QUANTUM WELL STATE OF CUBIC INCLUSIONS IN HEXAGONAL SILICON CARBIDE STUDIED WITH BALLISTIC ELECTRON EMISSION MICROSCOPY

DISSERTATION

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By

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* * * * *

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SiC is a polytypic material that may crystallize in many different close-packing sequences with cubic, hexagonal, or rhombohedral Bravais lattices. All SiC polytypes have wide bandgaps ranging from 2.39 eV in cubic SiC to 3.023 – 3.330 eV in common hexagonal polytypes. This, as well as many other properties favorable to electrical applications, makes SiC a very promising material in electronic device fabrication. However, the many lattice stacking sequences may impair the stability of SiC devices. In the hexagonal 4H polytype, it has been found that thin cubic SiC inclusions may be formed due to stacking fault expansion, and it has been proposed that the inclusions may behave as quantum wells because of the lower bandgap of cubic SiC.

We performed ultra-high vacuum ballistic electron emission microscopy (BEEM) measurements on $n$-type 4H-SiC samples containing double-stacking-fault cubic inclusions to characterize the electrical properties of individual inclusions. Thin Pt films are deposited in ultra-high vacuum on the sample surfaces to form Schottky contacts. A Schottky barrier height of $\sim$1.01 eV is observed over the inclusions in a background of normal 4H-SiC barrier height of 1.54 eV, which directly confirms the cubic inclusions support two-dimensional propagating quantum well states, and the 0.53 eV lowering of
barrier height indicates the two-dimensional conduction band minimum is located at
\(~0.53\) eV below the conduction band minimum of bulk 4H-SiC.

We also used BEEM to study the Schottky contact between Pt and \(p\)-type 4H-SiC,
and observed a second transmission channel in the BEEM spectrum that suggests a split-
off valence band at \(~0.11\) eV below the valence band maximum. We also measured the
barrier heights of \(p\)-type and \(n\)-type Schottky contacts prepared under identical conditions
and the results suggest the existence of an interfacial layer.

An earlier study of threading dislocations in GaN using BEEM is also described.
Although threading dislocations in GaN had been generally thought to be negatively
charged prior to our study, our high-resolution BEEM measurements yielded no evidence
of significant charge along the dislocations near the interface between Pt films and our
molecular beam epitaxy grown GaN sample.
Dedicated to my wife
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CHAPTER 1

OVERVIEW

In this work, the electrical properties of self-forming cubic inclusions in hexagonal silicon carbide (SiC) are studied using ballistic electron emission microscopy (BEEM) in ultra high vacuum (UHV). The quantum well behavior of the inclusions is directly confirmed, and the quantum well energy is estimated. Additionally, $p$-type Schottky contacts on SiC are studied using BEEM. The author’s contribution to an earlier project about charge accumulation along threading dislocations in gallium nitride (GaN) studied with BEEM is also presented in this dissertation.

SiC and GaN are wide-bandgap semiconductor materials of great use in the fabrication of electronic devices including power diodes, high-frequency (up to blue and ultra-violet) light emission diodes, and semiconductor lasers. Inclusions (planar defects) in SiC and threading dislocations (linear defects) in GaN, however, may impair the quality of devices. It has been observed that the formation of cubic inclusions results in the degradation of hexagonal SiC power diode after long hours of operation. Cubic inclusions of another type have also been found in $n$-type hexagonal SiC samples after high-temperature processing. Threading dislocations in GaN had generally been believed
to possess significant negative charge prior to our studies. Therefore, it is important to investigate these defects in SiC and GaN for more insights about the improvement of device quality, and BEEM as a local probe with high energy resolution and spatial resolution is a useful tool for this purpose.

One other aspect of great interest is that luminescence studies and theoretical calculations of cubic inclusions in hexagonal SiC have suggested they may behave like quantum wells. Our BEEM studies of cubic inclusions in high-temperature-processed hexagonal SiC samples directly confirmed the quantum well nature of this interesting physical system, in which there is no change in composition, density, or nearest-neighbor stacking across the quantum well boundaries, yet there are highly localized quantum well states in the cubic inclusions.

