Influence of Surface Roughness and Interfacial Layer on IR Reflectivity of 3C-SiC/Si

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INFLUENCE OF SURFACE ROUGHNESS AND INTERFACIAL LAYER ON
IR REFLECTIVITY OF 3C-SiC/Si

A Thesis

Submitted to the School of Graduate Studies and Research
in Partial Fulfillment of the
Requirements for Degree

Master of Science

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August 2012
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The use of thin films with high elastic modulus, fracture toughness and various physical properties find silicon carbide as an important material for technological applications. SiC exist in more than 200 polytypes, but only a few are useful for manufacturing semiconductor devices. Among various polytypes, 3C-SiC has been considered as a good choice of materials for developing high temperature, and high frequency devices for integrated electronics. The development of SiC as a microelectronic material has resulted in tremendous use in micro-electro-mechanical systems (MEMS) applications for harsh environmental conditions. This material of interest is the only IV-IV compound with zinc-blende structure that exists in nature. Aside the advantages listed above over other polytypes, 3C-SiC can also be grown heteroepitaxially on Si substrate giving the benefits for low-cost fabrication of large diameter wafers. 3C-SiC/Si (100) have been grown successfully by chemical vapor deposition (CVD) method without any hindrances due to structural difference in the lattice constants (~20%) and thermal expansion coefficient (8%) between the deposited 3C-SiC and the underlying Si substrate. The CVD method uses various deposition conditions to produce quality 3C-SiC/Si epilayers.

The purpose of the present work is to use the Fourier transform infrared (FTIR) spectroscopy to evaluate the thickness, structural and crystalline properties of the V-CVD grown 3C-SiC/Si (100) films. The results of infrared transmission and reflection spectra are analyzed using a modified effective medium theory by evaluating dielectric functions of the material. The spectra features as influenced by interfacial layer, surface roughness, film thickness, phonon damping, free
carrier concentrations, plasma damping constant, and the effect of two component effective medium model of crystalline grains and intergranular heterogeneous material when they co-exist in 3C-SiC are methodologically included in the calculation. The reflectance spectra can also be affected by plasma damping constant, and the effect of two component effective medium model of crystalline grains, and intergranular heterogeneous material when they co-exist in 3C-SiC.

The thickness estimates of the V-CVD grown 3C-SiC/Si (100) epilayers are possible by comparisons of the experimental and calculated reflectance and transmission spectra.

Valuable information about phonon characteristics of the 3C-SiC films can be obtain by the infrared spectroscopy technique, which provides useful tool in probing the material quality.
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CHAPTER I

INTRODUCTION

1.1 Why Silicon Carbide (SiC)

Silicon Carbide is a very important semiconductor material in electronic and optical devices applications for high power, high frequency and high temperature application [1-5].

Current research interests in silicon carbide are due to its several physical properties. These physical properties are wide bandgap, high saturated electron drift velocity, higher dielectric strength, high electron mobility, chemical stability and a high thermal conductivity. Silicon Carbide as a microelectronics material has mechanical properties which makes it a suitable material for MEMS application at high temperature[1].

Silicon Carbide exists in various structural forms with over 200 polytypes due to various periodic stacking patterns of Silicon Carbide layers. All the polytypes have structures with Silicon tetrahedrally surrounded by carbon or vise versa. Silicon Carbide band gaps ranges from 2.422V in 3C-SiC to 3.33eV in 2H-SiC[2, 5]. Among the various polytypes, the common polytypes are the zinc-blende β-SiC (3C-SiC) and the hexagonal 6H-SiC structures[4]

Silicon Carbide gained recognition in industrial application in late 1980s when it was used as a blue light emitting diode (LED) due to its indirect band gap, which was found to be the only popular electroluminescent light commercially available at that time. The introduction of Gallium Nitride (GaN) actually worked more efficiently with higher intensity than SiC due to its direct bandgap[3].
Small sizes (in millimeter) of silicon carbide were grown in the past using bulk growth method like sublimation or physical vapor transport[4, 6]. Epitaxial growth of silicon carbide thin films on silicon substrate is now available using epitaxial growth techniques like chemical vapor deposition (CVD) and molecular beam epitaxy (MBE)[4, 7, 8].

1.2 Literature Review

Silicon Carbide was first manufactured by Jöns Jacob Berzelius in 1824[3, 8] who happened to be known for his discovery of Silicon (Si). Berzelius in one of his samples discovered that Si and C have a chemical bond relationship between them which he published in a paper. In 1905, a French chemist named Henri Moissan discovered natural silicon carbide in meteorite[8]. Eugene and Alfred Cowles in 1885[3] invented the electric smelting furnace which was used to manufacture a convenient material as alternate for diamond used as cutting and abrasive material by Acheson. During this process, Acheson melted the mixture coke and sand (silica) in the furnace and discovered a new material which was crystalline in nature, very hard, high refractability and infusibility and was found to be a compound of carbon and silicon. This product was name Carborundum [3, 8] with empirical formula SiC. Acheson initial intention was not actualized by trying to recrystallise graphite in silica to make artificial diamond, by 1891 [47], the SiC production was commercialized in large scale. The Acheson process took place in the furnace (25m x 4m x 4m) [47] at temperature between 1600° and 1500°. The reaction formula of the process is

\[ \text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}. \]

The reaction of SiC as shown in Figure 1.1 shows that there are voids or pockets that are coated with hexagonal looking crystals [3].
Figure 1.1 The Acheson furnace process with the void where SiC crystal was found[3].
Aside the Acheson process of manufacturing SiC, other methods also exist in manufacturing SiC. One of the methods is the Carbothermal reduction\[47\] of silica to give pure $\beta$-SiC for the pigment and electronic industry. With time the method was modified to yield $\beta$-SiC in powder form, $\alpha$-SiC platelets commercially using silicon, carbon, and micron sized $\beta$-SiC within the range of 1900 to 2100$^0$. For production of $\alpha$-SiC platelets, the material was doped with dopants like Aluminium and Boron\[47\].

In the late 1960’s \[47\], there was existence of silicon carbide material in self-bonded, molded form with high silicon carbide content. During early 1970’s dense (less than 2 % porosity) silicon carbide materials were synthesized which happened to be the first dense silicon carbide. Prochazka in 1973 using boron and carbon additives sintered $\beta$-SiC to high densities at about 2100$^0$, which was the advent of sintered silicon carbide (SiC) in solid state. Alloying $\text{Al}_2\text{OC}$ and/ or $\text{AlN}$ with SiC was first introduced in 1981 to form solid solutions since $\text{Al}_2\text{OC}$ and/ or $\text{AlN}$ are carbides and nitrides. In 1982 (Omori et al.)\[47\], liquid phase sintering of silicon carbide was introduced with oxide additives for densifying silicon carbide. Due to this, many other people also tried to densify silicon carbide in the late 1980’s with $\text{Y}_2\text{O}_3-\text{Al}_2\text{O}_3$ sintering additive\[47\].

Acheson also happened to be the person who discovered the polytypism of silicon carbide after confirmation by professor Frazier that the hexagonal crystals Acheson found in the void were all silicon carbide in different crystalline form\[3\].

In 1955, a scientist at Philips Research Laboratories named J.A Lely tried to improve on the Acheson process of growing silicon carbide crystal known as Lely process which created the invention of silicon carbide based microelectronics\[3, 9\]. Before the Lely process the purity of crystal was uncontrollable which was rectified by Lely’s process to some extent and made Silicon Carbide more interesting material than Silicon and Germanium.
Tairov and Tsvetkov in 1978[3] invented the seeded sublimation growth technique also known as the modified-Lely technique. They used seed crystal and tried to transport material through temperature gradient from the powdered source to the seed.

In 1983[10] the first heteroepitaxial growth of 3C-SiC on large area Si substrate was carried out using various epitaxial growth methods. Heteroepitaxial growth of SiC on Si substrate always gives 3C-SiC due to the discrepancies in the lattice constant (approximately 20% between SiC and Si) and thermal coefficient (approximately 8% between SiC and Si)[10].
CHAPTER II

SILICON CARBIDE POLYTYPES AND STRUCTURES

The structure of silicon carbide can be represented by a tetrahedral structure with silicon atom surrounded by four carbon atoms (or vise versa) as shown in the Figure 2.1 below. The carbon atoms and silicon atoms are chemically bonded together by covalent bonding. The carbon atom is separated from the silicon atom by a distance of 1.89 Å while the carbon atoms are separated from each other by a distance of 3.08 Å as shown in Figure 2.2[3, 11]. Silicon carbide covalent bond contributes a total of 88% while the ionic bond contributes a total of 12% which makes the material partially ionic in nature. The tetrahedral structure of SiC is actually determined by sp³[12, 13] orbital hybridization.

