta H)^2 (\Delta T)^2}.$$  (5.11)

Here $\Delta G^*$ is the critical energy necessary to form a cluster with radius $r^*$. 
5.4. Importance of the Two-Step Growth Procedure

Both $\Delta G^*$ and $r^*$ shall decrease with decreasing temperature $T$ (i.e. increasing supercooling $\Delta T$, see Figure 5.15a). Furthermore, when $r > r^*$, $\Delta G_{\text{tot}}$ decreases with increasing radius; the opposite is true when $r < r^*$. This suggests that the larger nuclei will grow at the expense of smaller ones.

![Figure 5.15](image)

**Figure 5.15:** Effects of temperature $T$ on (a) nucleation parameters $r^*$, $\Delta G^*$, and (b) nucleation rate $\dot{N}$, after [8]. Note the different temperature axes.

The nucleation rate $\dot{N}$ depends on both the nuclei concentration and surface diffusion. It can be described by an Arrhenius equation [8]

$$\dot{N} \propto \exp \left( \frac{-\Delta G^*}{kT} \right) \exp \left( \frac{-\Delta G_s}{kT} \right). \quad (5.13)$$

If the temperature $T$ decreases in the region with small supercooling $\Delta T$, $\Delta G^*$ decreases but is still large (Figure 5.15a); the nucleation rate $\dot{N}$ shall increase until it reaches a maximum at some intermediate temperature (say $T_{\text{int}}$). Beyond this point, in the region where the supercooling $\Delta T$ is large, the nucleation rate shall decrease again as shown in Figure 5.15b.

The nuclei (clusters) can grow by ripening and coalescence. In the former
case, the primary driving force is the concentration gradient due to different vapor pressures of the different nuclei [125]

\[ p_r = p_0 \exp \left( \frac{2\gamma \Omega}{r k T} \right), \quad (5.14) \]

\[ N_r = N_0 \exp \left( \frac{2\gamma \Omega}{r k T} \right), \quad (5.15) \]

where \( \Omega \) is the atomic volume, \( N_r \) is the adatom concentration for clusters with a radius \( r \), \( p_r \) is the vapor pressure over the cluster. \( p_0 \) and \( N_0 \) correspond to the situation where there are no clusters (i.e. \( r \to \infty \)). Again, the bigger clusters will grow at the expense of smaller ones. In the case of coalescence, two or more clusters shall combine with each other in order to reduce the total energy. At some point, these cluster islands touch each other and a film forms.

If the growth is primarily diffusion-controlled, the growth rate \( \dot{r} \) is given by [125]

\[ \dot{r}^4 \propto \frac{1}{T} \exp \left( \frac{-\Delta G_s}{kT} \right). \quad (5.16) \]

The exponential term often dominates; and the growth rate \( \dot{r} \) shall decrease by decreasing temperature \( T \).

Also during the initial step, some Si atoms are replaced by carbon. This might have happened within the first few monolayers. Since Si is also deposited at this step, the process actually converts the pure Si planes in the substrate into an interfacial SiC buffer layer. The C and Si adatoms rearrange themselves, nucleate and grow into a single crystalline SiC film. To understand why this occurs, one needs to reexamine the over-simplified surface energy term in Equation 5.10.
Clearly for heteroepitaxy, there are three different surface or interfacial energies: i) the interfacial energy $\gamma_{ns}$ is associated with nucleus/substrate interface, ii) the surface energy $\gamma_{ng}$ for nucleus/gas, and iii) the surface energy $\gamma_{sg}$ for substrate/gas. They are related by Young’s equation

$$\gamma_{ns} = \gamma_{sg} - \gamma_{ng} \cos \theta,$$  \hspace{1cm} (5.17)

where $\theta$ is the contact angle. Hence, for heteroepitaxy, the second term in Equation 5.10 should be modified as

$$\Delta G_{\gamma} = 2\pi r^2 \gamma_{ng} + \pi r^2 \gamma_{ns} - \pi r^2 \gamma_{sg} = \pi r^2 \gamma_{ng}(2 - \cos \theta) \neq \pi r^2 \gamma. \hspace{1cm} (5.18)$$

For homoepitaxy, one can easily find that $\theta = 0$, $\gamma_{ns} = 0$, $\gamma_{ng} = \gamma_{sg} = \gamma$, and $\Delta G_{\gamma} = \pi r^2 \gamma$. Thermodynamics shows that the surface energy decreases with increasing temperature by [125]

$$\frac{d\gamma}{dT} = -\frac{S_s}{A'}, \hspace{1cm} (5.19)$$

where $S_s$ and $A$ stand for entropy of the surface and surface area, respectively. The interfacial energy $\gamma_{ns}$ is a combined property of the nucleus and the substrate. Parallel epitaxy, when the nucleus has the same orientation as the substrate, often gives a lower interfacial energy $\gamma_{ns}$ [94]. Hence, these nuclei are more stable than the disoriented ones. The lateral growth of the stable nuclei would also be faster in order to reduce the interfacial energy.

From this energy stand point, a single crystal buffer layer could form if the
growth conditions are right for the initial step. A higher growth temperature is often used in the second step to ensure a higher growth rate. Since it is homoepitaxy by nature, growth becomes much easier. The strain due to lattice misfit is primarily released by misfit dislocations. Still, microtwins, stacking faults and many other planar defects prevail in the epilayer.

But why are the SiC films grown on Si(111) substrates single crystalline, while those on Si(100) are polycrystalline?

Following the treatment given by Tu et al. [125], the surface energy (with respect to gas) is the excess potential energy necessary to break certain bonds. Hence, it depends on the orientation. By using Lennard-Jones potential, the authors estimated that $\gamma_{111} : \gamma_{100} : \gamma_{110} = 0.212 : 0.224 : 0.235$, for a simple cubic crystal. Here $\gamma_{111}$ stands for the surface energy of (111) plane and so on. As a result, the surface energies $\gamma_{ng}$ (for SiC nuclei) and $\gamma_{sg}$ (for Si substrate) are smaller for (111) surface than those for (100). The surface energy term in Equation 5.18 is also smaller in the case of (111) planes. Hence, Si(111) substrate might be more favorable to growth single crystal SiC films.

5.5 Summary on SiC Epitaxy on Si Substrates

Since it is important to precisely control and measure the substrate temperature during epitaxial growth, a simple statistical experiment was carried out. All factors, including the susceptor, grid and power levels, were found to have great effects on the substrate temperature. With a predetermined grid and susceptor, the temperature increases controllably with increasing power.
The two-step growth procedure was adopted for SiC epitaxy on Si(100) substrate. First, the chamber was baked around 1200°C for 10 min, while the carrier gas (a mixture of 8% H2 and 92% Ar) was flowing. Many different parameters were tried. The initial temperature was varied from 1000°C to 1275°C and the system was maintained at these temperatures for either 2 minutes or 5 minutes. The flow rates of the carrier gas and HMDS were FL3 = 2 slpm and FL5 = 5 sccm, respectively. The pressure during growth was kept constant at 100 Torr. The second step was fixed at 1300°C for 30 min. The XRD results show that the films are polycrystalline with two major SiC peaks—(111) and (200)—besides the (400) peak of the Si substrate.

Films grown on Si(111), both by two-step growth and one-step growth, exhibited only one SiC(111) peak besides Si(111) peak from the substrate in all XRD measurements. This indicates the films are single crystalline.

The morphology of these epilayers is comparable to what has been published in the literature.

A few GaN films were also grown on Si(111) with a SiC buffer layer using ammonia and TMG. XRD pattern clearly shows (111) peaks of Si, SiC and GaN. It indicates that GaN films are most likely single crystalline and epitaxial with respect to SiC and Si.

The benefit of the two-step growth procedure could possibly be explained by considering the interfacial energy and total energy change during the formation of a nucleus. A lower temperature for the initial step would provide a high nucleation rate and low growth rate; this is also the key to the buffer layer formation.
Part III

FIB and TEM Investigations of Ti Ohmic Contacts to SiC
Chapter 6

TEM Results on Ti Contacts

Dozens of site-specific TEM foils were prepared by FIB in situ liftout technique. Sample A is an as-deposited Ti contact to SiC with a top TaSi$_2$ diffusion barrier. The growth conditions (BQ343-08, Cab 100207) are similar to those described in Table 2.2 (page 16). Some of these samples were then exposed to a rapid thermal anneal (RTA) at 1000°C for 5 seconds; these are labeled B. The layered structure is TaSi$_2$(400 nm)/Ti(100 nm)/SiC for both samples. FIB and TEM results of these samples will be presented and compared in the next two sections (§6.1–§6.2).

One section (§6.3–§6.6) will be devoted to each of the four samples C–F (Cab 101607), which are more complex and each has a different annealing history (see Table 6.1). On top of the TaSi$_2$/Ti/SiC as in the above two samples, there are four more layers—Au/Ti/TaSi$_2$/Ti. The results will also be compared at the end of this chapter (§6.6.1). The diffusion aspect will be discussed in the next chapter.
Table 6.1: The multi-layer structure and annealing history of all the samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Layers</th>
<th>Annealing History</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>TaSi₂/Ti/SiC</td>
<td>as-deposited</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>1000°C for 5s</td>
</tr>
<tr>
<td>C</td>
<td>(Au/Ti/TaSi₂/Ti)</td>
<td>1h annealed: 650°C</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>1h at 650°C and 4h at 600°C</td>
</tr>
<tr>
<td>E</td>
<td>+(TaSi₂/Ti/SiC)</td>
<td>10h annealed</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>50h annealed</td>
</tr>
</tbody>
</table>

6.1 Sample A: As-deposited

SEM/FIB. Several TEM specimens were prepared for each sample. They are labeled as A3, where the letter (eg. A) stands for different samples, and the single digital is just a serial number for each specimen. A typical SEM image after AutoTEM in the FIB is shown in Figure 6.1a, where the multi-layer structure is clearly revealed. Besides the small bright dots from redeposition of Pt, the surface is smooth and clean. The specimens are ready for TEM examination when they are transparent to the electron beam.

Figure 6.1: Typical SEM images of the as-deposited sample A taken in the FIB with a magnification of (a) 7000x and (b) 350x.
FIB *in situ* liftout is way more difficult than it sounds. Figure 6.1b showcases 11 tries out of more than 30 on sample A. Initially, carbon tape was used to mount the sample on the SEM stub, which caused significant drift under the ion beam. As a result, Pt deposition and ion beam milling were both very difficult. This problem was partially solved by using silver paste instead. Another major problem of the system is that the micromanipulator is not very stable. For example, it may jump clockwise when it is rotated in the opposite direction. Certain procedures were also refined to avoid the collision of the membrane with its surrounding. Nevertheless, the success rate has increased to 90–100% now that INLO has been done at least once weekly for more than one year.