The BEEM technique, developed by Bell and Kaiser in 1988 [1], is an extension of scanning tunneling microscopy (STM) [2] that uses hot carriers injected from the STM tip to probe buried metal/semiconductor (M/S) interfaces and other heterostructures. Defects in the semiconductor, if electrically active, may alter the interface potential and be detected with BEEM. Additional information about the semiconductor band structure may also be obtained using BEEM.

Our BEEM experiments as well as macroscopic $IV$ and $CV$ characterizations of M/S contact samples described in this dissertation are performed in an UHV chamber with a base pressure of $\sim 1 - 2 \times 10^{-10}$ Torr to ensure sample cleanliness, where a sample can be repeatedly studied over several months with low noise, high resolution, and reproducible results. Thin metal films are deposited $in situ$ on semiconductor samples using e-beam evaporation in an adjacent UHV chamber.
Background information and experimental results of our work are presented in the following chapters:

Chapter 2, an introduction to SiC, covers several topics important to our study of cubic inclusions in hexagonal SiC. It begins with a detailed crystallographic review of polytypism, a prominent property of SiC. The general physical properties of different SiC polytypes are then reviewed, with emphasis on band structures and spontaneous polarization. Finally, the formation mechanisms and properties of cubic inclusions in hexagonal SiC are discussed, with both experimental findings and theoretical calculations summarized.

Chapter 3 deals with our experimental methods, mainly the technique of BEEM. Theories of Schottky contacts are briefly reviewed, and the equipment setup and data processing methods are also described.

The results of our experimental work in three different projects are presented in Chapter 4. The highlight is our study of double-stacking-fault cubic inclusions in 4H-SiC, whose quantum well behavior was directly confirmed using BEEM and the lowest quantum well energy was estimated to be at ~0.53 eV below the conduction band minimum (CBM) of 4H-SiC. Our BEEM study of Pt/p-type 4H-SiC contacts is then presented, in which we found evidence of a split-off valence band, and the comparison with Pt/n-type 4H-SiC contacts suggested the existence of an interfacial layer. Finally, we describe an earlier study of threading dislocations in GaN, in which NO significant negative charge was found along threading dislocations near the metal/GaN interface on our molecular beam epitaxy (MBE) grown GaN sample.
Chapter 5 summaries the work presented in this dissertation and discusses future directions.
CHAPTER 2

SILICON CARBIDE

SiC is a very promising semiconductor material for highly-demanding electronic devices (with respect to power, voltage, frequency, temperature, etc.), thanks to its wide bandgap, high breakdown electrical field, high carrier saturation speed, excellent thermal conductivity, and other proprieties favorable to electrical applications [3]. However, as-grown SiC still contains many defects. Recently, the long-term stability problem of SiC devices has attracted much attention since the first reports of hexagonal SiC power diode degradation after long hours of operation [4, 5]. Self-forming cubic inclusions have been found in the degraded diodes and some high-temperature-processed samples of hexagonal SiC, and the unique quantum well behavior of these inclusions is of great theoretical and experimental interest.

The phenomenon that SiC may crystallize in both cubic and hexagonal lattices is called polytypism. An introduction to polytypism and the physical properties of SiC polytypes will first be presented in this chapter before the cubic inclusions are discussed in details.
2.1 Polytypism

An important property of SiC is that it crystallizes in a number of forms. Generally this property is called polymorphism. However, the polymorphism of SiC is special in that all its different crystal forms have a same atomic plane in common and differ only in the stacking sequence along the direction normal to this plane. This kind of one-dimensional polymorphism is called polytypism. It is in SiC that the physical phenomenon of polytypism was first found [6], and SiC remains to be the most prominent polytypic material with more than 200 reported polytypes [7]. Other typical polytypic materials include zinc sulfide (ZnS) and cadmium iodide (CdI$_2$).