![Silicon carbide tetrahedral structure with silicon atom surrounded by four carbon atoms](image)

**Figure 2.1** Silicon carbide tetrahedral structure with silicon atom surrounded by four carbon atoms[3].
2.1  Silicon Carbide Polytypes

Silicon carbide possesses an important property that crystallizes it in different forms called polytypes without any change in its stoichiometry [9]. SiC polytypes has been known for many years as discussed earlier in chapter one. The polytypes can be viewed as chemically bonded compound of group IV consisting of 50% carbon atoms and 50%[13, 14] silicon atom as covalently bonded together, with each SiC polytypes preserving its unique electrical properties. With more than 200 SiC polytypes reported [8,13, 15], only few are grown in a duplicate form and useful for manufacturing semiconductor devices. Some of the common polytypes of SiC are the cubic 3C-SiC, the hexagonal 4H-SiC and 6H-SiC, and the rhombohedral 15R-SiC. Among the various polytypes, 3C-SiC has been considered as good choice of material for developing high temperature, high frequency integrated electronics. SiC can be represented by various periodic hexagonal structures of Si-C double layer structures along the c-axis. SiC polytypes are represented in a hexagonal coordinates system consisting of a1, a2, and a3[14]. The direction of the three a(s) are perpendicular to the c-axis direction as shown in Figure 2.3 below. The three a-
vectors are used to uniquely identify a plane or direction with the sum of reciprocal of $a_1$, $a_2$, and $a_3$ equal to zero. The angle between the three $a$-vectors is $120^0$ and they all contained in closed packed plane known as $a$-plane[11, 14].

![Hexagonal structure described by miller indices](image)

**Figure 2.3** Hexagonal structure described by miller indices[11].

Silicon carbide polytypes contains equal distribution of silicon and carbon except for the stacking sequences of the polytypes which determines the optical and electronic properties of these polytypes. The band gap for example for different polytypes differs, e.g. 2.39 eV for 3C-SiC, 3.023 eV for 6H-SiC, and 3.265 eV for 4H-SiC[3].

The stacking sequence of silicon carbide bi-layer can be repeated in a periodic manner in closed packed hexagonal layers. The hexagonal layers can be represented by hard spheres of the same radius[3] touching each other as shown in Figure 2.4. The position of the carbon atoms within the bilayer forms the hexagonal structure labeled “A” as shown in Figure 2.3, the next bilayer can be labeled “B” or “C”.

Figure 2.4 Example of closed packed hexagonal layer of hard spheres of the same radius. The first position is labeled “A” while the next is labeled “B” or “C”[3].

The stacking sequences of the various polytypes can be shown in Figure 2.5 below depending on the positions of the Si-C bilayers. The 3C-SiC is the simplest cubic structure which is also known as β-SiC with a stacking sequence of ABCABC along the [111] direction [8, 9], which is a common property of zinc blende structures. The non-cubic polytypes hexagonal (or α-SiC) and rhombohedral structures, 2H is the only hexagonal crystal with wurtzite structure and stacking sequence ABAB. The hexagonal structure is also known as α-SiC with 4H-SiC for example having a stacking sequence of ABCB while 6H-SiC is having a stacking sequence of ABCACBABCACB.

The number of layers before the stacking sequence repeats itself is attributed to the number in the notation of the crystal structures, the letters actually tells the type of structure of the polytypes[3, 14].
**Figure 2.5** Stacking sequence of 3H-SiC, 6H-SiC, 4H-SiC polytypes.
2.2 Polytypes Notations

Polytypes can be named using different notations such as ABC notation, ramsdell notation, Hägg notation, Zhdanov notation, and h-k notation to represent the various stacking sequences of the several polytypes.

2.2.1 ABC Notation

This is one of the methods used in naming silicon carbide polytypes using the letters “ABC”[3, 8, 9, 13, 14] notation. This can be used to represent the stacking layers of the Si-C bilayers bonded along the c-axis depending on the type of sites occupied in the layer. Polytypes can be represented by this form of notation by stacking the layers in a repeated manner. The ABC notation can be used to represent the $\beta$-SiC and $\alpha$-SiC depending on the arrangement of the bilayers of Silicon and carbon. The ABC notation however lacks the ability in representing polytypes with many layers in a periodic manner[13].

2.2.2 Ramsdell Notation

This is the conventional method used in denoting silicon carbide polytypes. This notation uses number[13, 16] of layers along the c-axis before repeating the sequence followed by the first letter of the Bravais lattice[12, 13]. The cubic lattice is denoted by C, hexagonal lattice by H, while the rhombohedral lattice is represented by R. Common silicon carbide polytypes represented by this notation are 3C (ABC), 2H (AB), 4H (ABCB), 6H (ABCACB), and 15R (ABCACBCABACABCB)[13] as shown in Figure 2.6 below. Unknown polytypes without any detail information about the stacking sequence can be named or represented using the Ramsdell notation which is an advantage over other polytypes notations. Aside 3C, 2H, and 4H, the Ramsdell notation however lacks uniqueness and enough information in determining the stacking order of the polytypes. 16H for example as shown in Figure 2.6 has been found to have
more than one stacking arrangements. In order to differentiate polytypes of this form, one can uniquely identify them by using a subscript e.g. alphabets or numbers in other which they occur.

**Figure 2.6** The periodic stacking sequence of different SiC polytypes in the (1120) plane. The dotted oval shape indicates the repetition of 15R minimum[13].

### 2.2.3 Hägg notation

This type of notation system differs from the previous notation systems we have examined earlier. This notation system uses the + and – sign to represent the various SiC polytypes. This shows that the closed-packed lattices can only be stacked in two ways using this notation. The arrangement of the + and – signs depend on the way the bilayers are stacked. The sign + is used
when the bilayers are stacked in this sequence, C on B, B on A, and A on C. The sign – is used when the bilayers are stacked in the following arrangements, B on C, A on C, and C on A. With this notation we can actually represent any of the notations above. The cubic periodic representation of 3C –SiC ABCABC sequence can be denoted by “++++++…”, the periodic hexagonal sequence of 2H-SiC ABAB can be represented with “+-+-…”, while rhombohedral structure like 15R can be represented by-+++--+++--+++-. This actually shows that the Hägg notation requires on 5 layers for 15R polytype while the ABC notation requires 15 layers. In Ramsdell notation, rhombohedral polytypes can be said to have 3n layer with n been a positive integer as compared to n-layer translation symmetry in Hägg notation [13, 16].

2.2.4 Zhdanov notation

Another notation system that is used in naming polytypes is Zhdanov notation system. This notation works on the basis of Hägg notation by using the number of times the signs occur in Hägg notation. Some of the Zhdanov notations using Hägg notation are, 11 for 2H, ∞ for 3C but according to the rule, 1 would have probably make more meaning, 22 for 4H, and 32 or 23 for 15R. Zhdanov notation can also be simplified for 2H and 4H hexagonal polytypes. 2H is denoted by <1>, while 4H is denoted by <2>, and etc.

The 16R that occurs in more than one form can also be represented by this notation, 16H₁ is denoted by (33)₂22, 16H₂ is denoted by 332332, 90R is denoted by (23)₄3322, and 6H is denoted by 33. Zhdanov also considered the stacking sequence of the non-basal tetrahedral planes of SiC in naming the polytypes. During this process he observed that the layers were represented by numbers denoting respective layers without any rotation while the repetition of the sequence is denoted by subscript.
The repetition of 15R minimum is shown by the layers enclosed in the dotted oval shape. The occurrence of of 16H₁ and 16H₂ is also shown with the subscript showing the order in which they occur[13].

2.2.5 Jagodzinski Notation

This is another type of polytype notation and can also be referred to as the h-k notation. It has been proven to be more efficient than the Zhdanov notation and can uniquely differentiate cubic layers from hexagonal layers. A quasi-cubic layer for example is represented with the letter k, while the hexagonal counterpart is represented with the letter h [13, 17]. Using this notation the various polytypes can be denoted in terms of h-k. 3C-SiC is denoted with k for example, 2H is denoted by h, and 4H is denoted by khkh.

Table 2.1 Various SiC polytypes notations (ABC, Ramsdell, Zhdanov, and Jagodzinski) of Silicon carbide tetrahedral structure

<table>
<thead>
<tr>
<th>Ramsdell notation</th>
<th>ABC notation</th>
<th>Zhdanov notation</th>
<th>Jagodzinski notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C</td>
<td>ABC</td>
<td>(∞)</td>
<td>(k)</td>
</tr>
<tr>
<td>2H</td>
<td>ABAB</td>
<td>(11)</td>
<td>(h)₂</td>
</tr>
<tr>
<td>4H</td>
<td>ABAC</td>
<td>(22)</td>
<td>(hk)₂</td>
</tr>
<tr>
<td>6H</td>
<td>ABCACB</td>
<td>(33)</td>
<td>(hkk)₂</td>
</tr>
<tr>
<td>15R</td>
<td>ABACBCACBABCBCAC</td>
<td>(32)₃</td>
<td>(hkhk)₃</td>
</tr>
</tbody>
</table>
The minimum repetition in this notation describes the number of unequal donor/acceptor sites about the electrical property which is an advantage of h-k notation. This can actually be demonstrated by 6H-SiC which is denoted as hkk with three different carbon sites, h,k_1, k_2, which has been used to experimentally to determine the ionization energy of nitrogen donor and one carbon site in 3C or 2H. Table 2.1 shows the notations discussed above for various SiC polytypes.

2.3 Silicon Carbide Tetrahedral Structure

The covalent bond that exists between silicon and carbon in the group IV elements of the periodic table has been described earlier to be due to sp^3 orbital hybridization. The hybridized bonding orbital formed by the atomic orbitals are different from each other in the ground state of the atom. Each of silicon and carbide atom have four nearest neighbor with each neighbor contributing one outer electron with each of the four neighbors. Semiconductor compounds in group II-V and II-VI also have this property to form a zinc-blende structure.