![Figure 6.2](image)

**Figure 6.2:** Typical STEM images of the as-deposited sample (A3).

**STEM-HAADF Imaging.** After carefully aligning the microscope, the region of interest was located and STEM images were recorded, as shown in Figure 6.2a. Only the very top part of specimen is transparent to the electron beam; fortu-
nately, this is also the desired ROI. Different camera lengths (CL) were used for the STEM images; however, no significant difference was found. Hence, the CL was fixed at 250 mm. At higher magnifications (Figure 6.2b), one can see the multi-layer structure more clearly and with a better resolution and contrast than those of an SEM image. Moreover, just as explained earlier in section §3.3, regions with heavier elements are brighter in the HAADF image, and vice versa. One can guess that the SiC substrate corresponds to dark layer at the very bottom in Figure 6.2b. The grey layer above it is most probably the Ti layer. The TaSi$_2$ layer is next up and appears very bright in the image. The very top layer is the Pt deposited in the FIB to protect the surface. However, XEDS data would be more reliable on the compositional details.

**XEDS Point Scan.** As usual, at least one point scan was obtained from each layer. A typical point scan in the TaSi$_2$ layer is shown in Figure 6.3a; the spectrum was collected from the point indicated by the small circle in the insert. The major peaks can be labeled as Ta-L and Si-K. Moreover, a simple quantification analysis shows that the Ta/Si ratio is about 28%/72% $\simeq 0.39$ (Figure 6.3b). The two small peaks around 6.4 and 7.1 keV belong to Fe-$K_{\alpha}$ and $K_{\beta}$, respectively. Their presence is a surprise and they could be attributed to the Tecnai pole piece.

---

1 The error of XEDS quantification can be attributed to several factors. i) Assume the X-ray peaks have a Gaussian distribution with an integrated intensity of $N$, then the standard distribution is given as $\sigma = \sqrt{N}$. For a 99.7% confidence or $\Delta N = 3\sigma$, the error can be estimated by $\text{Error} = \mp 300/\sqrt{N}$ (\%). [113]. One can collect the point scan for a long time to reduce this statistical error. For example, if the intensity is 10000 counts for 4 min, the error is about $\pm 3\%$. However, one can only use a rather short live time for a line scan; if the intensity is 1000, then the error is $\pm 9.5\%$. ii) There are also possible errors for the $k$-factors. iii) Some peaks might overlap, which shall introduce new errors. However, it is impossible to estimate the error due to the lack of standards. I would say the error for a typical point scan is a few percent; the error for a line scan is slightly larger.
6.1. **Sample A: As-deposited**

![Typical XEDS spectrum and quantification result](image)

*(a)*

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Uncertainty %</th>
<th>Correction</th>
<th>k-Factor</th>
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</thead>
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<td>0.000</td>
<td>100.000</td>
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<td>71.563</td>
<td>0.324</td>
<td>0.977</td>
<td>1.000</td>
</tr>
<tr>
<td>Fe(K)</td>
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<td>0.301</td>
<td>0.015</td>
<td>0.994</td>
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</tr>
<tr>
<td>Ta(L)</td>
<td>71.224</td>
<td>27.797</td>
<td>0.245</td>
<td>0.752</td>
<td>5.103</td>
</tr>
</tbody>
</table>

*(b)*

**Figure 6.3:** Typical XEDS (a) spectrum and (b) quantification result obtained from the point indicated by the circle in the TaSi$_2$ layer (specimen A3).
A point scan from the Ti layer (Figure 6.4a) shows a few strong Ti-K and weak Si-K peaks, while the atomic concentration of Ti and Si are about 94% and 2.5%. Traces of Ga and Cu are also found in the spectrum. The presence of Ga is because this ion was implanted in the FIB; Cu probably originates from the TEM copper half-grid which was used to mount the FIB-INLO membrane.

**Figure 6.4:** Typical XEDS point scan: (a) spectrum and (b) quantification result from the Ti layer (specimen A3).

Considering the additional spectra from the Pt layer and the SiC substrate (not shown here), the multi-layer structure (from SiC at the bottom) can be iden-
tified as: I) SiC substrate, II) Ti contact layer, III) TaSi₂ diffusion barrier, and IV) protection Pt layer deposited in the FIB. This also confirms our guess based on a simple HAADF image.

**XEDS Line Scan.** With the above information at hand, several line scans were then performed for each specimen. For example, 30 data points (i.e. spectra) were collected along the line with a length of 900 nm (as shown in Figure 6.5a). Since it usually takes a long time to collect a line scan, sample drift must be corrected with respect to the square indicated in the HAADF image.

From the above point scan results, the major elements in the sample were determined to be C, Pt, Si, Ta and Ti. The line scan data were processed by *EsVision*, which was also used to collect the data. Many so-called *k*-factors are also built in the program. Using Si as a reference element, the *k*-factors are of 5.644 for Au-L peak, 6.426 for C-K, 2.014 for O-K, 5.545 for Pt-L, 5.103 for Ta-L, and 1.272 for Ti-K, respectively. Since the atomic weight of each element is known, the program can compute the atomic concentration for each data point automatically. However, there are artifacts, as shown in Figure 6.5b, such as the Pt counts in the TaSi₂ layer and the Ta counts in the top protection Pt layer deposited in the FIB. The program was not able to separate the overlap of Pt-Lₐ and Ta-Lᵦ peaks (see Table 6.2). Nevertheless, one can estimate the thickness of this silicide layer to be roughly 640 nm from HAADF image or 630 nm from the full width at half maximum (FWHM) of Ta counts.

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**ii** Sometimes in the HAADF image for a line scan, no scale bar could be saved. It is an annoying software glitch. However, one can still use the line length as a scale reference.

**iii** When its vendor Emispec Systems, Inc. was acquired by FEI Company, the name has been changed to TIA (Tecnai Imaging & Analysis).
Figure 6.5: Typical XEDS line scan results across all the layers in specimen A3: (a) HAADF image, (b) atomic percent of some major elements.
Note that O counts are very close to zero throughout all the layers. C is present in the top Pt layer and SiC substrate. The composition within the TaSi$_2$ layer is not uniform since the counts of Ta and Si vary with position.

Table 6.2: Some major XEDS and EELS peaks.

<table>
<thead>
<tr>
<th>Element</th>
<th>EELS Edges (eV)</th>
<th>XEDS Characteristic Peaks (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>K 284</td>
<td>K (a,b) 0.283</td>
</tr>
<tr>
<td></td>
<td>K 532</td>
<td>K (a,b) 0.531</td>
</tr>
<tr>
<td></td>
<td>L$_{2,3}$ 99, K 1839</td>
<td>K$_{a}$ 1.740</td>
</tr>
<tr>
<td></td>
<td>L$_{2,3}$ 456</td>
<td>K$_{a}$ 4.508</td>
</tr>
<tr>
<td>O</td>
<td>L$_{2,3}$ 708</td>
<td>K$_{a}$ 6.400</td>
</tr>
<tr>
<td></td>
<td>L$_{2,3}$ 931</td>
<td>K$_{a}$ 8.041</td>
</tr>
<tr>
<td></td>
<td>L$_{2,3}$ 1115</td>
<td>K$_{a}$ 9.251</td>
</tr>
<tr>
<td>Si</td>
<td>O$<em>2$ 45, M$</em>{4,5}$ 1735</td>
<td>L$_{\alpha 1}$ 8.145</td>
</tr>
<tr>
<td></td>
<td>M$_{4,5}$ 2122</td>
<td>L$_{\alpha 1}$ 9.441</td>
</tr>
<tr>
<td></td>
<td>O$<em>3$ 54, M$</em>{4,5}$ 2206</td>
<td>L$_{\alpha 1}$ 9.711</td>
</tr>
<tr>
<td>Ti</td>
<td>L$_{2,3}$ 456</td>
<td>K$_{\beta}$ 1.838</td>
</tr>
<tr>
<td></td>
<td>L$_{2,3}$ 456</td>
<td>K$_{\beta}$ 4.931</td>
</tr>
<tr>
<td></td>
<td>L$_1$ (a,b) 0.530</td>
<td>L$_{\beta}$ 7.059</td>
</tr>
<tr>
<td></td>
<td>L$_{2,3}$ 1115</td>
<td>L$_{\beta}$ 8.907</td>
</tr>
<tr>
<td>Fe</td>
<td>L$_{2,3}$ 78</td>
<td>L$_{\beta}$ 10.263</td>
</tr>
<tr>
<td></td>
<td>L$_{2,3}$ 90</td>
<td>L$_{\beta}$ 10.263</td>
</tr>
<tr>
<td>Cu</td>
<td>L$_{2,3}$ 931</td>
<td>L$_{\beta}$ 10.263</td>
</tr>
<tr>
<td>Ga</td>
<td>L$_{2,3}$ 1115</td>
<td>L$_{\beta}$ 10.263</td>
</tr>
<tr>
<td>Ta</td>
<td>O$<em>2$ 45, M$</em>{4,5}$ 1735</td>
<td>L$_{\beta 1}$ 9.341</td>
</tr>
<tr>
<td></td>
<td>M$_{4,5}$ 2122</td>
<td>L$_{\beta 1}$ 11.069</td>
</tr>
<tr>
<td></td>
<td>O$<em>3$ 54, M$</em>{4,5}$ 2206</td>
<td>L$_{\beta 1}$ 11.439</td>
</tr>
<tr>
<td></td>
<td>L$_{\beta 2}$ 9.649</td>
<td>L$_{\beta 2}$ 11.249</td>
</tr>
<tr>
<td></td>
<td>O$<em>3$ 54, M$</em>{4,5}$ 2206</td>
<td>L$_{\beta 2}$ 11.582</td>
</tr>
</tbody>
</table>

Figure 6.6 shows a more detailed line scan across the Ti layer. The line spans 200 nm with 40 data points. In other words, one spectrum was collected every 5 nm from the starting point (see the cross in the HAADF image). The result is consistent with the above rough line scan and point scan data. The Si signal is quite weak in the middle of the Ti layer (between points B and C). This layer has an estimated thickness of 65–70 nm based on the HAADF image or 75 nm according to the FWHM of Ti-K X-ray counts. However, the Ti signal spreads much wider (about 120 nm between A and D). Two interfaces are clearly seen in the HAADF image (Figure 6.6a), one between A and B, and one between C and D. Ti concentration (at%) is above 4% between data points #5 and #28, which gives a thickness of 115 nm. In summary, not only does Si diffuse into the Ti layer from neighboring TaSi$_2$ and SiC layer, but Ti also counter-diffuses.
Figure 6.6: Typical XEDS line scan results across the Ti layer in specimen A3: (a) HAADF image, (b) atomic percent of some major elements.
By the way, the STEM and XEDS were usually performed with an extraction voltage of 4.5 keV, gun lens 1, spot size of 7–10 (nanoprobe) and #3 C2 aperture (100 μm). The stage was tilted to α = 15°.

Electron Spectroscopic Imaging (ESI). In the EFTEM and ESI mode, a spot size of 1–2 (microprobe) was used and the stage was not tilted. Figure 6.7d shows a zero-loss image of a ROI at the TaSi₂/Ti/SiC interface. Within the bright regions of Si and Ti map (Figure 6.7a–b), there is a higher concentration for these elements. For example, the upper-left corner of the Si map is very bright, which corresponds to the SiC region where there is a high Si concentration. Ta map (not shown) is not reliable, partially because of the high atomic number of Ta. Hence it has a high “critical ionization energy” $E_c$ (see also page 50) and a very low EELS signal. After Color Mix-ing the Si and Ti map, a Red(Ti)-Green(Si)-Blue(Ti) map was obtained (Figure 6.7c).iv The mixed RGB elemental map reveals not only the multi-layer structure, but also the chemical contents for each layer.