2.1.1 Tetrahedrally Bonded Structures

Silicon and carbon atoms in SiC are both tetravalent due to sp$^3$ orbital hybridization and form tetrahedral covalent bonds (to be more specific, 88% covalent and 12% ionic [8]) between the two types of atoms, i.e., each Silicon atom at the tetrahedral center is bonded with four Carbon atoms on the corners, and vice versa. Tetrahedral bond is prevalent among semiconductor materials, and most of these materials crystallize in either the diamond/zincblende (named after cubic ZnS) structure, or the wurtzite (named after hexagonal ZnS) structure, or both.

The diamond/zincblende structure consists of two interpenetrating face-centered cubic (fcc) lattices displaced along the [111] direction by 1/4 of the length of the cubic cell body diagonal so that each atom in one lattice forms tetrahedral bonds with four atoms in the other lattice (Figure 2.1). It is called the diamond structure if the material is elemental and zincblende if the two fcc lattices are occupied by different elements.
Figure 2.1: (a) The unit cell of an fcc lattice; (b) diamond/zincblende lattice. Thick solid lines in (b) represent the tetrahedral bonds between several atoms on the lattice sites; the two sites in the dotted oval is a basis of this lattice with respect to the fcc one.

Figure 2.2: (a) The unit cell of a simple hexagonal lattice. (b) hcp lattice, which consists of two identical simple hexagonal lattices (whose lattices parameters have to satisfy $c/a = 1.633$) interpenetrating as shown. (c) Wurtzite lattice. The two sites in the dotted oval is a basis of this lattice with respect to the hcp one.
The wurtzite structure is the hexagonal counterpart of the zincblende structure and consists of two hexagonal close-packed (hcp) lattices displaced along or against the stacking direction (known as the c-axis) by \(3/8\) of the \(c\) lattice vector (Figure 2.2). By definition, the wurtzite structure is dedicated to compounds. Interestingly, its elemental version does exist (embodied by carbon [9] and silicon [10] in some extremely rare situations) and is called the lonsdaleite structure [11].

It should be noted that the fcc lattice is also close-packed. This is evident in Figure 2.3 — the (111) plane of an fcc lattice is nothing but the two-dimensional (2D) close-packed lattice (in which any lattice point is surrounded by six evenly distributed closest points, and the two primitive vectors are of equal lengths and make an angle of \(60^\circ\) or \(120^\circ\)), and the three-dimensional (3D) fcc structure can be regarded as (111) planes close-packed along the [111] direction. Therefore, both the diamond/zincblende and the lonsdaleite/wurtzite structures are close-packed lattices with a basis, and the basis consists of a pair of atoms bonded along the stacking direction, as illustrated by the ovals in Figure 2.1 and 2.2.

The formation of close-packed structures in tetrahedrally bonded materials is not coincidental. Consider four cannonballs, there is only one close-packing arrangement, in which the ball centers mark the vertexes of a tetrahedron (Figure 2.4). Tetravalent atoms form tetrahedrons whose centers are also occupied, and the packing of these tetrahedrons (sharing vertexes, where atoms reside, but not sharing any faces or edges, otherwise the atoms on the vertexes would no longer be tetravalent) results in a close-packed lattice with a basis as described in the previous paragraph (Figure 2.5). On the other hand, a close-packed lattice is not necessarily formed by tetrahedral bond (e.g., CdI\(_2\)).
Figure 2.3: (a) 2D close-packed lattice. The dashed circles indicate a second layer close-packed above the first. (b) (111) planes of the fcc lattice are 2D close-packed lattices. The dotted lines are in the (110) plane and along the [111] direction.

Figure 2.4: Relationship between close-packing and tetrahedron. (a) Four close-packed cannonballs; (b) their centers form a tetrahedron; (c) tetravalent atoms occupy the center and the vertexes of the tetrahedron (the bonds are NOT along the tetrahedron’s edges).