In solid state physics diamond and zinc-blende structures are very important structures formed by interpenetration of two face-centered cubic (fcc) crystal lattices [13, 18, 19] along the [111] direction. The diamond structure such as silicon only occur in lattice of the same atoms while the zinc-blende structure as shown in Figure 2.7 below occur in such as SiC occur in two crystal lattices of silicon and carbon.
Aside from the zinc-blende structure, some semiconductor materials also crystallize in other structures known as rock-salt or wurtzite. The rock-salt structure is similar to that of zinc-blende but with different number of nearest neighbors (each atom with six nearest neighbors) by interpenetration of two fcc lattices as shown in Figure 2.8 (a) below. The wurtzite structure is made up of two interpenetrating hexagonal closed-packed (hcp) lattices along or against the c-axis as shown below in fig. 2.8. The wurtzite structure is similar to zincblende structure in that it possesses a tetrahedral arrangement of the four nearest neighbors.
Figure 2.8 (a) Rock-salt structure; (b) unit cell of hexagonal closed-packed structure; (c) two hcp lattices stacked on each other with lattice constant c/a; (d) Wurtzite lattice, the oval shape indicating the basis for this lattice.

The hexagonal SiC polytypes can be described by stacking of the hexagonal layers as shown in Figure 2.8. The crystal lattice of the hexagonal closed-packed structure is made up of two lattice constants a and c, where a denotes the distance between two neighboring atoms, while c denotes the repeated shortest distance along the stacking direction. The lattice constants ratio c/a for the
ideal hcp of hard spheres has been calculated from geometry to be $(8/3)^{1/2} = 1.633$[18]. The unit cell axial ratio of the lattice constants $c/a$ however differs from the ideal value of $c/a$ because atom are not really hard spheres.

2.4 Hexagonal Closed-Packed Structure

The structure might not be a Bravais lattice but has been ranked to be important as face-centered cubic and body-centered cubic Bravais lattices. The hexagonal closed-packed structure can be said to be made up of simple hexagonal Bravais lattice by stacking two -dimensional triangular nets directly above each other with the stacking direction along the $a_3$ which is also known as the c-axis as shown in Figure 2.9 below. The three primitive vectors are denoted as

$$a_1 = a_x, \quad a_2 = \frac{a}{2} x + \frac{\sqrt{3}}{2} a_y, \quad a_3 = c z$$

(2.1)

In the x-y plane, the first two generate a triangular lattice while the third stacks the planes a distance c above one another.

**Figure 2.9** Simple hexagonal Bravais lattice of two-dimensional triangular nets stacked over each other at distance c apart[18].
**Figure 2.10** The hcp crystal structure of two simple hexagonal Bravais lattices interpenetrating each other displaced vertically by a distance $c/2$ along the stacking direction c-axis. It is also displaced horizontally so that the points of one lie directly above the centers of the triangle formed by the other points[18].

The hexagonal close-packed structure can also be described as two simple hexagonal Bravais lattices interpenetrating each, the Bravais lattices are displaced from each other by

$$\frac{a_1}{3} + \frac{a_2}{3} + \frac{a_3}{2}$$

(2.2)

The formation of close-packed structures can also be described by considering cannonballs as shown in Figure 2.11 below. The close-packed structure formation can be considered by starting with a close-packed triangular lattice as the first layer. The second layer is formed by placing balls in the depressions left at the center of first layer other triangle. The same process is also repeated in forming the third layer by placing balls on the intermittent depressions in the second
layer. The third layer lies on the first layer while the fourth layer lies on the second layer as shown in Figure 2.11.

![Figure 2.11](image)

**Figure 2.11** Representation of the cannonball layers. The first layer is formed by four cannonballs to form a plane triangle lattice. Third layer lying on the first layer at sites of the type denoted by inset (a). The fourth layer lying on the second layer in inset (b) fourth layer balls lying directly above those in first, and fifth layer above those in second, and etc[18]

The close-packing structure formation using the cannonballs as discussed earlier can also be described in terms of the tetravalent atom forming tetrahedron with the centers (denotes the vertexes of a tetrahedron) involved as illustrated in Figure 2.12. The close-packed is formed by packing of the tetrahedron [13, 18] which is related to the one discussed above as shown in Figure 2.13.

![Figure 2.12](image)

**Figure 2.12** Formation of close-packed structure using the cannonballs to form tetrahedron. (a) Four close-packed cannonballs; (b) formation of tetrahedron from centers; (c) using tetravalent atoms to occupy the center and the vertexes of the tetrahedron[13].
2.5 Other Close-Packing Possibilities

Beside the close-packing possibility of hcp, there are also other close-packing possibilities by rearranging the stacking of the cannonballs as illustrated in Figure 2.11 above. This can be achieved by placing the third layer in the unused depressions of Figure 2.11 in both the first and second layer. This actually makes the fourth layer to be distributed in the depressions in the third layer precisely above the first layer balls, the fifth layer also precisely above the second layer and etc. the type of rearrangement gives a Bravais lattice which happens to be a face-centered cubic lattice as illustrated in Figure 2.14.

Figure 2.13 (a) Unconnected tetrahedron; (b) the upper layer is connected with respect to the lower layer[13].
Figure 2.14 Close-packing possibility in fcc lattice. (a) face-centered cubic Bravais lattice (110) planes in the [111] direction; (b) illustrating the close-packed spheres face-centered cubic with spheres touching one another along the face diagonal of the cube [13, 18].

2.6 Physical Properties of SiC

SiC is a very important material due to its various physical properties. The various stacking of Si and C atoms in the SiC crystal lattice is responsible for various optical and electronic properties of SiC for various technological needs. The optical and electronic properties of silicon carbide vary also for different SiC polytypes due to various stacking arrangement as mentioned earlier. SiC also exhibits some physical properties which make them useful in micro-electro-mechanical systems (MEMS) application for different environmental condition. SiC is known for its wide-band gap property which is responsible for responsible for the high temperature operation of SiC devices over other semiconductor material. The tetrahedral covalent bonding between Si and C is also responsible for the for the high frequency operation resulting in higher critical electrical
field and higher thermal conductivity. Table 2.2 actually shows the various electrical properties of 3C, 4H, and 6H-SiC polytypes as compared to pure Si and GaAs.

**Table 2.2** Electronic properties of selected SiC polytypes compared to Si and GaAs[10].

<table>
<thead>
<tr>
<th>Property</th>
<th>Silicon</th>
<th>GaAs</th>
<th>4H-SiC</th>
<th>6H-SiC</th>
<th>3C-SiC</th>
<th>2H-GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
<td>1.1</td>
<td>1.42</td>
<td>3.2</td>
<td>3.0</td>
<td>2.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Relative dielectric constant</td>
<td>11.9</td>
<td>13.1</td>
<td>9.7</td>
<td>9.7</td>
<td>9.7</td>
<td>9.5</td>
</tr>
<tr>
<td>Breakdown field</td>
<td>0.6</td>
<td>0.8</td>
<td>//c-axis: 3.0</td>
<td>//c-axis: 3.2</td>
<td>1.8</td>
<td>2.5</td>
</tr>
<tr>
<td>( N_H = 10^{17} \text{cm}^{-3} ) (MVcm(^{-1}))</td>
<td>( \perp c )-axis: 2.5</td>
<td>( \perp c )-axis: &gt; 1</td>
<td>( \perp c )-axis: &gt; 1</td>
<td>( \perp c )-axis: &gt; 1</td>
<td>( \perp c )-axis: &gt; 1</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity (W/cm(^{-1})K)</td>
<td>1.5</td>
<td>0.5</td>
<td>3-5</td>
<td>3-5</td>
<td>3-5</td>
<td>1.3</td>
</tr>
<tr>
<td>Intrinsic carrier concentration (cm(^{-3}))</td>
<td>(10^{10})</td>
<td>(1.8 \times 10^6)</td>
<td>(10^{-7})</td>
<td>(10^{-5})</td>
<td>(10)</td>
<td>(10^{-10})</td>
</tr>
<tr>
<td>Electron mobility at ( N_D = 10^{16} \text{cm}^{-3} ) (cm(^2)V(^{-1})s(^{-1}))</td>
<td>1200</td>
<td>6500</td>
<td>//c-axis: 800</td>
<td>//c-axis: 800</td>
<td>750</td>
<td>900</td>
</tr>
<tr>
<td>Hole mobility at ( N_A = 10^{16} \text{cm}^{-3} ) (cm(^2)V(^{-1})s(^{-1}))</td>
<td>420</td>
<td>320</td>
<td>115</td>
<td>90</td>
<td>40</td>
<td>200</td>
</tr>
<tr>
<td>Saturated electron velocity ((10^7 \text{cm} \text{ s}^{-1}))</td>
<td>1.0</td>
<td>1.2</td>
<td>2</td>
<td>2</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Donor dopants and shallowest ionization energy (meV)</td>
<td>P: 45</td>
<td>Si: 5.8</td>
<td>N: 45</td>
<td>N: 85</td>
<td>N: 50</td>
<td>Si: 20</td>
</tr>
<tr>
<td>Acceptor dopants and shallowest ionization energy (meV)</td>
<td>As: 54</td>
<td>P: 80</td>
<td>C: 80</td>
<td>B: 300</td>
<td>B: 300</td>
<td>Al: 270</td>
</tr>
<tr>
<td>2005 Commercial wafer diameter (cm)</td>
<td>30</td>
<td>15</td>
<td>7.5</td>
<td>7.6</td>
<td>15</td>
<td>None</td>
</tr>
</tbody>
</table>

Table 2.2 above actually shows the various electrical properties of selected polytypes of SiC as compared to Si and GaAs which makes them more important for various technological needs. 3C-SiC as seen above possesses the highest electron mobility which makes it a very important
material for various industrial applications. SiC properties are discussed below for detail understanding of each property.