### 6.2 Sample B: Rapid Thermally Annealed

**SEM/FIB.** In a typical SEM image of sample B (Figure 6.8a), one can see that it is not as smooth as that of A (Figure 6.1b). There are many small white patches on the surface of this annealed sample. At high magnification (Figure 6.8b), they appear as (distorted) hexagonal pits with a size about 1 μm surrounded by some

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iv There was a software glitch when I recorded the Si and Ti maps, which have different sizes–511 pixels by 511 pixels for Si and 510x510 for Ti. Hence, the Gatan DigitalMicrograph program couldn’t be used to mix these maps. I used ImageMagick to resize both images to 512x512 as Si.pdf and Ti.pdf. They are mixed by the command “convert Ti.pdf Si.pdf Ti.pdf -combine TiSiTi.pdf”. In the final result, green stands for Si; both red and blue are assigned to Ti.
Figure 6.7: Elemental map of specimen A3: (a) Si map, (b) Ti map, (c) RGB map and (d) Zero-Loss image (see text for details).
white shadow.

![Figure 6.8: Typical SEM images of sample B: (a) 350x and (b) 7000x.](image)

A spectrum was obtained within one of the pits (Figure 6.9a), where the major elements are shown to be Si, Ta and Ti. A map of them is shown in Figure 6.9b. It seems that there is a lower concentration of Ta and Si in the craters, which is also evident in the line scan (Figure 6.9c). Moreover, the density of these pits is so high that they can not be related to micropipes in the SiC substrate.
Figure 6.9: a) A typical XEDS spectrum obtained from a hexagonal pit in sample B. (b) An elemental map, and (c) a line scan of the same sample.
XEDS Point Scan. In a typical STEMF image of the annealed sample (see the insert to Figure 6.10), one can also see a layered structure. There might be some precipitates in both the TaSi$_2$ layer (bright dots) and the Ti layer (dark dots). The XEDS spectrum from a gray point within the TaSi$_2$ layer is similar to that of the as-deposited sample. The Ta/Si ratio is now estimated as $31/68 \approx 0.46$. This value and that of the as-deposited sample (i.e. 0.30) are both smaller than the stoichiometric value 0.50 for TaSi$_2$.

![XEDS Spectrum and Quantification Result](image.png)

**Figure 6.10:** Typical XEDS point scan: (a) spectrum and (b) quantification result obtained from a gray point in the TaSi$_2$ layer (specimen B6).
**Figure 6.11:** Typical XEDS point scan: (a) spectrum and (b) quantification result obtained from a white point in the TaSi$_2$ layer (specimen B6).

An XEDS scan from a white point within the same layer gives a Ta/Si ratio of $38/60 \approx 0.63$ (Figure 6.11). It indicates that there is an excess of Ta compared with the stoichiometric silicide TaSi$_2$. Nevertheless, it is consistent with the HAADF image, where the heavy element Ta appears brighter than the light element Si. By the way, the scale bar is 50 nm for all the point scans in specimen B6.
6.2. Sample B: Rapid Thermally Annealed

The spectrum in the Ti layer is very different from that of as-deposited sample since the Si signal is now very strong. Quantification of a typical scan obtained from a gray point shows that the atomic concentrations of Ti and Si are about 56% and 40%, respectively (Figure 6.12). The origins of Cu, Fe and Ga peaks were explained before (page 107). Since these peaks are primarily due to the FIB and TEM systems, they will be called system peaks from now on.

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**Figure 6.12:** Typical XEDS point scan: (a) spectrum and (b) quantification result obtained from a gray point in the Ti layer (specimen B6).

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Uncertainty %</th>
<th>Detector Correction</th>
<th>k-Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (K)</td>
<td>27.160</td>
<td>39.565</td>
<td>0.204</td>
<td>0.977</td>
<td>1.000</td>
</tr>
<tr>
<td>Ti (K)</td>
<td>65.315</td>
<td>55.788</td>
<td>0.343</td>
<td>0.985</td>
<td>1.272</td>
</tr>
<tr>
<td>Fe (K)</td>
<td>0.171</td>
<td>0.125</td>
<td>0.027</td>
<td>0.994</td>
<td>1.434</td>
</tr>
<tr>
<td>Cu (K)</td>
<td>3.598</td>
<td>2.316</td>
<td>0.082</td>
<td>0.997</td>
<td>1.688</td>
</tr>
<tr>
<td>Ga (K)</td>
<td>3.753</td>
<td>2.202</td>
<td>0.098</td>
<td>0.998</td>
<td>1.945</td>
</tr>
</tbody>
</table>
Chapter 6. TEM Results on Ti Contacts

Figure 6.13: Typical XEDS point scan: (a) spectrum and (b) quantification result obtained from a dark point in the Ti layer (specimen B6).

The atomic concentrations of a dark point in this area is 40% and 47% for Ti and Si, respectively, which gives a Ti/Si ratio of 0.85 (Figure 6.13). This is consistent with the HAADF images, where Si should look darker than the heavier element Ti. The high concentration of Si indicates that there must be substantial diffusion of Si into Ti layer for the rapid thermally annealed sample.
Figure 6.14: Typical XEDS point scan: (a) spectrum and (b) quantification result obtained within the SiC layer (specimen B6).

Figure 6.14a shows a typical spectrum obtained from a spot in the SiC layer. The C-K and Si-K peaks dominate the rest of the peaks. Quantification renders the concentrations of C and Si, which are 69 at% and 31 at%, respectively. The deficiency of Si can be attributed to Si out-diffusion into the neighboring Ti layer and silicide formation.
Chapter 6. TEM Results on Ti Contacts

XEDS Line Scan. A line scan (800 nm and 40 points) across all the layers of the annealed sample is shown (Figure 6.15). Based on the quantification results (see also the point scan), the layers can be identified as: I) SiC, II) Ti, III) TaSi$_2$, and IV) Pt. Again, there are systematical artifacts, such as Pt counts within the TaSi$_2$ layer, because of the overlap of Pt-L$_\alpha$ and Ta-L$_\beta$ peaks. The thickness of the TaSi$_2$ layer is estimated to be $\approx$570 nm based on the HAADF image, and 560 nm from FWHM of Ta counts (data points #5–32). The modulation of Ta counts is correlated to contrast change of the TaSi$_2$ layer in the STEM image. There is a higher concentration of Ta in the regions that looks brighter in the HAADF image. Moreover, the Si count reaches a local minimum when the Ta count peaks.

A more detailed line scan (250 nm and 50 points) across the Ti layer for the annealed sample is shown in Figure 6.16. The Si signal is always strong throughout this Ti layer (except 3 data point in the middle). If we link the HAADF image and spectra in EsVision and examine closely, we find that the valley of the Si count corresponds to the points where they appear dark in the Ti layer. This might also be the end of the diffusion path of Si from the substrate into the neighboring Ti layer. Ta concentration is also relatively high throughout this Ti layer, with only a few exceptions. The thickness of Ti(Si) layer is estimated to be 120 nm based on the HAADF image or 115 nm on FWHM of Ti counts. Last, oxygen concentration is virtually zero in the Ti and SiC layers.

ESI. Figure 6.17e shows a typical EFTEM zero-loss image of the TaSi$_2$/Ti/SiC interface. It is complementary to the HAADF image of the same area (see Figure 6.15a, for example). The darker spots within the Ti layer in HAADF image appear
Figure 6.15: An XEDS line scan from the annealed specimen B4: (a) HAADF image, (b) atomic percent of some major elements.
Figure 6.16: Typical XEDS line scan results across Ti layer in specimen B4: (a) HAADF image, (b) atomic percent of some major elements.
6.2. Sample B: Rapid Thermally Annealed

brighter in the ZL image. Elemental map (ESI) of C, Si and Ti are shown in Figure 6.17a–c; there is a higher concentration of each element in the brighter region. A RGB map (Figure 6.17d) was generated by overlap of these three maps and assigning Red, Green and Blue to C, Si and Ti, respectively. Ti (in blue) is predominant in the middle layer, where there are also Si signals (in green). Si is very strong both in the SiC layer and in the TaSi$_2$ layer. However, the C signal is hardly seen in this RGB map although there is a clear contrast in the carbon map.

![Figure 6.17: (a) C-, (b) Si-, (c) Ti-, (d) RGB map, and (e) ZL image of specimen B6.](image)
6.2.1 Comparison between Samples A and B

The results are summarized as follows for samples A and B.

**SiC substrate.** Oxygen was not detected in the SiC substrate in the as-deposited sample A nor in the RTA sample B (see Figure 6.10).

**Ti contact layer.** There exist two clear interfaces on both sides of the Ti contact layer for both samples. The lower interface is between the SiC and Ti layers, where C and Si were found besides Ti. Although no HRTEM lattice images were attempted for titanium silicides and/or carbides, their presence has been demonstrated not only in our work by STEM, XEDS and ESI, but also by numerous publications by other investigators (eg. [52, 81, 98]). In the upper interface between the Ti and TaSi$_2$ layers, high concentrations of Si, Ta and Ti were detected.

In the very center of this Ti layer (between the above two interfaces), the Si signal is negligible for the as-deposited sample A (eg. between points B and C in Figure 6.6). However, the Si and Ta signals are very strong throughout the Ti layer for the annealed sample B except at a few data points (see Figures 6.16). This indicates a substantial diffusion of C, Si and Ta into the Ti layer.

**TaSi$_2$ diffusion barrier.** No C, O, or Ti was found in the as-deposited sample A (see Figure 6.5). However, a few percent of O and Ti (but no C) were found in the RTA sample (see Figure 6.15). This suggests a stronger Ti out-diffusion even when the sample was rapid annealed at 1000°C for just 5 seconds.

The SEM images show that the as-deposited surface is rather smooth; while there are hexagonal pits on the surface of the RTA sample.
6.3 Sample C: 1 Hour Annealed

**SEM/FIB.** As mentioned at the beginning of this chapter, samples C–F have four more layers than samples A and B. Moreover, sample C was annealed at 650°C for 1 hour in air; sample D was further annealed for an additional 4 hours at 600°C; sample E was further annealed for a total duration of 10 hours; and sample F was annealed for a total time of 50 hours. The SEM images of top surface for all these samples (C–F) are nearly the same; two typical images are shown in Figures 6.18a and 6.18b. There are numerous bright wires that form a complex web on the gold surface. The diameter of these wires is about 1–2 µm.

Several XEDS spectra (not shown here) were carried out on the smooth Au surfaces and on the wires. They have an almost identical composition—Au with traces of Si (and O). Hence, the contrast in these top-view SEM images is very likely topographical contrast. When two trenches were cut from both sides of a membrane, a cross-section view could be obtained (see Figure 6.18c). Many dark features can be seen underneath the Au wires, which implies lighter elements as their constituents. The size of these dark features is too small so that no XEDS measurements could be taken in the FIB.

**STEM-HAADF.** A typical HAADF image clearly shows the multi-layer structure (Figure 6.19). The bright regions at the bottom and either side are due to the greater thickness. Thin area in the middle looks brighter; this indicates that there are heavier elements (light elements will appear darker in the image).