Figure 2.5: (a) Untwinned tetrahedrons; (b) upper row are twinned tetrahedrons with respect to those in the lower row.
Further analysis of 3D close-packing possibilities reveals that given a “seed” tetrahedron and a close-packing direction, any additional tetrahedrons will have only two choices of orientation: either the same as the original, or rotated by 180° about the stacking direction (Figure 2.5). The former is called untwinned tetrahedron, the latter twinned. Exclusively untwinned tetrahedrons build the diamond/zincblende lattice, while alternating layers of twinned tetrahedrons form the wurtzite lattice.

SiC can take either the zincblende form or the wurtzite one, but there are a number of additional SiC polytypes, all of which have a close-packed lattice with a basis.

2.1.2 Close-Packing Possibilities

Although there is only one possible configuration of 2D close-packed lattice, the number of variations in 3D close-packing arrangements is virtually infinite, which gives rise to the phenomenon of polytypism.

Any 3D close-packed lattice is formed by the stacking of 2D close-packed lattice planes (known as the basal plane) along the direction normal to it (the c-axis). Consider the stacking of two planes first. Given the first plane (Figure 2.6, in which the lattice sites are denoted with the letter A), lattice points of the second plane may either reside above the sites denoted with the letter B or those with the letter C, but they cannot reside above both sites B and sites C simultaneously, because the distance between adjacent B and C sites is smaller than the close-packing distance. If the second plane resides above B sites, for example, then the third plane also has two choices: A, or C. Every additional plane has two possible stacking locations, and the total number of possible variations in 3D close-packing arrangements explodes exponentially with the number of 2D layers.
Figure 2.6: Possible sites in the stacking of 2D close-packed planes.

Figure 2.7: Axes in the Miller-Bravais index and the hexagonal coordinate system.

Figure 2.8: (a) Determination of coordinates in the hexagonal coordinate system.
(b) $\frac{1}{3}[11\bar{2}0] = \frac{1}{3}[01\bar{1}0] + \frac{1}{3}[10\bar{1}0]$ (upper vectors) or $\frac{1}{5}[21\bar{3}0] + \frac{1}{15}[\bar{1}210]$ (lower ones).
Miller-Bravais Index and the Hexagonal Coordinate System

Due to the hexagonal symmetry of the basal plane, it is convenient to use the Miller-Bravais index, a 4-axis variation of the conventional Miller index, to describe planes in non-cubic close-packed lattices. The first three axes lie in the basal plane and make 120º with one another, while the fourth is the c-axis (Figure 2.7). The Miller-Bravais index of any plane is still defined as the smallest set of integers proportional to the reciprocals of the plane’s intercepts on all axes (the sum of the first three indexes is always zero, which is not difficult to prove in trigonometry). This index system better reflects the hexagonal symmetry: e.g., the three crystallographically equivalent planes indicated with dashed lines in Figure 2.6 are now collectively indexed as the \{11\overline{2}0\} planes, while their conventional Miller indexes are [110], [\overline{2}10], and [1\overline{2}0], respectively.

The four axes used in the Miller-Bravais index also define a hexagonal coordinate system, in which a vectors can be represented using four coordinates that are quite count-intuitively defined. For example, should the lattice vector $a$ in Figure 2.8 be [1100] or [00\overline{1}0]? To make the coordinates unique, and to be consistent with the Miller-Bravais index system, the coordinates of a vector must be proportional to the Miller-Bravais index of the plane perpendicular to it. As illustrated in Figure 2.8, the vector $a$ is actually $\frac{1}{3}[11\overline{2}0]$ in this coordinate system. Two other vector [01\overline{1}0] and [21\overline{3}0] are also shown, and it can be derived that $\frac{1}{3}[11\overline{2}0] = \frac{1}{9}[21\overline{3}0] + \frac{1}{9}[12\overline{3}0] = \frac{1}{5}[21\overline{3}0] + \frac{1}{15}[1\overline{2}10]$.