2.6.1 Mechanical and Chemical Properties

Silicon carbide as shown in chapter one has been described as a very hard material used as abrasive or cutting material. SiC has high Young modulus that of 424GPa that enables it to withstand stress under harsh environmental condition. SiC also possess a very high melting point which makes it to withstand high temperature. Chemically, SiC is chemically inert and does not any material if possible a room to react with it at room temperature (25°C). SiC does not also exist in the liquid phase but rather sublimes from solid to gaseous state into Si, Si$_2$C, and SiC$_2$ at temperature above 1,800°C[3].

2.6.2 Critical Field

The critical field is another important property that determines the breakdown (also known as catastrophic breakdown) of SiC under a very strong field for various high power electronic applications. Critical field property of SiC determines how high the critical must be before breakdown take place[3]. The breakdown field for the selected polytypes as been quoted in table 2.2 as compared to other semiconductor materials. 3C-SiC for example has critical field ten times the one of SiC[3]. The high critical field of silicon carbide as compared to silicon can be explained in terms of the blocking voltage ability of the material. The SiC high critical field as compared to Si enhances the power device blocking voltage region to be approximately to be ten times thinner and heavily doped[10], this factor ensures a decrease in the resistance of the blocking region at the same voltage rating.
2.6.3 Thermal Conductivity

This is another important factor for high power and high frequency operation of silicon carbide devices. The thermal conductivity parameter helps to conduct heat away from the material. SiC ability to operate at high temperature with increase in energy radiation efficiency and temperature difference between the cooling environment and the device enables more cooling effect of the material with the help of the cooling devices like cooling fan, heat sink, and etc[10]. SiC has been quoted severally to have higher thermal conductivity than copper (with thermal conductivity better than any other metal) at room temperature. The thermal conductivity of SiC and copper are, \(4.9 \text{ W/(cm-K)}\)[3] for reported thermal conductivity value of SiC , and copper has thermal conductivity of \(4.0 \text{ W/(cm-K)}\). Doping can actually decrease the thermal conductivity of some crystal but they are all still above the thermal conductivity of copper at room temperature.

2.6.4 Saturated Electron Velocity

The saturated electron velocity is an important property of SiC crystal. The frequency and application range of SiC and its polytypes are determined by the saturated electron velocity. In high frequency operation of SiC, the saturated electron velocity is considered to be more important that the breakdown electric field strength. The saturated electron velocity in SiC is considered to be twice that of silicon material. High channel current for microwaves devices can only be attained by high saturated electron velocity. The various saturated electron velocity for the selected polytypes (3C, 4H, and 6H-SiC) can be viewed from table 2.2 above. The values of 4H and 6H-SiC are equal and different from 3C-SiC due to anisotropy of SiC polytypes electrical properties.
2.6.5 High Temperature Operation

Temperature effect on semiconductor material and devices is a very important parameter. SiC as compared to other semiconductor material like Si has a wide bandgap energy and low intrinsic carrier concentration. These properties are responsible for silicon carbide to be operated at higher temperatures greater than that of silicon. Usually at negligible intrinsic carrier concentration the conductivity of the semiconductor device is controlled by doping and the semiconductor can operate functionally in this temperature range. The semiconductor device might not operate properly if the intrinsic carrier concentration exceeds the doping of the device at high temperature[10]. The need for high power, high temperature devices has found SiC as a useful material operating at higher temperature than other semiconductor materials.

2.7 Electronic Band Structure

In studying the electronic dynamism of SiC polytypes it is expedient to know the band structure of the polytypes. The band gap is used to determine many physical properties like optical properties, transport properties and etc. The detail information about the band structure from the top of the valence bands and the bottom of the conduction bands in 3C, 2H, 4H, and 6H polytypes is needed to describe the electron and hole dynamism of the polytypes. In 1964, Choyke, Hamilton, and Patrick discovered that the electronic energy gap depends linear on the hexagonality[20] contribution (in percentage) of the polytypes. Due to lack of availability of high-quality single crystals or perfect epitaxial layers, experimental studies of the electronic properties of SiC polytypes have been very low. The combination of both experimental and theoretical studies revealed the band structure of SiC and other semiconductors considering the huge change of the conduction bands in various polytypes. The first Brillouin zone for the cubic,
hexagonal and rhombohedral crystal is shown in Figure 2.15 for clarity of the subject on band structure from LDA calculation[9].
Figure 2.15 First Brillouin zone of (a) fcc; (b) Hexagonal and (c) Rhombohedral crystal [13].

It has been shown lately from first principle that the local density approximation (LDA)[9] calculation has been used for various SiC polytypes for studying their electronics properties. The band structure of 3C, 2H, 4H, and 6H is illustrated in Figure 2.16 from LDA calculation.
Figure 2.16 Band structures of (a) 3C-, (b) 2H-, (c) 4H-, and (c) 6H-SiC [20].
It has been revealed theoretically that the conduction bands minima of the four polytypes are located off center of the Brillouin zone, while the valence bands are located at the center of the Brillouin (r-point). This indicates that the band gap of these polytypes are indirect band gaps. These minima are not easy to measure directly but have been assigned due to the band model consistency with experimental results. The conduction band minimum for cubic 3C-Sic is located at X-point, 2H at K-point, 4H at M-point, and between M- and L-point for 6H-SiC (as indicated in Figure 2.17)[9].

![Conduction bands of 6H-SiC along L-M line](image)

**Figure 2.17** Conduction bands of 6H-SiC along L-M line[9].

A magnified image of the 6H-SiC conduction bands minimum along L-M line as shown in Figure 2.17, the minimum is about 40% from M-point along the L-M line.
Silicon carbide polytype 4H-SiC conduction band is also illustrated in Figure 2.18 below. Experimental reasons also show that the minimum of 4H-SiC is not located at M or L-M line but located at an F position. However, there was no indication for the minimum found at k point in the plane, DFT-LDA band structure, and after adding the quasiparticle.

**Figure 2.18** Conduction band of 4H-SiC near the minimum[9].

The band gap values that was experimentally determines years back and confirmed also by a recent X-ray spectroscopy experiment are 3.25eV for 4H, 2.416eV for 3C, 3.023eV for 6H, and 3.33eV for 2H-SiC. It has also been revealed also that the LDA calculation within the density functional theory (DFT) frequently underestimates the band gap of semiconductor and insulator. The LDA calculation which is approximately 1eV underestimation for the four polytypes are
2.19eV for 4H, 1.30eV for 3C, 1.98eV for 6H, and 2.13eV for 2H SiC. However this can also be consistent with experiment by including a quasiparticle (QP)[20] shift to improve the band gap. In different polytypes this has given the approximate accurate ordering of band gaps and the location of the minimum of the conduction band.

2.8 Phonon Dispersion

For proper understanding and explanation of different SiC properties, it is necessary to relate the concept of polytypes with phonons. With the help of phonon contribution to the free energy is very important due to closeness of the various phases of SiC electronic energies, which can be used in stabilizing the various polytypes[21, 22]. The theoretical tools[9] for calculation of phonon frequencies aside the experimental tools are now available. The experimental tools employed for these calculations are infrared absorption, Raman spectroscopy, low temperature photo luminescent experiment, neutron scattering experiments and inelastic X-ray experiments. The experimental tools listed above are not only limited for investigating the modes at high symmetry points in the Brillouin zone but can also be used to investigate the phonon dispersion generally. Lattice dynamics can be illustrated with the help of phonon frequency dispersion relations. However, the understanding of dynamic matrix $D$ is very important in calculating lattice vibration with the help of the eigenvalues and eigenvectors[21]. However, the linear-response theory have been suggested for obtaining dynamical matrices at arbitrary wave vectors alongside the application of computational effort as compared the unperturbed bulk self-consistent calculation[23]. Recently, many groups have tried to probe the structural and electronic properties of SiC from ab initio , but only a few of the lattice dynamics ab initio calculations are available[22, 23]. The ab initio calculation of the crystal lattice vibration can be done by using LDA method due to its ability in administering the energy difference between the
several structural phases of SiC due to small atomic displacement. This method is good but the
disadvantage is the increased computational load which is proportional to the size of systems
more than that used for band structure calculation [9, 22, 24]. Density-functional perturbation
theory (DFPT) is a powerful tool in determining the band structure at any wave vector \( \mathbf{q} \) in the
Brillouin zone of the phonon frequencies and eigenvectors [22, 23]. The wave vector of phonon
modes at high symmetry point in the BZ, DFPT can be used within the framework of the linear-
response theory or real-space frozen phonon method can also be used for that particular \( k \)-point
by making use of small super-cells to construct dynamic matrix \( D \). For nearly a decade now,
phonon dispersion for 3C-SiC and 2H-SiC have been reported using LDA calculations despite
the computational loads experienced [9, 22]. Aside 3C- and 2H-SiC polytypes, 4H-SiC and 6H-
SiC polytypes phonon dispersion can also be predicted using the empirical approaches. Fitting of
the experimental data of \( \Gamma \)-point can be used in getting the parameters of these empirical models
or by using the first-principle phonon results of smaller 3C-SiC and 2H-SiC. This can be done
by using the local-coupling transfer procedure fitting method to construct force constant of 4H-
SiC in terms of the 3C-SiC and 2H-SiC polytypes force constants calculated with LDA
 technique, which was in agreement with the experimental method and empirical calculations[9].
A detailed study of 3C-, 2H-, 4H-, and 6H-SiC was carried out recently using the \textit{ab initio} real-
space super-cell force constant (SCFC)[9] approach in predicting the full phonon dispersion. The
source of numerical errors using this method is attached to the truncation of real space force
constant matrices. Calculating the force-constant matrix for a larger super-cell model before it is
truncated to increase the real space range can actually be used to reduce the errors. Born
effective charges (BEC) \( Z^* \) [25] are induced in ionic solid like silicon carbide due to phonon, the
frequencies of certain longitudinal phonon mode is altered by the microscopic electrostatic
interaction of $Z^*$ the longitudinal-optical-transverse-optical (LO-TO) splitting[9, 21, 26, 27]. This splitting can be corrected by Kunc and martin algorithm based on intermolecular force constant. With this method the phonon band-structures of the polytypes of SiC listed above have been calculated as shown in Figure 2.19 below[9].
Figure 2.19 Phonon dispersions of (a) 2H-SiC, (b) 4H-SiC, (c) 6H-SiC, and (d) 3C-SiC [21].