STEM-HAADF images might be very simple; but still, one needs to be careful with these TEM results. On May 29, 2008, I accidently discovered that the
Figure 6.18: Typical SEM images of as-annealed sample C: top view at (a) 250x, (b) 5000x, and (c) a cross-section view after AutoTEM.
scale bar of the STEM images was wrong. In Figure 6.20, the scale bar is 500 nm. Hence, the Au layer (very bright layer with embedded dark feature) can be estimated to be merely 750 nm instead of the true value of 2 µm.

![Figure 6.19: STEM HAADF images of specimen C4 at 8500x.](image)

![Figure 6.20: Another STEM image for specimen C3 at magnification of 12 kx. Note the wrong scale bar.](image)
**XEDS Point Scan.** As shown in the inserts to Figure 6.21, the very top grey layer was Pt deposited in the FIB to protect the surface. The labeling for each layer is a direct result from all the following XEDS point scans for this specimen C3. In the bright gold layer underneath, there are some dark irregular patches. A typical point scan spectrum from the bright region within the Au layer (Figure 6.21a) shows that it consists of mainly Au. Signals of Cu and Fe (system peaks) were explained in the previous sections. On the other hand, the spectrum obtained from the dark patches gives 29 at% of O and 71 at% of Si (Figure 6.21b). Only a small Au-M peak is visible besides the system peaks of Cu, Fe and Ga.

At this magnification (68 kx), the top Ti layer underneath Au is too thin for an XEDS point scan.

Figure 6.22a shows a typical point scan spectrum from the upper TaSi$_2$ layer. Here, one can find strong O-K (30 at%) and Au-M peaks besides the major Si-K (46 at%) and Ta-L (23%) peaks. Note that the Ta/Si ratio is now very close to the stoichiometric value 0.50. The high oxygen concentration indicates a substantial inward-diffusion of oxygen from Air into this TaSi$_2$ layer through the top Au layer. This is an alarming result!

The Au-M peak is missing of the spectrum from the lower TaSi$_2$ layer below the next Ti layer (Figure 6.22b). The atomic concentration of O, Si, and Ta are 8%, 56% and 31%, respectively. Now the Ta/Si is 0.55, greater than the stoichiometric value 0.50; the deficiency of Si suggests that it should have diffused into two adjacent Ti layers.
Figure 6.21: Typical XEDS point scans in the Au layer for specimen C3 from (a) a bright spot, and (b) a dark spot.
Figure 6.22: Typical XEDS point scans for specimen C3 within (a) the upper and (b) the lower TaSi₂ layer.
Figure 6.23a shows a typical point scan obtained from the Ti contact layer. The magnification of the HAADF image is 270 kx and scale bar is 100 nm. There are strong Si-K (37 at%) and Ti-K (50 at%) peaks; it suggests the formation of titanium silicide phase. System peaks of Cu, Fe and Ga are also visible.

Figure 6.23b show a typical point scan obtained from the SiC substrate. The atomic concentration of C and Si are 65% and 28%, respectively. Again, there is a deficiency of Si; some of it might have diffuse outward from the SiC substrate into the Ti contact layer above.

Based on these point scans, the multi-layer structure (see the insert to Figure 6.23b) has been demonstrated to be: I) the SiC substrate, II) Ti contact layer, III) the lower TaSi₂ diffusion barrier, IV) a thin strip of Ti (the middle Ti layer), V) the upper TaSi₂ layer, VI) the top Ti layer, VII) a thick Au layer, and VIII) the top protection Pt layer deposited in the FIB.

**XEDS Line Scan.** Figure 6.24 shows a line scan (700 nm and 35 data points) across the top TaSi₂ layer and the quantification output. There are substantial amounts of Au, Si and Ta at the Ti interface between the top Au and TaSi₂ layers. This silicide layer has three distinguishable regions, a dark one in between two bright sub-layers. Oxygen at a atomic concentration greater than 10% exists in the whole layer; this suggests a strong inward diffusion of oxygen, which also penetrates the thick Au layer. Within the dark sub-layer, one can see greater amounts of Si and O, but Ta concentration is relatively low; the composition is close to what have been found in the point scan from the dark patches within the Au layer (see Figure 6.21b in page 130). Once again, the chemical contents are consistent with the HAADF image contrast.
Figure 6.23: Typical XEDS point scan for specimen C3 within (a) the Ti contact layer, and (b) SiC substrate.
Figure 6.24: Typical XEDS line scan results across the top TaSi$_2$ layer in specimen C3: (a) HAADF image, (b) atomic percent of some major elements.
Following the next thin Ti layer, there is another TaSi$_2$ layer, whose line scan (800 nm and 40 data points) is shown in Figure 6.25. The oxygen and titanium concentrations are negligible within this layer. However, there is a high concentration of Si and Ta throughout the Ti contact layer with no exceptions. Recall the results of RTA sample B (page 121), there exists a thin region in the middle of the Ti contact layer where Si and Ta concentration are low. This difference suggests that 1h annealing shall promote further inward diffusion of Ta or Si and outward diffusion of Si into this Ti layer. Only the C and Si concentrations are significant within the SiC substrate; this ought to be.

**Figure 6.25:** Typical XEDS line scan across the lower TaSi$_2$ layer in specimen C3.
6.4 Sample D: 5 Hour Annealed

**XEDS Point Scan.** Figure 6.26a shows a point scan spectrum obtained within the dark region between the Au and top TaSi$_2$ layer, which is similar to the one from the Au layer for specimen C3 (Figure 6.21b). Both O and Si show strong K peaks. However, there is also a significant C-K peak (to the left of O-K) for specimen D4, which does not appear in specimen C3. A small Au-M peak is also visible besides (the system peaks of) Cu, Fe and Ga.

The spectrum from the lower TaSi$_2$ layer (Figure 6.26b) is also slightly different from that of specimen C3 (Figure 6.22b). Au-M peaks are now present for specimen D2, which do not appear in specimen C3. This suggests a more significant Au inward diffusion for the sample undergone larger annealing. Oxygen does not appear in the point scan for this specimen D2.

**XEDS Line Scan.** Figure 6.27 shows the typical line scan (660 nm for 44 data points) for specimen D2. The results are similar to those of specimen C3 (see Figures 6.24 and 6.25). High concentrations of Au and O are present in the top TaSi$_2$ layer close to the Au side. However, we need to be cautious with the atomic concentration of Au for all these line scans. For example, the Au concentration is 0 for data points 9–14, which is not reasonable. In fact, Figure 6.27a shows the spectrum obtained for data point #11 (indicated by the cross in the insert). Here Au-M peak dominates instead of the Au-L, which is also true for many other data points. Unfortunately, the $k$ factor for Au-M is defined as zero in EsVision (aka TIA). As a result, one has to use the Au-L to generate a might-be-unreliable atomic concentration profile.
Figure 6.26: Typical XEDS point scan for specimen D2 within (a) the top Au and (b) the lower TaSi$_2$ layer.
6.4. Sample D: 5 Hour Annealed

Figure 6.27: Typical XEDS line scan results for specimen D2: (a) a spectrum and HAADF image, (b) atomic percent of some major elements.
EELS spectrum. Since there are a number of heavy elements (eg. Au, Pt and Ta) in these samples it is not easy to perform EELS and ESI unless the specimen is extremely thin. Nevertheless, several EELS spectra were collected for specimen D2, with an extraction voltage of 3.8 keV, gun lens 6, spot size 8–10 (microprobe, 5–6 for heavy elements) and the #2 C2 aperture.

The top Au layer was examined under EFTEM mode carefully (Figure 6.28b), where the bright region appears dark in the STEM HAADF images (Figure 6.28a). The beam positions, when the EELS low-loss and core-loss spectra were recorded, were marked by the two circles (#1 and #2) in both images. Figure 6.28c shows a typical low-loss spectrum obtained from circle #2 with a drift tube of 32 eV, where one can see a plasmon peak around 20 eV and a small hump around 110 eV. The spectrum from circle #1 (in the dark region of the STEM image) is very similar, except that there are additional features at higher values of energy loss. These features are clearly shown in the spectrum obtained with a drift tube of 80 eV (Figure 6.28d), where a visible peak appears around 110 eV and there are two shoulders at 130 eV and 160 eV. These features are due to the presence of Si within the bright regions of the EFTEM image (they are dark in the STEM image). The C edge around 300 eV is evident in the spectrum obtained with a drift tube of 270 eV (Figure 6.28e). With a drift tube of 500 eV (Figure 6.28f), the O edge also shows up. In other words, EELS low-loss and core-loss spectra can confirm that there are mainly C, O and Si within circle #1; this confirms the results obtained by the STEM images and XEDS analyses.

EELS spectra were also recorded from the TaSi$_2$/Ti/SiC region. If one focuses the beam in another circle #1 as indicated in the EFTEM image (Figure 6.29a),
Figure 6.28: (a) STEM HAADF image indicating the spots whose EELS spectra were collected; (b) EFTEM version for specimen D2. (c) EELS spectrum with a drift tube of 32 eV for Si from circle #2. Spectra for circle #1 with a drift tube of (d) 80 eV for Si; core-loss spectra obtained with a drift tube of (e) 270 eV for C and (f) 500 eV for O.
Figure 6.29: (a) A zero-loss image for specimen D2. EELS spectra from circle #1 (indicated in the ZL image) with drift tube of (b) 32 eV for Si and (c) 450 eV for Ti. Spectra from circle #2 with drift tube of (d) 32 eV for Si, and (e) 110 eV for Si and C. (f) Spectrum from circle #3 with drift tube of 32 eV for Si.
where it is inside the Ti layer, a typical low-loss spectrum with drift tube of 32 eV is obtained ((Figure 6.29b). There are a strong peak around 20 eV and a shoulder at 50 eV. The plasmon peaks are compatible to that of a Si standard. In the spectrum obtained with drift tube of 450 eV (Figure 6.29c), one can see a clear Ti edge around 460 eV. The edge around 530 eV is due to O.

The spectrum from circle #2 with drift tube 32 eV, which is in the SiC layer, is slightly different (Figure 6.29d). The peak at 20 eV remains, but the shoulder at 50 eV is gone. However, one can see a small hump around 110 eV, which can be enlarged with a drift tube 110 eV (Figure 6.29e). The peak split around 120 eV can be used to identify Si. The edge around 300 eV energy loss is definitely carbon.

For circle #3, which is in the TaSi$_x$ layer, only a low-loss spectrum was recorded (Figure 6.29f). In this case, there are two shoulders at 40 eV and 50 eV besides the major peak at 20 eV. This can be attributed to the different bonding of Si-Ta from that of Si-Ti or Si-C.

**ESI.** After obtaining the EELS spectra, one can be more confident with ESI, aka elemental maps. An example is given for the bright region in the top gold layer (see the EFTEM image in Figure 6.30e). Because, Au M edge has an energy loss of 2206 eV and it will give a very small intensity, Au O-edge with an energy loss of 54 eV was used to record Au map. It is a surprise that the dark particle in the EFTEM image, which consists mainly of Au, does not appear bright in this Au map as it ought to. However, if one examines the Si peaks closely in Figures 6.28c—d, one can see the strong peak around 20 eV and a small hump around 110 eV. The background around 50 eV is still quite strong, which must
have contributed to the Au (O-edge) map. The O map was obtained for its K-edge (energy loss 532 eV); while Si map was obtained from its L-edge (energy loss of 99 eV). Using the Gatan DigitalMicrograph, one can assign a different color to each of these three elements and obtain a RGB map as shown in Figure 6.30d, where red stands for Au, green for O and blue for Si.