3D Close-Packing

Most of the 3D close-packing arrangements are disordered, i.e., no periodicity in the stacking along the c-axis. Disordered crystals have also been observed in SiC [12].
However, ordered crystals (with possible defects, of course) are the common case for materials grown under stable conditions. The fcc and hcp lattices happen to be two extremes of the ordering along the $c$-axis: the fcc lattice has the stacking sequence \ldots ABCABCABC\ldots extended all the way in one direction in the $(1\bar{2}0)$ plane [Figure 2.9(a); also see Figure 2.3(b), where the $(1\bar{1}0)$ plane in rectangular coordinates belongs to \{11\bar{2}0\} in hexagonal coordinates], while the hcp lattices is stacked like \ldots ABABAB\ldots with a turn every layer [see Figure 2.2(b) and 2.9(b)]. All other ordered stacking possibilities fall in between these two extremes: one repeat contains both “quasi-cubic layers”, where a concerned layer and its two neighboring layers occupy three different types of sites and are stacked along one direction in the $(1\bar{1}20)$ plane, and “quasi-hexagonal layers” (or hexagonal turns), where the two neighboring layers occupy the same type of sites and hence form a turn in the stacking direction [13]. These two types of layers are illustrated in Figure 2.9(c).

Concerning the relative numbers of quasi-cubic layers and hexagonal turns, a term “hexagonality” is defined as the percentage expression of the number of hexagonal turns divided by the total number of layers in a close-packed lattice [14]. The hcp lattice has a hexagonality of 100\%, fcc 0\%, and others (including both ordered and disordered configurations) in between.

The fcc lattice is a Bravais one, but all other close-packed lattices, including the hcp one, are non-Bravais, and have to be described as a Bravais lattice with a basis. The underlying Bravais lattice of a non-Bravais close-packed lattice is either hexagonal, in which the three primitive vectors can be chosen so that two of them span the 2D close-packed basal plane [Figure 2.3(a)] and the third lies along the $c$-axis [Figure 2.2(a)], or
Figure 2.9: The stacking in the (1120) plane of (a) the fcc lattice; (b) the hcp lattice; (c) a lattice containing both quasi-cubic layers (dashed circles) and hexagonal turns (shaded circles). Note that the distance between adjacent sites in the same layer in this plane is $\sqrt{3}$ of the hexagonal lattice constant (see Figure 2.6).

Figure 2.10: A rhombohedral unit cell spanned by the 3 primitive lattice vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$. The angle between the vectors cannot be $60^\circ$, $90^\circ$, or $109^\circ 28'$, otherwise the lattice becomes cubic. The basal plane and the $c$-axis are indicated by the axes of a hexagonal coordinate system.
rhombohedral (a.k.a. trigonal), in which three primitive vectors can be chosen so that they have equal lengths and make equal angles with one another (and also make equal angles with the basal plane). Figure 2.10 illustrates a rhombohedral unit cell. Details about how to determine whether the Bravais lattice of a non-cubic close-packed structure is hexagonal or rhombohedral will be discussed in Section 2.1.4.

Previously it was mentioned that tetrahedrally bonded materials crystallize in close-packed lattices with a basis containing two atoms bonded along the c-axis. This “basis” should not be confused with the basis needed for describing a non-Bravais close-packed lattice in term of a Bravais one. The two bases are on different levels and can be combined to directly describe a tetrahedrally bonded structure with a Bravais lattice.

### 2.1.3 SiC Polytypes

Among the over 200 known SiC polytypes, 1 (and only possibly 1) is cubic, and all others have hexagonal or rhombohedral Bravais lattices. Hexagonal and rhombohedral SiC polytypes are collectively called α-SiC, while the cubic one is also known as β-SiC. SiC crystals with disordered stacking, in which it doesn’t make much sense to establish a Bravais lattice, can also be regarded as different polytypes.