Phonon density of states can also be calculated from these phonon dispersions as shown in Figure 2.20[2] below for 3C-, 2H-, 4H, and 6H-SiC polytypes. This was first discussed by Van Hove through the use of topological consideration [9, 28].
Figure 2.20 Phonon density of states for (a) 3C-SiC, (b) 2H-SiC, (b) 4H-SiC, (c) 6H-SiC polytypes [2].

The correct experimental determination of the general phonon dispersion faced some constraints until recently. The dispersion along the stacking direction omission for the polytypes is the r-L
direction in cubic crystal or $\mathbf{r}$-A direction in the hexagonal crystals [9, 28, 29]. Using the optical experimental data, it is possible to predict the $\mathbf{r}$-point phonon frequency of 3C-, 2H-, 4H-, 6H-, and 15R-SiC polytypes by folding the phonon dispersion of 3C-Sic in the direction of $\mathbf{r}$-$\mathbf{L}$[30-32]. Fig 2.21 actually confirms this agreement by theoretical[9] phonon axial dispersions of 3C-, 2H-, 4H-, and 6H-SiC polytypes plotted within the framework of the first Brillouin zone of 3C.

**Figure 2.21** Phonon dispersions along the axial direction when back folded. The elastic limit is depicted by the two straight lines[9].

Thus, LDA calculation reveals that that 3C-, 2H-, 4H, and 6H-SiC polytypes have a likely dispersion in the axial direction[9].
Aside the theoretical calculations of phonon dispersions, experimental approach was also used which seems difficult and challenging. Phonon dispersion was not experimentally determined for SiC polytypes except 6H-SiC by Raman scattering which was later also used for 3C-, 2H-, 4H-, 6H-, 15R-SiC, and 21R-SiC polytypes [33-35]. Dorner et al. [36] in 1998 used inelastic neutrons scattering to measure 6H-SiC dispersion relations for two mutually perpendicular symmetry directions (Δ(Γ-A) and Σ(Γ-M)). It is also possible to measure the dispersion curves by inelastic X-ray scattering method [9, 37]. Serrano et al. [9, 32] used this method to measure the phonon dispersion of 3C-SiC as shown in Figure 2.22 below which was also in agreement with the theoretical calculation.

![Graph](a)
This IXS method was also used for 4H-SiC along $\Gamma$-$A$ direction and basal $\Gamma$-$M$ and $\Gamma$-$K$-$M$ directions as shown in Figure 2.23 below.

![Phonon dispersion in (a) 3C-SiC, and (b) 4H-SiC. Solid lines indicate calculated measurement while circles represents experimental measurements][9].

**Figure 2.22** Phonon dispersion in (a) 3C-SiC, and (b) 4H-SiC. Solid lines indicate calculated measurement while circles represents experimental measurements[9].

**Silicon Carbide Growth Techniques**

SiC commercialization[12, 38] in the production of substrate (bulk)[12] is a major advantage as a wide bandgap semiconductor material. One major limitation of bulk SiC is the problem of large
diameter and quality [3, 12, 38]. The epitaxial growth technique is a useful technique in overcoming the limitations of large diameter and high quality SiC substrate[12]. The innovations in SiC based technological and electronic device applications are due to the commercial availability of SiC substrate of large diameter and quality[38].

2.9 Bulk SiC Growth

Some of the SiC bulk growth techniques like the Acheson and Lely process have been discussed in chapter one. Aside from bulk growth techniques already discussed, there are other methods also used in fabricating bulk SiC. The modified Lely process known as Seeded sublimation technique based on physical vapor transport. This technique is mostly used with source materials like powdered SiC[12].

2.9.1 Seeded Sublimation Growth

Seeded Sublimation Process as originally reported by Tairov and Tsvetkov[3, 6, 9] has been reported to be a successful method in growing crystals of SiC. This method is also known as the modified-Lely-method by introducing a seed crystal into the growth cavity[9] under close-to-uniform thermal condition[3]. Seeded sublimation method takes place by placing the seed wafer in the direction facing the SiC powder source[9] in a closed system, the crucible is then heated for sublimation of SiC to take place at a very high temperature[3]. The main gases that sublime during the process are Si, Si$_2$C, and SiC$_2$ and the temperature determines the ratio between the gases. The sublimated gases condense epitaxially on the seed crystal at low ambient temperature. The seeded sublimation process is illustrated in Figure 2.24 below.
Figure 2.23 (a)Diagram of seeded sublimation growth method[3], (b) Schematic diagram of the modified-Lely-method of Seeded sublimation method[6].

The temperature of the growth process is maintained between 2200-2500°C with a temperature gradient maintained across the growth cell with an argon over pressure[9] of about 600 Torr to
avoid crystallization. This temperature also ensures that the number of materials that will remain inert for the growth time is limited[38].

The growth method was confirmed by many laboratories for growing Silicon carbide wafers of large diameter. Cree using this method [6, 9] actually increased the diameter and the quality of the Silicon carbide wafers. Cree presented the first silicon carbide wafers in late 1999 up to 100mm (4-in) in diameter. The purpose of increasing the diameter is to reduce cost of SiC devices with the help of existing Si or GaAs manufacturing equipment[6]. However, the seeded sublimation growth technique still faces some major challenges like growing of boules on off-axis substrates which need to be eliminated. This will only come to reality if the wafer is improved, combined with polishing procedure and the need for epitaxial technique.

2.9.2 High Temperature Chemical Vapor Deposition

Another technique similar to the seeded sublimation growth technique is the HTCVD presented in 1995 for growing SiC boules. The only difference between HTCVD and seeded sublimation growth technique is that HTCVD uses gases as source of material instead of powder[3]. This method has been designed to achieve epitaxial quality material in a bulk growth process[38]. The HTCVD technique apparatus can be illustrated as been made up of three zones namely:

1. Entrance zone
2. Sublimation zone and
3. Growth or condensation zone.

The process gases are majorly silane, hydrocarbon (ethylene) diluted in a helium carrier gas flow which is very low. These gases are dispersed towards a substrate or seed-crystal holders[39]. Figure 2.25 illustrate the HTCVD system.
**Figure 2.24** (a) HTCVD process[3], (b) The schematic diagram of the HTCVD process[38].

Silane and hydrocarbon are used at very high concentration in order for homogeneous nucleation to dominate the process. Silane decomposes to form Si liquid droplets or solid microcrystal and the hydrocarbon also takes part in this reaction to form micro particles of Si$_x$C$_y$ as the gases
proceeds to the hot part of the injector. This reaction can also take place without the inclusion of a hydrocarbon. The reaction between the hot silicon and graphite walls helps to supply the carbon needed for this process which however not the way in achieving high growth rate[3].

High growth rates can also be maintained by minimizing the precursor losses by maintaining a very high susceptor wall temperature. Once the formed microparticle Si$_x$C$_y$ is in the sublimation zone, the microparticle sublimes to form Si, Si$_2$C, and SiC$_2$ similar to seeded sublimation growth[3].

2.10 SiC Epitaxial Growth Techniques

The epitaxial growth of SiC is one of the most promising[40] method in growing SiC with well developed fabrication technology. Epitaxial growth technique involves the growing of crystalline film layer on a crystalline substrate[41]. This layered growth have a great number of defects[40] due to lattice mismatch[40, 41] and different coefficient of thermal expansion between SiC and Si. Lattice mismatches (20%) and different coefficient of thermal expansion (8%)[42] leads to surface roughness, wafer bending, misorientations, defects like stacking faults, twin and cracks which hinders high quality growth of SiC on Si substrates.

The various epitaxial growth techniques used are the liquid phase (LPE) and vapor phase (CVD and MBE)[12]. For this study, we shall focus on CVD epitaxial growth technique for growing 3C-SiC.