Figure 6.30: Typical elemental maps of (a) Au, (b) O and (c) Si for specimen D2; (d) the resulting RGB (Au-O-Si) map, and (e) zero-loss image of the same region.
SAD. Some selected-area diffraction (SAD) patterns were taken with a camera length of 890 mm and different exposure times. Figure 6.31a shows the diffraction pattern obtained from a Au particle indicated by circle #3 in Figure 6.31d. It is clearly a single crystal. However, the EFTEM bright region (e.g. circle #4) within the Au layer is amorphous (Figure 6.31b). Based on XEDS results, it consists mainly of C, O and Si. The SiC substrate is a 4H single crystal (Figure 6.31c).

![SAD patterns and EFTEM image](image)

**Figure 6.31:** SAD patterns obtained from specimen D2.
6.5 Sample E: 10 Hour Annealed

XEDS Line Scan. The STEM images and XEDS point scans of sample E are very similar to what have been shown for sample D. Figure 6.32 shows a typical line scan (1500 nm for 50 data points) for specimen E3. The two Si peaks in the top Au layer correspond to the two dark regions. Three distinctive Ti layers are also visible. The topmost one resides between the top Au layer and the upper TaSi$_2$ layer, where a thick interface has been formed. Note also the high concentration of Au and O in this region; however, the Ti concentration is negligible. The middle one is between the two TaSi$_2$ layers, where the Ti concentration is merely 2 at% within a 30 nm thick strip. Furthermore, this layer is very wavy. In other word, it is not as abrupt and smooth as that in samples C and D, which was annealed for 1h and 5h, respectively. The lower one is between the second TaSi$_2$ and SiC substrate. The C, Si and Ta (besides Ti) concentrations are relatively high; this result is similar as that of samples C and D.

ESI. From the zero loss image within the Au layer shown in Figure 6.33e, one can see three large dark particles. Again, Au O-edge with an energy loss of 54 eV was used to record Au map. The brightest parts of the Au map coincide with these particles; while O and Si signals are brighter at other places (Figure 6.33a–c). The resulting RGB map is quite reasonable (Figure 6.33d). These results confirm the information that was obtained from the STEM-XEDS mode.
Figure 6.32: Typical XEDS line scan results for specimen E3: (a) HAADF image, (b) atomic percent of some major elements.
Figure 6.33: Typical elemental map of (a) Au, (b) O and (c) Si of specimen E4. (d) The resulting RGB (Au-O-Si) map. (e) A typical zero-loss of the same region.
6.6 Sample F: 50 Hour Annealed

**XEDS Line Scan.** The line scan profile of specimen F5 (2600 nm for 52 data points; Figure 6.34) is very similar to those for samples C–E. Note the C counts in the top Au layer and O in the upper TaSi$_2$ layer. Moreover, O count peaks at the interface between the two TaSi$_2$ layers. This interface appears darker in the HAADF images, which means there exist some light elements in this region. C, Si and Ti dominate in the lower Ti contact layer above the SiC substrate; Ta concentration is also high throughout this thin layer.

![Figure 6.34: A typical XEDS line scan for specimen F5.](image-url)
**ESI.** Figure 6.35 shows typical ESI results of the TaSi$_2$/Ti/SiC interface. There are strong signals of C in the SiC substrate as well as in parts of the Ti layer. Si is everywhere in this region, including in the SiC, Ti and TaSi$_2$ layers (Figure 6.35b). Ti signal is the strongest in the center layer (i.e. Ti layer; Figure 6.35c). The Ta signal is also strongest within the Ti layer instead of within the TaSi$_2$ layer. It is another prove that Ta map is very difficult to obtain and it is possibly erroneous (Figure 6.35d). The C-Si-Ti RGB map and ZL image are also shown in Figures 6.35e and 6.35f, respectively. Some titanium silicide and/or carbides must have also formed during the long annealing process.

![ESI results](image.png)

**Figure 6.35:** Typical elemental map of (a) C, (b) Si, (c) Ti and (d) Ta from specimen F5. (e) The resulting RGB map and (f) zero-loss image of the same region.
SAD. The diffraction patterns are similar to those of sample D (Figure 6.31).

6.6.1 Comparison of Samples C–F

In this section, TEM results for samples C–F, which have been annealed for 1–50 hours, are summarized and compared, including HAADF images, XEDS point and line scans, and ESI. By combining these techniques, the structure of the complex multi-layer Ti alloy contacts to SiC is revealed as follows.

SiC substrate. A few percent of O and Ta are present for samples that have been annealed for at least 1 hour (see Figure 6.27); this is in contrast with the results for the as-deposited sample A and the RTA sample B. A clear interface exists between SiC and Ti in all samples, where one can find C, Si and Ta besides Ti. XEDS spectra and EELS analyses suggest that titanium silicides and/or carbides must have formed.

Ti contact layer. All the elements within the TaSi$_2$/Ti/SiC region, i.e. C, Si, Ta and Ti, are detected throughout the Ti contact layer. This suggests a substantial diffusion of C, Si and Ta into the Ti layer. The oxygen counts can be attributed to “an artifact of the deposition process” according to [78]. Furthermore, the thickness of Ti(Si) is roughly the same 120 nm for all annealed samples.

The lower TaSi$_2$ diffusion barrier. The Ti signal in the TaSi$_2$ is contained within the interface for all samples. In all samples, the oxygen concentration can be neglected. Both C and Au signals are found in sample D (5h annealing) and sample E (10h), but not in sample C (1h) or F (50h). This is not well understood.

The middle Ti layer. This thin Ti layer resides between the two TaSi$_2$ layers. Both Si and Ta are found throughout this layer; these atoms must have diffused from
the adjacent TaSi$_2$ layers.

**The upper TaSi$_2$ and Ti layer.** In samples C–F, there is an additional TaSi$_2$ sacrificial diffusion barrier. A thick interface is formed near the top Au layer, where high concentrations of Au and O can be found.

**Top Au layer.** A typical SEM image shows that there are many cross-linked Au wires with a feature size of 1–2 µm on the surface (see Figure 6.18). The surface looks rather smooth everywhere else. There are also many irregular dark patches underneath these wires, as shown in a typical cross-sectional SEM/TEM image. XEDS and EELS analyses show that these features are mainly comprised of Si, O and/or C, which are all light elements. SAD patterns suggest that this new phase is poly-crystalline; while the Au layer is single crystal.
Chapter 7

Failure Mechanism

Based on the TEM findings presented in the previous chapter, there are many species undergoing diffusion in and/or out the complex contact region. Generally speaking, Au and O diffuse inward; while Si, Ta and Ti shall diffuse in both directions.

7.1 Thermodynamics Approach

But first, let us recall some thermodynamics. Consider a simple reaction, \( aA + bB \rightarrow cC + dD \), where \( a, b, c, \) and \( d \) are stoichiometric coefficients (some real numbers); \( A, B, C, \) and \( D \) stand for different substances. The Gibbs free energy change is given by [76]

\[
\Delta G = cG_C + dG_D - aG_A - bG_B.
\] (7.1)

If \( \Delta G < 0 \), the above reaction shall occur spontaneously. By using the activity \( a_i \) for each substance, we can write \( G_i = G_i^0 + RT \ln a_i \), where \( G_i^0 \) is the free energy at...
Chapter 7. Failure Mechanism

a reference state (usually at room temperature and atmosphere pressure). Thus,

$$\Delta G = \Delta G^0 + RT \ln K,$$  \hspace{1cm} (7.2)

where $\Delta G^0$ can be expressed in a similar equation as (7.1) with the corresponding superscripts. The constant $K$ is defined as

$$K = \left(\frac{a_C a_D}{a_A a_B}\right).$$  \hspace{1cm} (7.3)

The activities are often close to unity; thus, we have $\Delta G = \Delta G^0$ from Equation 7.2. At equilibrium, $\Delta G = 0$. Denote $K_{eq}$ as the equilibrium constant and we can rewrite Equation (7.2) as

$$\Delta G^0 = -RT \ln K_{eq}.$$  \hspace{1cm} (7.4)

Now consider the real case. Si and most metals tend to oxidize in air, as shown in the following examples (data after [48]):

$$\text{Si} + \text{O}_2 \longrightarrow \text{SiO}_2 (\alpha-\text{quartz}) \hspace{1cm} \Delta G^0 = -910.7 \text{ kJ/mol}; \hspace{1cm} (7.5a)$$

$$2\text{Ta} + \frac{5}{2}\text{O}_2 \longrightarrow \text{Ta}_2\text{O}_5 \hspace{1cm} \Delta G^0 = -2046 \text{ kJ/mol}; \hspace{1cm} (7.5b)$$

$$\text{Ti} + \text{O}_2 \longrightarrow \text{TiO}_2 (\text{rutile}) \hspace{1cm} \Delta G^0 = -944 \text{ kJ/mol.} \hspace{1cm} (7.5c)$$

The Gibbs free energy data are hard to obtain for silicides. Murarka tabulated the heat of formation $\Delta_f H^0$ for some silicides in his book [64]; the values are $-120 \text{ kJ/mol}$ and $-134 \text{ kJ/mol}$ for $\text{TaSi}_2$ and $\text{TiSi}_2$, respectively. Most silicides also tend to oxidize, including $\text{TaSi}_x$ and $\text{TiSi}_x$ (and $\text{CSi}$).
7.2 Kinetics Approach

However, Au does not usually form a silicide or an oxide at the relatively low temperature under consideration (ie. \( T = 600^\circ C \); the melting point is 1063°C), but it is nothing perfect. Given that \( \Delta G_f = 0.98 \text{eV} = 1.57 \times 10^{-19} \text{J} \), for the fcc Au crystal [48], site fraction of mono-vacancies can be easily calculated as \( X_v \simeq \exp(-13.03) \) from Equation (5.5), or 2 vacancies per million atoms at \( T = 600^\circ C \)!

7.2 Kinetics Approach

Diffusion occurs when an atom jumps into a neighboring defect, be it a vacancy or interstitial lattice site. It may also happen when two neighboring atoms swap positions. It was found that the diffusivity (i.e. diffusion coefficient \( D \)) is also temperature dependent according to (recall Equation 5.6 in page 94):

\[
D = D_0 \exp(-\Delta H/(kT)).
\] (7.6)

Table 7.1 lists the pre-exponential factor \( D_0 \) and activation energy \( \Delta H \) for some important diffusion phenomena.

**Table 7.1**: Some important diffusion data.

<table>
<thead>
<tr>
<th></th>
<th>Self Diffusion</th>
<th>Diffusion in Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
<td>Si</td>
</tr>
<tr>
<td>( D_0 ) (cm(^2)/s)</td>
<td>0.04</td>
<td>1460</td>
</tr>
<tr>
<td>( \Delta H ) (eV)</td>
<td>1.76</td>
<td>5.02</td>
</tr>
</tbody>
</table>

\(^a\) Compiled after [48, 50, 125].
\(^b\) Interstitial diffusion at 700–1300°C.
\(^c\) Substitutional diffusion.