**ABC Notation**

Using the letters A, B, and C to denote stacking layers (in SiC, a stacking layer is a silicon-carbon bilayer bonded along the c-axis) according to the type of sites occupied in a layer, any polytype can be represented by writing down the stacking of layers within a repeat. For example, β-SiC is ABC (or any rotation of these three letters, depending on where one starts to count). However, this is not convenient for polytypes with many
layers in a repeat. Also, the ABC notation of a polytype is not unique (e.g., ABCB is equivalent to ABAC and ACBC).

**Ramsdell Notation**

The most commonly used notation system of SiC polytypes, proposed by Ramsdell [15] in 1947, is the number of layers in a stacking repeat in the ABC notation followed by the initial of the underlying Bravais lattice. The zincblende form (β-SiC) is therefore named 3C, wurtzite form 2H, and so forth. Other common SiC polytypes include 4H (with ABCB stacking), 6H (ABCACB), and 15R (ABCACBCABACABCB). The stacking sequences of these polytypes are illustrated in Fig. 2.11.

The Ramsdell notation system is easy to use, but it is an over-simplification and doesn’t contain sufficient information to uniquely determine the stacking order except for 3C, 2H, and 4H. More than one stacking arrangements have been found in 16H (see Figure 2.11), 51R, etc. In this situation the polytypes sharing the same Ramsdell notation are distinguished by adding a subscript (in the styles of 1, 2, … or a, b, …) based on the order they were found. On the other hand, when the detailed stacking sequence of a polytype is unknown, the Ramsdell notation is the only choice to name it.

Other notation systems are more precise but consequently less concise then the Ramsdell one. They are alternatives to the ABC notation system in describing the exact stacking sequence of polytypes, and are very useful under certain circumstances.

**Hägg notation**

The Hägg notation system emphasizes the fact that a layer in close-packed lattices only has two choices of stacking sites, given the underlying layer. Instead of using three symbols to represent the three types of sites, Hägg [16] used + and − signs to denote a
Figure 2.11: The stacking repeats (in the ABC notation) of several SiC polytypes illustrated in the (1120) plane. The real minimum repeat of 15R is encircled in the dotted oval. The tetrahedrons associated with a 4H repeat are also illustrated. Other than 3C, the repeat of any polytype in this figure starts at a hexagonal turn, but this is just for comparison purposes in this particular figure, and a repeat may start at any layer.
layer’s choice of sites. If a B layer is stacked on top of an A layer (cyclic stacking), the B layer is denoted with the + sign. C on B and A on C are indistinguishable from B on A and are therefore also denoted with +. Anti-cyclically stacked layers (C on A, B on C or A on B) goes with the − sign (sometimes they are denoted as A’, B’, and C’). This way, any ABC notation can be converted into the Hägg notation. For example, 4H (ABCB) as illustrated in Figure 2.11 becomes − + + + (or + + − −, since the first + sign in several consecutive + ones is conventionally chosen as the starting point of a repeat).

A direct conversion of 15R yields − + + + − + + − + + − + + + −. In this view, it is apparent that the smallest repeat contains only 5 layers (+ + + −)! The ABC notation requires 15 layers because every repeat has to start with the same letter, but as far as lattice translation symmetry is concerned, it is no problem to translate an A site to a B or C site (see the arrow in Fig. 2.11). Therefore, the Hägg notation system reveals more symmetry of than the ABC one. All rhombohedral polytypes have 3n (n is a positive integer) layers in the Ramsdell notation and an n-layer translation symmetry as revealed in the Hägg notation. This is not a coincidence and will be discussed in the next section.

Since interchanging the + and − signs the Hägg notation doesn’t make a different lattice, 15R may alternatively be denoted as + + − −. Sometimes a subscript of 3 is used, like (+ + − −)₃ or (+ + − −)₃.