2.10.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is one of the techniques used in growing crystalline films epitaxially. This process involves chemical reaction and transportation of gaseous compounds to the substrate surface to give deposition of the material. the substrate temperature is kept between 1400 to 1600$^\circ$C[12] and the gas pressure is between 0.1 to 1 atm. During the process, the
precursors are diluted in a carrier gas and placed in the reaction chamber. In the reaction chamber, the gasses diffuse through a boundary layer to the surface and the reactants absorb to the surface. Deposition takes place during chemical reaction and the absorbed species are desorbed, hence diffusing out the bye-product[41]. CVD process is illustrated in Figure 2.25 with the substrate placed on a graphite susceptor inside the deposition chamber[12].

![Figure 2.25 CVD chamber](image)

Figure 2.25 CVD chamber (1. water cooled deposition chamber; 2. induction heaters; 3. graphitic susceptor; 4. SiC heated substrate; 5. residual gases exit) [12].

The heteroepitaxial growth of 3C-SiC on Si substrate can be done using a horizontal wall low-pressure chemical vapor deposition (LPCVD)[41-43] system. The carrier gas was purified hydrogen with reactants gases like silane and propane. The growth was performed at 1200°C, 97mbar and at the growth rate of 4µm[42].
CHAPTER III
EXPERIMENTAL

The material of interest is the IV-IV 3C-SiC semiconductor compound. The main focus of this study is to ensure that the theoretical modeling calculations are in agreement with existing experimental data using similar parameters to confirm that the theoretical modeling can actually be used to find the reflectance and transmission of 3C-SiC. The features of the spectra was examined by influencing it with film thickness, interfacial layer, surface roughness, and free carrier concentration. Hence the CVD grown 3C-SiC/Si (100) epilayer thickness can be estimated by comparing the calculated reflectance and transmission spectra with that of experimental.

3.1 SiC Bulk Samples

Bulk samples of SiC can be grown experimentally by one of the growth techniques (Seeded sublimation or HTCVD) discussed in the previous chapter. These methods are commonly used through sublimation of a SiC source (powder or solid) placed in the hot zone of the crucible. The vapor species collected are transported to a cooler region for deposition of the crystal from the vapor phase[12]. The optical properties can also observe with the effect of free carrier concentration and film thickness.

3.2 Reflectance of CVD SiC Film

Another way of growing SiC aside the bulk growth technique is by growing SiC crystalline films epitaxially. CVD exist in various types which include: thermal CVD, which consist of low pressure (LPCVD) and atmospheric pressure (APCVD), and plasma enhanced (PECVD)[41]. Holm et al[44] observed the infrared reflectance of cubic SiC films grown on silicon substrates which actually provided a quick and non-destructive evaluation of the films. They recorded the
infrared reflectance spectra at near-normal incidence on a Perkin-Elmer model 180 spectrophotometer over the spectra range from 400-4000 cm\(^{-1}\). They experimented without polishing the back of the substrate (rough surface). Different buffer layers spectra were measured in the range 20 to 90 nm.

**Figure 3.1** Experimental reflectance spectra for four SiC films grown on surfaces at near normal incidence. The thicknesses of the film are (1) 6.1 \(\mu\)m, (2) 12.7 \(\mu\)m, (3) 12.0 \(\mu\)m, and (4) 5.0 \(\mu\)m [44].
The spectra of the four-thick samples with as-grown, specular surfaces can be seen from Figure 3.1 above.

Looking at all the spectra observed, spectrum 1 is the closest to ideal spectra recorded with thickness of 6.1µm and surface roughness of 6nm. They observed that the fringe contrast decreases with frequency increase beyond the restsrahlen region which also appeared at all the spectrum measured.

The fringe contrast as observed in spectrum 2 decreases faster beyond the restsrahlen region, hence approaching zero at $\omega = 4000\text{cm}^{-1}$ making the reflectance 20% which is the reflectivity of semi-infinite SiC. This actually reveals that the addition of SiC-Si interface to the total reflectance declines as $\omega$ goes to 4000 cm$^{-1}$. The interface optical roughness could be responsible for this action, diffusely scattering the light instead of specularly reflecting it with scattering losses proportional to the frequency increase. Normally the fringe contrast is expected to decrease as the frequency decreases due to the refractive index of SiC becoming that of silicon. Unexpected high reflectivity (probably from a conducting layer between the film and the substrate) at the SiC-Si interface may also be responsible for the large fringe contrast increase as the frequency decreases.

Higher than normal fringe contrast were observed in spectrum 3 below $\omega_T$ and above $\omega_L$ which makes it different from all other spectra with higher contrast below $\omega_T$. This feature could also be explained by the presence of conducting layer but with a very high carrier concentration. The contrast should have been higher than the one shew above but coincident phenomena actually modified this spectrum.

The result of large carrier concentration was actually illustrated in spectrum 4 which were optically and electrically determined.
Holm et al were able to get from the infrared spectral the surface roughness information at the film surface and information about the conducting layer between the film and the substrate interface. They were also able to determine the free carrier concentration and the film thickness from the reflectance spectra[44].

Feng et al[43] also determine the IR reflectance spectra of 3C-SiC by growing SiC on Si substrate using vertical vapor deposition (V-CVD) at Auburn university.

They observed in their measured spectra decreasing interference fringes above the reststrahlen above for an interfacial layer. This fringes contrast is determined in ideal sample reflectance by the refractive index between the film and substrate. For a real sample defects may occur but for an ideal sample the epitaxial film is the same with the interfaces optically sharp and parallel. When \( n_f < n_s \) for SiC grown on Si substrate the fringe contrast is determined by

\[
(R_{\text{max}} - R_{\text{min}}) / (R_{\text{max}} + R_{\text{min}}), \\
R_{\text{max}} = \left[ \frac{(n_s - 1)}{(n_s + 1)} \right]^2, \\
R_{\text{min}} = \left[ \frac{(n_s - n_f)}{n_s + n_f} \right]^2. 
\]

(3.1)

They tried to model this effect by varying the doping concentration in both the film and the substrate but the difference in the free carrier concentration could not account for the minimized effect.

Feng et al used their modified model to calculate the reflectance spectra and did an excellent fitting comparism with the measured spectrum as illustrate in Figure 3.2 below. They considered a transition layer between the film and the substrate, the transition layer thickness of about 2.4% of the film thickness.

When the refractive index of sample a121 used for this measurement is larger than \( n_f \) with an average factor of 1.2, a decreasing contrast is observed[43] or an enhanced fringe contrast when \( n_f \) is lower than the refractive index. The speed at which the contrast decreases is determined by the refractive index and the transition layer thickness.
Figure 3.2 IR reflectance spectrum of 3C-SiC on Si substrate. Theoretical (solid line) and experimental (dotted line)[43].

The effect of the transition layer negligible when the when the thickness of the transitional layer is very small, hence the fringe extreme remain almost constant.

Feng et al[43] concluded that surface roughness (of about 0.08\,\mu{}m) scattering also affects the reflectance of sample a121 aside the transition layer. Surface roughness decreases the reflectivity at higher frequency and as photon frequency increases the interference fringes becomes smaller[43] as shown in Figure 3.3.
Figure 3.3 IR reflectance spectrum of 3C-SiC on Si. Theoretical (solid line) and experimental (dotted line) showing the effect of surface roughness[43].
CHAPTER IV
THEORETICAL MODELING

Studying the optical properties of a semiconductor material like infrared reflectance gives us more information about the semiconductor material. The infrared reflectance spectra actually gives information about the film thickness, carrier concentration, surface roughness and the effect of two component effective medium when crystalline grains and intergranular materials were assumed to co-exist[43].

4.1 Dielectric Function

The dielectric function as discussed earlier is a very important factor in calculating the reflectance spectra as discussed earlier. The optical response of a semiconductor to infrared radiation can be explained by the interactions of matter with radiation due to wave vector and frequency-dependent dielectric function when light is shine on it. Two major factors actually add up to the dielectric response function $\epsilon(\omega,q)$. The first factor is the effect of the free charge carrier $[\epsilon_e(\omega,q)]$ from either the electrons in the conduction band or the holes in the valence band. The second factor is the effect lattice $[\epsilon_i(\omega,q)]$ due to lattice vibrations or optical phonons. The limiting case shows that as $q$ becomes zero, the dielectric function can be expressed as[5]:

$$\epsilon(\omega) = \epsilon_e(\omega) + \epsilon_i(\omega)$$  \hspace{1cm} (4.1)

The above equation can also be written using complex notation to express the complex dielectric function as

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$$  \hspace{1cm} (4.2)
The complex dielectric function above shows both the real and imaginary part which helps to describe the optical properties of the medium at all photon energies[28]. \(\epsilon_1(\omega)\) is the real part and \(\epsilon_2(\omega)\) is the imaginary part which is due to the absorption of energy as a function of frequency. This absorption influences the reflectivity spectrum directly[5].