First, consider diffusion within the Ti contact layer between SiC and TaSi\(_2\) layers. Ti concentration C varies with position \( x \) for all the line scans; the concent-
tration peaks in the middle and decades as it spreads out in space. Although not precisely, this Ti distribution can be simulated by a Gauss function (see Figure 7.1 for specimen B4):

\[
C = C_0 + \frac{A}{w\sqrt{\pi/2}} \times \exp\left(-\frac{2(x - x_c)^2}{w^2}\right). \tag{7.7}
\]

**Figure 7.1:** Ti concentration versus distance in an XEDS line scan for specimen B4.

The simulated peak position is located at \(x_c = 125\) nm, which is the center point of this line scan (see also the HAADF image, Figure 6.16a in page 123). The FWHM of the Gaussian curve is 99 nm, which is close to what has been found—120 nm based on the image or 115 nm on Ti concentration.
This can be easily explained by solving the non-steady-state diffusion equation, i.e. Fick’s second law of diffusion:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C). \quad (7.8)$$

If the diffusivity $D$ does not depend on the concentration $C$, we can write:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (7.9)$$

in one dimension $x$. In the case of Ti diffusion into neighboring layers of TaSi$_2$ and SiC, the source of Ti is a finite amount $Q$. In other word, we need to consider the following boundary condition:

$$\int_{+\infty}^{+\infty} C(x, t)dx = \int_{+\infty}^{+\infty} Q\delta(x)dx = Q, \quad (7.10)$$

where $\delta(x)$ is the delta function. The initial condition is evident:

$$C(x, 0) = Q\delta(x). \quad (7.11)$$

Hence, the solution to Equation (7.9) is a standard Gaussian function:

$$C(x, t) = \frac{Q}{2\sqrt{\pi Dt}} \times \exp \left( \frac{-x^2}{4Dt} \right). \quad (7.12)$$

For a certain time $t$, the formula reduces to Equation (7.7).

One would speculate that it is also possible to compute the diffusivity $D$ if there are enough data for different times. However, the TiSi$_x$ thickness in the
lower Ti layer for all the annealed samples (i.e. B–F) is roughly the same 120 nm. The atomic concentration of Ti within this interface did drop over time—a maximum 96 at% for 5s specimen B4, 83 at% for 1h specimen C3, and 44 at% for 5h specimen D2. Since the thickness of this Ti layer is barely 100 nm as-deposited, Ti has already diffused beyond this Ti layer during the annealing process. This was demonstrated by all the XEDS spectra. The other possible explanation is that the diffusivity $D$ has changed over time because of the chemical reaction at the interfaces. Hence, the diffusion length, $x = 2\sqrt{Dt}$, is not proportional to $t^{1/2}$.

Next, consider Si distribution within this Ti layer and the SiC substrate. There is a valley of Si signal in the middle of Ti layer, which can be used to estimate the diffusion length of Si from SiC and TaSi$_2$ into Ti. For one data point in the line scan of specimen E3 with 10h annealing (at 600°C), there is only a few percent of Si (see Figure 6.32); while about 20% Si was found somewhere within the Ti layer for sample B, which was only annealed for 5 seconds at 1000°C (Figure 6.16b). The Si distribution suggests that Si atoms out-diffuse from SiC into Ti (recall that Ti atoms diffuse into SiC); a new phase TiSi$_x$ forms at the interface between the Ti layer and SiC substrate. On the other side, Si atoms within the TaSi$_2$ layer diffuse inward to form another TiSi$_x$ interface above the Ti layer. The latter titanium silicide interface for all the annealed samples can also form by possible Ti out-diffusion into the TaSi$_2$ layer.

A few percent of oxygen was also found within this Ti contact layer. Okojie et al. attributed this to “an artifact of the deposition process” [78]. No oxygen was detected within the TaSi$_2$ layer above the Ti contact, at least for the samples that have been annealed for 1h (C), 10h (E) and 50h (F). It seems that this excess
oxygen is confined to the vicinity of the Ti layer. This should be avoided in future processing as it might impose long term reliability issues.

As a side story, about ten years ago, several colleagues of mine were working on silicon-on-insulator (SOI) devices at the Ion Beam Laboratory in Shanghai Institute of Metallurgy, Chinese Academy of Sciences. Oxygen ions were implanted into a silicon wafer, which was then annealed to form an insulating SiO$_2$ layer within Si. However, this insulating layer was never smooth and clean. The industrial-grade implanting facility was examined and found to have no problem of leak and the like. The new high-end annealing furnace and clean quart tube were properly working. After days (or weeks) of trouble shooting, there is still not a clue. Then, someone said, "It must be dirty". As it turned out, dust was the real culprit. The wafers were cleaned in one room, and subsequently transferred to another room to be implanted. Moreover, the furnace sat on another floor. Hundreds of thousands of RMB $\text{yuan}^1$ had to be spent to convert a section of the lab into a large clean room. Viola!

In samples C–F, at the interface between the upper TaSi$_2$ and top Au layers, a high concentration of Au and O could be found. It is evident that Au in-diffuses from the top Au layer. More than 10% of oxygen was also detected within the upper TaSi$_2$ sacrificial layer; this oxygen has been built up during annealing. In other words, oxygen diffuses inward through the top Au layer and reacts with TaSi$_2$. With a closer look at the HAADF images and XEDS point/line scans, silicon oxide might have been formed at this interface, which corresponds to the dark features in HAADF images (and bright features in the EFTEM micrographs).

$^1$1 RMB yuan $\simeq$ 1/8 US dollar at that time.
No significant Ti aggregation was found at the Au surface, which confirms that the 400 nm TaSi$_2$ layer contains the Ti within the contact region [81]. However, in the case of Pt(300 nm)/TaSi$_2$(200 nm)/Ti(100 nm)/SiC studied previously, about 60 at% of Ti was found on the surface after 200h annealing at 600°C in air [80, 84]. The surface has been oxidized and experiments show that the oxide growth follows a parabolic law, $x \propto \sqrt{t}$. In other words, this is a diffusion-controlled process. However, in our case, the top Au layer acts differently from the Pt layer. Although there is substantial diffusion of oxygen into the upper TaSi$_2$ layer, the oxide thickness in samples C–F does not follow the parabolic rule.

Si continues the out-diffusion from the silicide layers until it encounters oxygen in the upper TaSi$_2$ layer and top Au layer. The formation and ubiquitous presence of silicon oxide are similar to what have happened in the TaSi$_2$ layer. It causes a large volume expansion within the Au layer. At some critical point, the integrity of lattice can not be withheld any more and blisters appear on its surface. With many of these blisters, a network of Au wires form on the Au layer.

### 7.3 Failure Mode and Failure Mechanism

Table 7.2 summaries the many possible failure modes, failure defects, failure mechanisms and failure causes for electronic devices [77].

In our case, the failure mode is probably due to the formation of an SiO$_x$ insulating layer at the Au/TaSi$_2$ interface; this will cause an “open circuit” or increase the resistivity dramatically. The failure mode can also be attributed to “high temperature failure”. The failure mechanism is proposed as follows.
### Table 7.2: A summary of failure mode, defects, mechanism and causes, after [77].

<table>
<thead>
<tr>
<th>Reported Fault</th>
<th>Analysis</th>
<th>Failure Mechanism and Cause</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Open-circuit (OC)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Missing interconnects</td>
<td>Mask errors</td>
</tr>
<tr>
<td></td>
<td>Corrosion</td>
<td>1. Moisture (internal gas; poor seal)</td>
</tr>
<tr>
<td></td>
<td>Mechanical damage, scratching</td>
<td>2. Contaminants + moisture</td>
</tr>
<tr>
<td></td>
<td>Open bond</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Package stress</td>
</tr>
<tr>
<td></td>
<td>Open metallization</td>
<td>4. Al/ Au intermetallic formation</td>
</tr>
<tr>
<td></td>
<td>Metallization microcracks</td>
<td>5. Fatigue failure</td>
</tr>
<tr>
<td></td>
<td>Local disruption of interconnects</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Die cracking</td>
<td></td>
</tr>
<tr>
<td><strong>Short-circuit (SC)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surface contamination</td>
<td>Stress, migration in as-deposited metallization</td>
</tr>
<tr>
<td></td>
<td>Isolation layer pin holes</td>
<td>1. Electrical overstress</td>
</tr>
<tr>
<td></td>
<td>Hillocks</td>
<td>2. Electrostatic discharge</td>
</tr>
<tr>
<td></td>
<td>Local disruption of interconnects</td>
<td>3. Electrostatic discharge</td>
</tr>
<tr>
<td></td>
<td>Metal spikes</td>
<td>1. Enhanced diffusion along dislocations</td>
</tr>
<tr>
<td></td>
<td>Metal shorts</td>
<td>2. Poor contact alloying</td>
</tr>
<tr>
<td></td>
<td>Package lead short</td>
<td>3. Overstress giving spiking</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4. Electrothermal overstress</td>
</tr>
<tr>
<td><strong>Leakage</strong></td>
<td>Surface contamination</td>
<td>1. Surface leakage</td>
</tr>
<tr>
<td></td>
<td>Processing defects</td>
<td>2. Ionic contamination at oxide/silicon interface</td>
</tr>
<tr>
<td></td>
<td>Voltage overstress</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hot spots</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Metal spikes</td>
<td>Metal diffusion along crystal defects</td>
</tr>
<tr>
<td><strong>High temperature</strong></td>
<td>Defective die-attach</td>
<td>Thermal overstress</td>
</tr>
<tr>
<td>failure**</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Even if there are no “processing defects” such as oxygen contamination and poor film quality, oxygen still can penetrate the 2µm thick Au overlayer. Oxides will form within the Au layer; this causes the formation of Au blisters and a complex network of Au wires on the surface. The rough surface will result in a poor connection between the contact pads and contact wires, which are not welded together (see Figure 2.8).

Also by the high-temperature in-diffusion of oxygen, a majority of the upper TaSi₂ layer have very high concentrations of O and Au. With time and the high temperature, this process shall degrade the diffusion barrier.

The Ti contact layer has also gone through dramatic changes. The Ti concentration drops over time while C, Si and Ta concentrations increase. This shall change the resistivity of the device, which can also make the pressure measurement unreliable according to Equations 2.3–2.11.
Part IV

Conclusions
Chapter 8

Conclusions and Suggestions for Future Work

8.1 Conclusions on the First Half of the Thesis (SiC Heteroepitaxy on Si)

The low pressure MOCVD reactor was re-designed and constructed in-house. Compared to the original reactor, it contained the following major modifications. First, the leakage problems of the old system were examined closely and made leak-proof. Second, many more flanges and fittings were acquired in order to install a new and bigger quartz tube. Third, the gas cylinders were secured in a cabinet with an exhaust to a chemical hood. The bubblers were also secured by two sets of leak-proof valves. Finally, the one exhaust of the system was connected to a cold trap, which also sat in the chemical hood. All these made the reactor substantially safer and more reliable.

The factors that control the substrate temperature were investigated by a sim-
ple statistical experiment. With a fixed susceptor and fixed positioning, the desired growth temperature can be reached by adjusting the power and grid levels.

By using hexamethyldisilane (HMDS) as the (single) precursor and a mixture of 8% H2 and 92% Ar as the carrier gas, SiC was epitaxially grown on Si(100) and Si(111) substrates. The two-step growth procedure was adopted for SiC epitaxy on (100) Si. XRD results demonstrated that these films were polycrystalline with two major SiC peaks—(111) and (200)—besides the (400) peak of the Si substrate. Films grown on (111) Si exhibited only the SiC (111) peak besides the Si peaks; this indicates the films are single crystalline. The morphology of all the films was comparable with what has been found in the literature. The benefit of the two-step growth procedure could be explained by considering the interfacial energy and total energy change during the formation of a nucleus. The high nucleation rate and low growth rate are also keys in this initial low temperature step by producing a single crystalline buffer layer.

A few GaN films were also grown on Si(111) substrates with SiC buffer layers using ammonia and trimethylgallium (TMG). XRD patterns clearly showed only single (111) peaks of Si, SiC and GaN with no other peaks in the spectra.

8.2 Conclusions on the Second Half of the Thesis (Ti Ohmic Contacts to SiC)

The FIB (focused ion beam) liftout technique was used to prepare numerous site-specific TEM thin foils of Ti ohmic contacts to SiC. Each contact, (Au/Ti/TaSi2/Ti/TaSi2/Ti/SiC, had a different annealing history. The thin foils were then
studied by various modes of transmission electron microscopy (TEM), including HAADF (High-Angle Annular Dark Field) imaging, XEDS (X-ray Energy Dispersive Spectroscopy), EELS (Electron Energy-Loss Spectrometry), ESI (Electron Spectroscopic Imaging), and SAD (selected-area diffraction).

The results show that the Ti contact layer interacts with the adjoining SiC to form a distinguishable interface for all samples. In every cases, C, Si and Ti were detected at the interface between SiC and Ti. For the as-deposited sample, no C or Si was detected in the middle of the Ti layer; this indicates that there is no significant Si or C diffusion into this layer. However, the Si concentration is very high for all the annealed samples. Although the thickness of this interface remains roughly the same (~120 nm), the atomic concentration of Ti within this interface did drop over time — a maximum 96 at% for 5s annealed sample, 80 at% for the 1h sample, and 40 at% for the 5h sample. In the other interface, formed between the Ti and TaSi$_2$ layers, high concentrations of Si, Ta and Ti were detected.

The TaSi$_2$ diffusion barrier was able to contain the Ti from out-diffusing into the surface and in-diffusion of oxygen.

In samples with seven-layer contact (i.e. an additional multilayer of Au/Ti/TaSi$_2$/Ti to the original TaSi$_2$/Ti/SiC multilayer), which had also been annealed for 1–50 hours, a thick interfacial layer had formed between the upper TaSi$_2$ layer and the overlying Au layer. Both HAADF images and XEDS spectra demonstrated the existence of high concentrations of Au and O.

Within the Au layer, a new phase had formed, which appears as dark patches in STEM images. XEDS and EELS studies suggest that these patches consist mainly of C, O and Si. SAD patterns suggest that the Au layer is single crystalline,
but the embedded new phase is poly-crystalline. The new phase also drives the formation of blisters on the surface, which cross link and form a complex web of gold micro-wires.

The failure mechanism is probably the high-temperature in-diffusion of oxygen and out-diffusion of Si. Moreover, the reactions change the resistivity of the device, which can make the pressure measurements unreliable.

8.3 Suggestions for Future Work

The following three suggestions are made for SiC heteroepitaxy: i) a tilted susceptor towards the gas flow; ii) separate precursors to control the Si/C ratio; iii) a more powerful coil or RF generator to raise the growth temperature.

As for the FIB/TEM studies of Ti contacts, W(CO)$_6$ could be used to form a tungsten (W) weld instead of Pt to avoid the overlap with Ta and Au peaks in XEDS. Possibly, thinner TEM foils could be prepared with a low-energy ion milling machine which would allow HRTEM images to be obtained from all the interfaces and new phases identified. Micro-diffraction patterns could also determine the composition and structure of these new phases. EELS line scan would also help if this is possible on the Tecnai. Moreover, samples with longer annealing times need to be examined, especially at the interface between the upper TaSi$_2$ layer and the overlying Au layer.

For the SiC pressure sensor fabrication, it would be better if all processing steps could be done within the same clean room. A lower base pressure in the sputtering system would be favorable. These might reduce or even prevent oxygen contamination.
Appendix A

Procedures for MOCVD Epitaxy

1. Checking system and loading sample:

1.1. Check vent lines and make sure there is no blockage;

1.2. Keep all valves closed including gas cylinders (especially 29–34);\(^\text{i}\)

\(^\text{i}\)The first Version 1.0 was written by Changrong Li on November 2, 2004.

\(^\text{ii}\)Note that valves 7 and 12 are three-way valves.
1.3. Load samples:
   1.3.1. Open viewing window.
   1.3.2. Load freshly-cleaned wafer(s) on the susceptor and place it in the center of the RF coil;
   1.3.3. Close viewing windows.

2. Pumping to base pressure:
   2.1. Turn on the mechanical pump and open valve 1; iii
   2.2. Open valve 2 to purge quartz tube;
   2.3. Purge all gas input lines:
      2.4.1. Evacuate HMDS line (Open 4,5, 7–10 if they are closed);
      2.4.2. Evacuate NH$_3$ line (Open 4, 11–14 if closed);
      2.4.3. Evacuate carrier gas line (Open 15 if closed);
      2.4.4. Evacuate TMG line (Open 4, 16 and 17 if closed);
      2.4.5. Evacuate TMA line (Open 4, 16, 18 and 19 if closed);
      2.4.6. Evacuate remain lines (Open 4, 16, 20–23 and 25–28 if closed);
      2.4.7. Open valve 3 and turn on Turbo pump if needed.
   2.4. Backfill with Ar to 100–760 Torr.—Close 2, 10 and 23—Open 36 and then 23—Close 36);
   2.5. Repeat 2.3, 2.4, 2.5, 2.3 and 2.4 consequently;

3. Baking:
   3.1. Check RF source and make sure that main switch is off, heating coil is in position, Power is set to 0, and Grid 55 (You can use other values);

---

iiiMake sure the N$_2$ gas cylinder is open and pressurized for all pneumatic valves.
3.2. Set valve 2 to setpoint A (ie. 100 Torr);

3.3. Pass H$_2$/Ar carrier gas—Open 4, 11, FL3, 15, 24 and 35;

3.4. Baking:

3.4.1. Turn on cooling water (> 35 psi) and cooling fan;

3.4.2. Turn ON main switch (Filament/Yellow light $\mapsto$ on, Panel relay/-Green $\mapsto$ on);

3.4.3. Hit “START” (Plate on/Red light $\mapsto$ on);

3.4.4. Slowly adjust Power to 40 and turn on pyrometer;

3.4.5. Adjust Power to baking temperature $T_0$ about 1200°C for 10 minutes.

3.5. Options:

3.5.1. SiC growth $\Rightarrow$ 4.1;

3.5.2. AlN growth $\Rightarrow$ 5.1;

3.5.3. GaN growth $\Rightarrow$ 6.1.

4. Growing SiC:

4.1. Adjust Power to SiC growth temperature $T_1$;

4.2. Make sure carrier gas is ready. If not, open 4, 11, FL3, 15, 24 and 35;

4.3. Open 5, 7, 8, 9, FL5, 20 and 23 (Make sure 10 is closed);

4.4. Open HMDS outlet (ie. valve 29) slowly, and wait for about 1 min;

4.5. Open HMDS inlet (ie. valve 30) slowly, and then close bypass valve 9;

4.6. One step or two steps:

4.6.1. One-step-growth: Keep at $T_1$ for desired growth time $t_1$ $\Rightarrow$ 4.7.

4.6.2. Two-step-growth: Keep at $T_1$ for $t_1$; Open 9, adjust temperature to $T_2$, close 9, and keep for $t_2$.

4.7. Open 9, close 30, close 29;
4.8. Close 5, 7, 8, and 20;

4.9. Options:

4.9.1. For AlN growth ⇒ 5.1;

4.9.2. For GaN growth ⇒ 6.1;

4.9.3. For SiC only ⇒ 7.1.

5. Growing AlN:

5.1. Adjust Power to AlN growth temperature $T_3$ (say 500°C);

5.2. Make sure carrier gas is ready. If not, open 4, 11, FL3, 15, 24 and 35;

5.3. Open NH3 line: Open 12, 13 and 37 (Make sure 14 is closed);

5.4. Open 18, 19, FL2 and 16;

5.5. Open TMA outlet (27 & 33) slowly, and wait for about 1 min;

5.6. Open TMA inlet (28 & 34) slowly, and then close bypass valve 19;

5.7. Keep for desired growth time $t_3$;

5.8. Open 19, close 28 and 34, and then close 33 and 27;

5.9. Close 21, 18 and 16;

5.10. Close 37, 13, 12 and 11;

5.11. Options:

5.11.1. For GaN growth ⇒ 6.1;

5.11.2. For AlN growth only ⇒ 7.1.

6. Growing GaN:

6.1. Adjust Power to GaN growth temperature $T_4$ (say 950°C);

6.2. Make sure carrier gas is ready. If not, open 4, 11, FL3, 15, 24 and 35;

6.3. Open NH3 line: Open 12, 13 and 37 (Make sure 14 is closed);

6.4. Open 16, 17, 18, FL1 and 22;
6.5. Open TMG outlet (26 & 32) slowly, and wait for about 1 min;

6.6. Open TMG inlet (25 & 31) slowly, and then close bypass valve 17;

6.7. One step or two steps:

6.7.1. One step: Keep for desired growth time \( t_4 \Rightarrow 6.8; \)

6.7.2. Two steps: Keep \( T_4 \) for \( t_4 \); Open 18, adjust temperature to \( T_5 \), close 18, keep for \( t_5 \).

6.8. Open 17, close 25 and 31, and then close 32 and 26;

6.9. Close 22, 17, 18 and 16;

6.10. Close 37, 13, 12, 11, and then \( \Rightarrow 7.1. \)

7. **Unloading sample and shutting down:**

7.1. Change carrier gas to Ar—slowly open 36 and close 35 and 24;

7.2. Cooling:

7.2.1. Slowly adjust *Power* to 0; Hit “OFF” (Red light \( \Rightarrow \) off); Main switch \( \Rightarrow \) OFF (Yellow light \( \Rightarrow \) off, Green light \( \Rightarrow \) off);

7.2.2. When \( T < 500^\circ C \), turn off cooling water and cooling fan;

7.2.3. Close valve 2 and let base pressure adjust to about 1 atm (760 Torr.);

7.2.4. Stop cooling gas—Close 36, 15, 11 and 4;

7.2.5. Turn off the mechanical pump and close valve 1;

7.2.6. Stop \( N_2 \) gas for all pneumatic valves.

7.3. Open viewing window and unload sample;

7.4. Options:

7.4.1. Reload sample by going through steps 1.3.2–2.3;

7.4.2. Or stop growth—close viewing window and turn off the Power.
Appendix B

Miller-Bravais Indices

Miller-Bravais and Weber indices are widely used to describe directions and planes in hexagonal systems. By definition, plane \((hkil)\) intersects the axes \((a_1, a_2, a_3\) and \(c)\) at \(a/h, a/k, a/i\) and \(c/l\), respectively (Figure B.1). Here \(a\) and \(c\) are lattice parameters, and \(i = -(h + k)\) [22]. Direction \([hkil]\) can be defined by a vector \(\overrightarrow{OP} = h\vec{a}_1 + k\vec{a}_2 + i\vec{a}_3 + l\vec{c}\), where \(\vec{a}_1\) is the unit vector along the \(a_1\) axis, and so on. Note there is a 3-fold symmetry between the three axes \(a_1, a_2, a_3\). Frank proposed to define the unit vectors as \(\vec{a}_1 = \frac{a}{3}[2\overline{1}\overline{1}0], \vec{a}_2 = \frac{a}{3}[\overline{1}2\overline{1}0], \vec{a}_3 = \frac{a}{3}[\overline{1}\overline{1}20],\) and \(\vec{c} = c[0001]\) [25].