The complex refractive index \(n^*(\omega)\) can be related to the complex dielectric function as:

\[
n^*(\omega) = n(\omega) + ik(\omega) = [\epsilon(\omega)]^{1/2}
\]

(4.3)

Where the optical constant \(n(\omega)\) is the index of refraction and \(k(\omega)\) is the extinction coefficient which is also known as the attenuation index[5, 28]. The complex dielectric can also be written as:

\[
\epsilon(\omega) = \epsilon_\infty [1 - \frac{\omega_p^2}{\omega(\omega+i\gamma)}] + \frac{s_\omega^2_{\text{TO}}}{\omega_p^2 - \omega^2 + i\omega\Gamma},
\]

(4.4)

where \(\omega\) is the infrared frequency, \(\epsilon_\infty\) is the high frequency dielectric constant, \(\gamma\) is the plasma coefficient and \(\Gamma\) is the phonon damping constant, \(\omega_{\text{TO}}\) is the transverse optic-phonon frequency(also known as TO phonon frequency), \(S\) is the oscillator strength and \(\omega_p\) is the bulk plasma frequency which can be expressed as

\[
\omega_p = \sqrt{\frac{4\pi\eta e^2}{m^*\epsilon_\infty}}
\]

(4.5)

Where \(\eta\) is the free carrier density in cm\(^{-3}\), \(m^*\) is the effective mass and \(e\) is the charge.

4.2 Superlattice

The measurement of reflection and transmission at near normal incidence using FIR spectroscopy can be used to study the optical constants in compound semiconductor[5]. The dielectric function varies due to anisotropy of the uniaxial crystal relative to the polarization with
the plane of the surface. The dielectric tensor $\epsilon_{\text{SL}}$ according to long-wavelength theory for a Superlattice (SL) including isotropic layers for a uniaxial crystal can be expressed as

$$\epsilon_{\text{SL}} = \begin{bmatrix} \epsilon_{\perp} & 0 & 0 \\ 0 & \epsilon_{\perp} & 0 \\ 0 & 0 & \epsilon_{\parallel} \end{bmatrix}$$

(4.6)

The above tensor shows that the dielectric function is uniform first two columns of the diagonal axis when polarized along x- or y-axis but different in the z-axis. The z-axis is placed along the optical axis perpendicular to the plane of the superlattice. For any large wavelength as compared to the SL period $d (=d_1 + d_2)$, the electromagnetic boundary conditions give[5, 45]

$$\epsilon_{\perp}(\omega) = \frac{d_1 \epsilon_1(\omega) + d_2 \epsilon_2(\omega)}{d_1 + d_2}$$

(4.7)

and

$$\epsilon_{\parallel}(\omega) = \frac{(d_1 + d_2)\epsilon_1(\omega)\epsilon_2(\omega)}{d_1\epsilon_2(\omega) + d_2\epsilon_1(\omega)}$$

(4.8)

The layer thickness of the alternating layer of the SL is represented with $d_1$ and $d_2$, while $\epsilon_1$ and $\epsilon_2$ are the complex dielectric function which can be calculated from the known parameters of the SL materials.

The reflectance and transmission spectra of SL or multilayer can be calculated using the effective medium dielectric tensor described above. The reflectance of polarized radiation for the SL grown on substrate for s and p polarization can be obtained by

$$R = \left| \frac{(1-A)\cos B - i(C-D)\sin B}{(1+A)\cos B - i(C+D)\sin B} \right|^2,$$

(4.9)
For s polarization,

\[ A = \sqrt{\epsilon_s - \sin^2 \theta_i} \cos \theta_i \]  

(4.10)

\[ B = 2\pi \hbar \omega \sqrt{\epsilon_\perp \sin^2 \theta_i} \]  

(4.11)

\[ C = \left( \frac{\epsilon_s - \sin^2 \theta_i}{\epsilon_\perp - \sin^2 \theta_i} \right)^{1/2} \]  

(4.12)

\[ D = \frac{\sqrt{\epsilon_\perp - \sin^2 \theta_i}}{\cos \theta_i} \]  

(4.13)

and for p polarization,

\[ A = \frac{\sqrt{\epsilon_s - \sin^2 \theta_i}}{\epsilon_s \cos \theta_i} \]  

(4.14)

\[ B = 2\pi \hbar \omega \left( \frac{(\epsilon_\parallel - \sin^2 \theta_i) \epsilon_\perp}{\epsilon_\parallel} \right)^{1/2} \]  

(4.15)

\[ C = \left( \frac{\epsilon_\perp \epsilon_\parallel (\epsilon_s - \sin^2 \theta_i)}{\epsilon_\parallel^2 (\epsilon_\parallel - \sin^2 \theta_i)} \right)^{1/2} \]  

(4.16)

\[ D = \left( \frac{\epsilon_\parallel - \sin^2 \theta_i}{\epsilon_\perp \epsilon_\parallel \cos^2 \theta_i} \right)^{1/2} \]  

(4.17)

The complex dielectric function if the substrate is represented with \( \epsilon_s \), \( h \) is the total thickness of the SL and \( \omega \) is the frequency. The incident angle is represented with \( \theta_i \).
4.3 Thin films

When the FIR penetration depth radiation is approximately 3µm in nontransparent materials, the reflectivity of the thin films gives structural information of the film constituents and the substrate. The dielectric function knowledge helps in calculating or determining the reflectivity and transmission spectra of the material.

**Figure 4.1** Semiconductor thin film grown on a thick substrate. The s and p component of the FIR radiation incident direction are at oblique angle (45°) to the thin film surface of thickness $d \ll \lambda$ grown on thick substrate[5].
The reflectance and transmission of a thin film grown on a substrate is illustrated in Figure 4.1 with three medium air-film-substrate system. The dielectric functions $\varepsilon_1$ is unity for air medium, $\varepsilon_2$ is the dielectric function of the thin film $\varepsilon_{tf}$ and $\varepsilon_3$ is the dielectric function of the substrate.

The complex dielectric function of the thin film in response to the infrared radiation can be expressed in the following form

$$\varepsilon(\omega) = (n + ik)^2 = \varepsilon_\infty \left[ 1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i \gamma_{TO} \omega} - \frac{\omega_p^2}{\omega(\omega + i \gamma_p)} \right]$$  \hspace{1cm} (4.18)

Here $n$ is the refractive index, $k$ is the extinction coefficient, $\omega$ is the infrared frequency, $\varepsilon_\infty$ is the high-frequency dielectric function, $\gamma_p$ is the plasma damping constant, $\gamma_{TO}$ is the phonon damping constant, $\omega_p$ is the plasma frequency, $\omega_{LO}$ is the transverse optical frequency and $\omega_{LO}$ is the longitudinal phonon frequency.

The reflectance of the thin film grown on a substrate can be calculated from the normal incidence reflectance in the following form[44]

$$R = \frac{A1 - 2B1\cos\phi + 4KfC1\sin\phi + D1\chi^2}{A2 - 2B2\cos\phi + 4KfC2\sin\phi + D2\chi^2}$$  \hspace{1cm} (4.19)

$$\chi = \exp(-4\pi nfd/\lambda)$$  \hspace{1cm} (4.20)

$$\phi = 4\pi nfd/\lambda$$  \hspace{1cm} (4.21)

$$A1 = [1 - n_f^2 + K_f^2 + 1](n_f + n_s)^2 + K_f^2]$$  \hspace{1cm} (4.22)

$$B1 = (n_f^2 + K_f^2 - 1)(n_f^2 + K_f^2 - n_s^2) + 4n_sK_f^2$$  \hspace{1cm} (4.23)

$$C1 = n_s(n_f^2 + K_f^2 - 1) - (n_f^2 + K_f^2 - n_s^2)$$  \hspace{1cm} (4.24)

$$D1 = [(n_f + n_s)^2 + K_f^2][(1 + n_f)^2 + K_f^2]$$  \hspace{1cm} (4.25)

$$A2 = [(1 + n_f)^2 + K_f^2][(n_f + n_s)^2 + K_f^2]$$  \hspace{1cm} (4.26)

$$B2 = (n_f^2 + K_f^2 - 1)(n_f^2 + K_f^2 - n_s^2) + 4n_sK_f^2$$  \hspace{1cm} (4.27)
\[ C_2 = (n_f^2 + K_f^2 - n_s^2) + n_s(n_f^2 + K_f^2 - 1) \]  \hspace{1cm} (4.28)

\[ D_2 = [(1 - n_f)^2 + K_f^2][(n_f - n_s)^2 + K_f^2] \]  \hspace{1cm} (4.29)

Here \( n_f \) is the index of refraction and \( k_f \) is the extinction coefficient of the film. The film thickness is \( d \), the wavelength of the infrared radiation is \( \lambda \), and \( n_s \) is the index of refraction of the substrate.
CHAPTER V
RESULTS AND DISCUSSION

The complex dielectric model as discussed can be used to calculate the reflectance and transmission spectra of 3C-SiC as discussed earlier. The reflectance spectra is influenced by the film thickness, surface roughness, phonon damping constant, plasma damping factor, carrier concentration and the effect of three component medium co-existing in SiC sample. The theoretical calculated spectra provides information for comparing the theoretical model with experimental spectra with the help of IR spectroscopy. The results of this study have been carried out using the C++ programs.

5.1 IR Reflectance Spectra for Different Thickness

The IR reflectances for different thicknesses of 3C-SiC on Si have been calculated including the

Figure 5.1 Calculated reflectance of 3C-SiC on Si for different thickness, (a) Bulk SiC, (b) 5µm, (c) 25µm, (d) 15µm, (e) 0.55µm, and (f) 0.055µm.
spectrum of the bulk SiC. Figure 5.1 illustrates the calculated reflectance spectra for bulk SiC and different thickness.