Now, we have the foundations to describe a hexagonal system and these are all we need, as we can simply embrace the beauty of vector geometry.

First, we have \(\vec{a}_m \cdot \vec{a}_n = (\frac{3}{2}\delta_{mn} - \frac{1}{2})a^2, \vec{c} \cdot \vec{a}_m = 0,\) and \(\vec{c} \cdot \vec{c} = c^2\) (where \(m, n = 1, 2, \text{ or } 3\)). By imposing \(h + k + i = 0\), we can derive that (let \(\lambda^2 = 2c^2/3a^2\))

\[
OP = (\overrightarrow{OP} \cdot \overrightarrow{OP})^{1/2} = \sqrt{3(h^2 + k^2 + hk + \frac{1}{2}\lambda^2l^2)a^2}.
\] (B.1)
The angle $\alpha$ between two directions $[defg]$ and $[DEFG]$ is

$$\alpha = \arccos \frac{Dd + Ee + \frac{1}{2}(De + Ed) + \frac{1}{2}(Gg\lambda^2)}{\sqrt{d^2 + e^2 + de + \frac{1}{2}(g\lambda)^2} \sqrt{D^2 + E^2 + DE + \frac{1}{2}(G\lambda)^2}}. \quad \text{(B.2)}$$

Moreover, the normal to plane $(hkil)$ can be expressed as $[hkil/\lambda^2]$. The angle $\beta$ between two planes $(hkil)$ and $(HKIL)$ can be derived similarly as

$$\beta = \pi - \arccos \frac{Hh + Kk + \frac{1}{2}(Hk + Kh) + \frac{1}{2}(Ll/\lambda^2)}{\sqrt{h^2 + k^2 + hk + \frac{1}{2}(l/\lambda)^2} \sqrt{H^2 + K^2 + HK + \frac{1}{2}(L/\lambda)^2}}. \quad \text{(B.3)}$$

Finally, the acute angle $\varphi$ between direction $[defg]$ and plane $(hkil)$ is complementary to the angle between this direction and the plane normal. Hence, it is given by

$$\varphi = \arcsin \frac{dh + ek + \frac{1}{2}(dk + eh) + \frac{1}{2}gl}{\sqrt{d^2 + e^2 + de + \frac{1}{2}(g\lambda)^2} \sqrt{h^2 + k^2 + hk + \frac{1}{2}(l/\lambda)^2}}. \quad \text{(B.4)}$$
Similar to the notations \{hkl\} and \langle uvw \rangle, \{hkil\} and [defg] describe a family of planes and directions, respectively. For example, \{2\bar{1}\bar{1}0\} stands for three planes (2\bar{1}\bar{1}0), (\bar{1}2\bar{1}0) and (\bar{1}\bar{1}20), which are related by a 3-fold rotation symmetry about the \textit{c}-axis. [2\bar{1}\bar{1}0] stands for three related directions [2\bar{1}\bar{1}0], [\bar{1}2\bar{1}0] and [\bar{1}\bar{1}20]. By the way, the correspondences for planes and directions are given as:

\[
\begin{align*}
(hk il) &\rightarrow (hk l), & [hk il] &\rightarrow [(h-i)(k-i)l]; \\
(uv w) &\rightarrow (u v (-u-v) w), & [uv w] &\rightarrow [(2u-v)(2v-u)(-u-v)3w].
\end{align*}
\]
Appendix C

Ion-Solid Interaction

Figure C.1: Collision cascade caused by a 30 keV Ga ion, after [127].

When an incident ion beam bombards a stationary target, it can transfer energy and momentum by elastic interaction (refer to nuclear stopping power) and inelastic interaction (electron stopping power). The interaction is usually not limited to one pass, but leads to a collision cascade as shown in Figure C.1.
**Nuclear Stopping Power.** The stopping cross-section can be divided into nuclear (i.e. elastic) and electronic (or inelastic) stopping power

\[
S \equiv -\frac{1}{N} \left( \frac{dE}{dX} \right) = -\frac{1}{N} \left( \frac{dE}{dX} \right)_n - \frac{1}{N} \left( \frac{dE}{dX} \right)_e \equiv S_n + S_e. \tag{C.1}
\]

To estimate the nuclear stopping power, we can adopt the classic treatment of a simple two-body problem ([29, 45]). The scattering angle \( \Theta \) can be easily calculated in polar coordinates for a central force motion:

\[
\Theta = \pi - 2 \int_{r_{\text{min}}}^{\infty} \frac{p \, dr}{r^2 \sqrt{1 - V(r)/E_c - p^2/r^2}}, \tag{C.2}
\]

where \( r_{\text{min}} \) is the minimum approaching distance, \( p \) is the impact parameter (Figure C.2b), and the initial value of \( \Theta \) equals \( \pi \). The total energy \( E_c \) in the center of mass system can be expressed by \( \dot{r} \equiv dr/dt \) and \( \dot{\Theta} \equiv d\Theta/dt \) as:

\[
E_c = \frac{1}{2} \mu (r^2 + r^2 \dot{\Theta}^2) + V(r), \tag{C.3}
\]

where \( \mu \) and \( V(r) \) are the reduced mass and the potential, respectively.

![Figure C.2: Schematic of two-body elastic collision in the (a) laboratory and (b) center-of-mass coordinates, modified from [134].](image-url)
However, it was not easy to find single potential function $V(r)$ that is suitable for the general interatomic screening function:

$$\Phi_I = \frac{V(r)}{Z_1Z_2e^2/r},$$  \hspace{1cm} (C.4)

where $Z_1$ and $Z_2$ are atomic numbers of the ion and target atom, respectively.

Ziegler, Biersack and Littmark [134] were able to find a quite accurate universal potential function (Figure C.3)

$$\Phi_U = 0.18175e^{-3.1998x} + 0.50986e^{-0.94229x} + 0.28022e^{-0.4029x} + 0.02817e^{-0.20162x},$$  \hspace{1cm} (C.5)

where $x$ is defined as $r/a_U$. Here $r$ is interatomic distance, the universal screening length is given as $a_U = 0.8854a_0/(Z_1^{0.23} + Z_2^{0.23})$, and $a_0$ is the Bohr radius.\textsuperscript{1} Note the screening function have the form of

$$\Phi_I(x) = \sum_{i=1}^{n} a_i \cdot e^{-b_i x},$$  \hspace{1cm} (C.6)

where $a_i$ and $b_i$ are fitting parameters, and $\sum_{i=1}^{n} a_i = 1$ so that $\Phi_I(0) = 0$.

They also derived a universal reduced nuclear stopping power [134]:

$$S_n(\epsilon) = \begin{cases} 
\ln \epsilon 
& \text{for } \epsilon > 30, \\
\frac{\ln(1 + 1.1383\epsilon)}{\epsilon + 0.0132\epsilon^{0.21226} + 0.19593\epsilon^{0.5}} 
& \text{for } \epsilon \leq 30.
\end{cases}$$  \hspace{1cm} (C.7)

\textsuperscript{1}Bohr gave an amazing estimation as $a_{12} = a_0/(Z_1^{2/3} + Z_2^{2/3})^{1/2}$ in 1940, which has been the best formula for nearly 30 years [13].
The solid line shows the universal nuclear stopping power, which fits well with the experimental data as shown by solid circles (after [134]).

The reduced energy $\epsilon$ is defined as

$$\epsilon \equiv \frac{a_U E_0 M_2}{Z_1 Z_2 e^2 (M_1 + M_2)},$$

where $M_1$ and $M_2$ are the mass of the ion and target atom, respectively; $E_0$ is the kinetic energy of the incident ion.

**Electronic Stopping Power.** The electronic stopping power of a charged incident ion by the electron cloud of the target atom can be expressed as

$$S_e = \int I(v, \rho) (Z_1^+(v))^2 \rho \, dV,$$
where $Z_1^*$ is the screened charge of the particle, $dV$ is the volume element, and $I(v, \rho)$ is the interaction function between a particle of unit charge with velocity $v$ and a free electron gas of density $\rho$. It can be estimated that

$$S_e(E) = \begin{cases} 
N \cdot K_1 E^{1/2}, & \text{for low energy ion;} \\
N \cdot K_1 E^{-1} \ln(K_2 E), & \text{for high energy ion.}
\end{cases} \quad (C.10)$$

The terms $K$ are functions of $Z_1, Z_2, M_1$ and $M_2$.

**Range Distribution.** With knowledge of the total stopping power $S$ (see equations (C.1), (C.7) and (C.10)), one can calculate the range $R$ from

$$R \equiv \int \mathrm{d}R = \int \mathrm{d}X = \int_0^E \frac{dE}{dX} = \frac{1}{N} \int_0^E \frac{dE}{S}. \quad (C.11)$$

There are two important ranges as shown in Figure C.1, the projected range $R_p$ and lateral range $R_l$. For a 30 keV Ga$^+$ ion, $R_p$ is about 10–100 nm and $R_l$ is about 5–50 nm for different target materials. A Monte Carlo computer program to simulate slowing down and scattering of energetic ions in amorphous targets has been published by Biersack and Haggmark [12]. Nowadays, the stopping power can be calculated within an error less than 10% for low-energy heavy ions, and less than 2% for high-energy light ions [134].
Bibliography

[1] (No author). Intrinsic celebrates micropipe-free SiC and goes to 100 mm. III-Vs Review, 18:18, 2005.


Colophon

Among many other TeXnicians in the universe, I’d like to thank the grand master Professor Donald Ervin Knuth. Some 30 years ago he, a renowned Case alumnus, invented TeX, which is the engine that produces this PDF document behind the scene. Well, to be moderate, I am not an expert on TeX. Hence, what I really used is pdflatex by Hàn Thế Thanh, an extension to LaTeX by Leslie Lamport, which is a collection of macros that makes TeX accessible to a great audience. The beautiful Palatino PostScript font was enabled by the PSNFSS collection by Walter Schmidt. The hyperlinks are color-coded in cyan for references, violet for URL, and orange for everything else.

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