From the calculated IR reflectance spectra above, the peak rises and spread out as the thickness increases. A good reststrahlen band is observed at different micrometers. The thickness of the epitaxial film determines the fringe spacing and is given by

\[ d = \frac{1}{2n_f \Delta \omega} \]  

(5.1)

Here, \( \Delta \omega \) is the spacing in wave number between the two consecutive maxima and minima of the fringe in the interference pattern.

For accuracy, \( \Delta \omega \) can be known over a frequency interval that is made up of different maxima. This can be done when Equation (5.1) takes the general form

\[ d = \frac{m}{2n_f \Delta \omega} \]  

(5.2)

Here, \( m \) represents the number of complete cycles included in the interval \( \Delta \omega \).

5.2 IR Reflectance Spectra for Different carrier concentration

The IR reflectance spectra shows two changes with different plasma frequency \( \omega_p \) and different free carrier concentration \( \eta \) at \( \gamma_p = 300 \text{ cm}^{-1} \). The first reflectance minimum appeared near \( \omega_{LO} \) (973 cm\(^{-1}\)) for undoped system. The reflectance minimum shifts to high frequency side and the reststrahlen band spread out as \( \omega_p \) increases. \( \omega_p \) and \( \eta \) are related by the equation (4.5). The different value of the concentration and related plasma frequency can be found in table 5.1 as illustrated in Figure 5.2 and Figure 5.3.

| Table 5.1 Different values of carrier concentration and related \( \omega_p \) (in cm\(^{-1}\)) |
|-----------------|--------------|--------------|--------------|--------------|--------------|--------------|
| \( \omega_p \) (cm\(^{-1}\)) | (a) 2100     | (b) 1500     | (c) 1200     | (d) 900      | (e) 500      | (f) 100      |
| \( \eta \) (cm\(^{-3}\))  | 1.03x10\(^{20}\) | 5.23x10\(^{10}\) | 3.35x10\(^{19}\) | 1.88x10\(^{19}\) | 5.82x10\(^{18}\) | 2.33x10\(^{18}\) |
Figure 5.2 Calculated IR reflectance spectrum of 3C-SiC on Si with different $\omega_p$ at $\gamma_p = 300$ cm$^{-1}$. The different $\omega_p$ are (a) 2100, (b) 1500, (c) 900, (e) 500, (f) 100.

Figure 5.3 Carrier Concentration $\eta$ and plasma frequency $\omega_p$. 

$\epsilon_\infty = 6.7$

$m^* = 0.31 m_0$

$n$-3C-SiC
d = 7.7 µm
5.3 IR Reflectance Spectra for Different Phonon Damping Constants

The effect of phonon damping factor has great significance on the reflectance peak, with large damping factors leading to lower reflectance. With large $\gamma_{TO}$ the interference fringes will spread out. The increase of the TO resonance is due to the presence of crystalline defect that introduces dissipative process.

![Figure 5.4](image)

**Figure 5.4** Calculated IR reflectance spectra of 3C-Si on Si with different $\gamma_{TO}$ (cm$^{-1}$) of (a) 50, (b) 30, (c) 15, (d) 9, (e) 5, and (f) 3.

5.4 IR Reflectance Spectra for Different Plasma Damping Factors

The effect of plasma damping factor helps us to determine the carrier mobility of the film reflectance.
As the mobility decreases the band narrows, while reflectivity becomes smaller at lower frequency. This can be represented as follows

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

(5.3)

**Figure 5.5** Calculated IR reflectance of 3C-SiC on Si for different plasma damping factors \( \gamma_p \) (in \( \text{cm}^{-1} \)) at \( \omega_p = 500 \text{ cm}^{-1} \) (a) 800, (b) 400, (c) 100.

5.5 IR Reflectance Spectra Due to Surface Roughness

As discussed earlier in the experimental approach that the fringe contrast decrease as the frequency increases beyond the restsrahalen due to surface roughness. The effect of surface roughness of the film can be seen from Figure 5.6 below. Loss of reflectance and decreasing contrast of interference fringes may be due to the surface roughness of the film which can be represented as:

\[ R = R_0 \exp[-16(\pi \delta/\lambda)^2] \]  

(5.4)
Here, in the above equation, $R_0$ is the ideal reflectance of the film, $\lambda$ is the wavelength, and $\delta$ is the surface roughness of the film measured in $\mu$m. This theoretical modeling actually agrees with the work done by Feng et al. and Holm et al. Hence, the effect of surface roughness on the reflectance cannot be overlooked [43, 44, 46].

![Figure 5.6](image)

**Figure 5.6** Calculated IR Reflectance spectra for different surface roughness of the film at 6.0 $\mu$m thickness with surface roughness of:

(a) $\delta = 0.0 \mu$m, (b) $\delta = 0.08 \mu$m, and (c) $\delta = 0.15 \mu$m.

### 5.6 IR Reflectance Spectrum due to Interfacial Layer Effect

The presence of interfacial layer between the film and the substrate is also very important. The effect of interfacial layer on the interference fringes when it is large or very small. The presence
of interfacial layer between the film and the substrate does not only lead to high reflectivity below the restsrahlen band but also above the restsrahlen band as shown in Figure 5.7.

![Figure 5.7 IR reflectance spectrum of 3C-SiC/Si in the presence of interfacial layer.](image)

From fig. 5.7, it shows that the IR reflectivity of the sample has higher contrast as compared to other samples discussed earlier. The interfacial layer thickness and refractive index helps in determining the speed of the contrast. With the interfacial layer thickness very small, the interference contrasts appear as normal for an ideal sample.

5.7 Two-component effective medium model

The calculated IR spectra can also be analyzed with the use of modified three-component effective medium. Holm et al also observed this phenomenon with the sensitivity of the reflectance at the top of the restsrahlen peak to slight surface roughness. Thus at about $\omega = 900$ cm$^{-1}$ increase in surface roughness makes the dip to become a deep notch. This feature can also
be seen from Figure 5.8 and Figure 5.9 with the dips occurring around 900 cm\(^{-1}\) using the calculated IR spectrum.

\[ \sum_{i=1}^{3} f_i \left[ \epsilon_i(\omega) - \epsilon(\omega) \right] = 0, \]

\(\text{Figure 5.8 IR reflectance spectrum of 3C-SiC/Si (100) for two different components of SiC.}\)

This calculation was done using the three-component effective medium model as said earlier with three effective mediums. The mediums are pores, crystalline grains, and intergranular materials. However in this study, the effect of pores was not considered. These mediums were assumed to add up in a SiC sample with the effective dielectric function evaluated from the self consistency condition in the form

\[ \epsilon(\omega) = \frac{\sum_{i=1}^{3} f_i \epsilon_i(\omega)}{1 + 2 \sum_{i=1}^{3} f_i}, \]

Where \(\epsilon_i\) is the ith component dielectric function, \(f_i\) is the volume fraction, and \(\epsilon\) is the effective dielectric function.
Figure 5.9 IR spectrum of 3C-SiC/Si (100) for two different components of SiC.

This IR reflectance was carried out by varying the volume fractions $f_i$ (1-3), $\omega_{TO}$ and $\omega_{LO}$ frequency of the intergranular material to give the features observed in Figure 5.8 and Figure 5.9. The volume fraction $f_2$ (of Figure 5.8) is 0.5% for intergranular material with 940cm$^{-1}$ and 980cm$^{-1}$ $\omega_{TO}$ and $\omega_{LO}$ respectively higher than that of crystalline SiC. The fraction $f_2$ was responsible for the little notch observed.

Likewise for Figure 5.9 the volume fraction $f_2$ is 2.5% for intergranular material with 940cm$^{-1}$ and 980cm$^{-1}$ $\omega_{TO}$ and $\omega_{LO}$ respectively higher than that of crystalline SiC. We were able to see a clear notch at higher $f_2$ value.
CHAPTER VI
CONCLUSION

We have been able to carry out study on infrared (IR) reflectance of 3C-SiC grown on Si (100) theoretically using IR reflectance methodology to model the reflectance spectra with the influence of surface roughness, film thickness, free carrier concentration, plasma damping constant, plasma frequency, and interfacial layer. This study have been carried out using C++ program to model the complex dielectric function in calculating the reflectance spectra to give result in agreement with experimental spectra observed by Holm and Feng [43,44].

With the calculated reflection spectra, we have been able to gather information related to the surface roughness and interfacial layer between the thin film and the substrate. We also noticed that with increase in frequency, the interference fringes contrast decreases when surface roughness is included in the calculation, which actually was in agreement with the experimental spectra observed. From the IR reflectance spectra, we noticed that as the thickness changes, the spectrum also changes with different fringe spacing and number of peaks without surface roughness.

We were able to study the effect of phonon damping constant and plasma damping factor on the IR reflectance spectra of 3C-SiC/Si. It shows clearly from our study that reflectance was directly proportional to phonon damping constant. The interference fringes tend to spread out at high phonon damping constant. We also observed that decrease in the carrier mobility narrows the band.

We noticed that the introduction of interfacial layer between the film and the substrate leads to high reflectivity below the restsrahlen band but also above the restsrahlen band. The interfacial layer thickness and the index of refraction determine the decreasing speed of the contrast.
Finally we observed the effect of intergranular material with higher TO and LO frequencies as compared to crystalline SiC. The volume fraction of intergranular material was responsible for the notch observed at the peak of the restsrahlen band.
REFERENCES


31. Halac, E.; Burgos, E.; Bonadeo, H. Static and dynamical properties of SiC polytypes. 