A variant of the Hägg notation uses arrows (↑ and ↓) in place of + and − signs, and the two types of layers are called “parallel spin” and “antiparallel spin” layers. The “spin” language here is just an analogy, and nothing is really flipped down in a ↓ layer — ↑ and ↓ rather represent the twinned relationship between the tetrahedrons formed by a pair of atoms in a concerned layer with 3 atoms in the layer below it (see Figure 2.11).
**Zhdanov notation**

The Zhdanov notation system [17] is a simplification of the Hägg one by counting the numbers of consecutive like signs in the latter and writing down the numbers sequentially — 4H is denoted as 22, and 15R as 32 or 23 [or (23)_3]. It is quite convenient without any lack of stacking information: for example, 16H₁ is (33)_222, 16H₂ is 332332, 18H is (22)_33, 21R is 43, 24R is 53, 27H is (23)_3(33)_2, 33R is 3332, 90R is (23)_43322, 174R is (33)_36(33)_34, and 393R is simply (33)_2132! As can be seen from the examples above, 4H (22), 6H (33), and 15R (23) are the basic “building blocks” of many polytypes. 3C is denoted as ∞, although the author believes 1 would be a better choice.

In some literature the Zhdanov notations for some low-number hexagonal polytypes are further simplified as <1> for 2H, <2> for 4H, etc. However, there is no real advantage in doing so, because it is only applicable to very few polytypes. The use of this simplification by some people is probably one of the reasons why 3C is denoted as ∞ instead of 1.

**h-k Notation**

The h-k notation system (a.k.a the Jagodzinski notation system [18]) is more complex than the Zhdanov one but does a better job in the simplification mentioned in the previous paragraph (so that 3C would naturally not be confused with 2H). In this system, a layer is denoted with the letter h if it is a hexagonal turn and with the letter k if it is quasi-cubic. By this means, 4H (ABAC) is converted into khkh, or simpler, kh (this simplification actually reveals a hexagonal symmetry containing a screw axis and will be discussed in the next section). Every layer in 2H is an h layer whereas every layer in 3C is k, and hence 2H and 3C are denoted as h and k, respectively.
An additional advantage of the $h$-$k$ notation system is that the minimum repeat in this system reflects the number of inequivalent donor/acceptor sites concerning electrical properties. For example, 6H-SiC is denoted as $hkk$ and contains 3 different types of carbon sites: $h$, $k_1$, and $k_2$, which have experimentally determined nitrogen donor ionization energy of 81.0 meV, 137.6 meV, and 142.4 meV, respectively [19]. There is only one type of carbon site and one type of silicon site in 2H- or 3C-SiC, while the number is 5 in 15R-SiC. The inequivalence of sites comes from the differences in the relative locations of neighboring atoms from short range to long range [13], as is evident in Figure 2.11.

All the notation systems discussed above apply not only to SiC polytypes but also to close-packed structures in general. For example, the GaN samples to be discussed in Section 4.3 are of the 2H (Wurtzite) polytype.

2.1.4 Bravais lattice of Close-Packed Structures

To begin with, consider the minimum symmetry a close-packed lattice has to have. Careful inspection of Figure 2.6 reveals that any close-packing arrangement has a 3-fold rotation symmetry about the $c$-axis through any site (A, B, and C), and a reflection symmetry about the $\{1\bar{1}20\}$ planes (represented by the three dashed lines in Figure 2.6). These minimum symmetries correspond to the crystallographic point group $3m$, which belongs to the trigonal crystal system. Additional symmetries in certain polytypes may put them into a different point group and sometimes a different crystal system.

For any given lattice, the choice of a Bravais lattice along with a basis to describe it is not unique. For example, the fcc lattice, though by itself a Bravais one, can be
described as a simple cubic lattice with a basis containing four lattice points. By choosing a bigger basis, the corresponding Bravais lattice may (but not necessarily) display a higher symmetry because some asymmetries may be hidden in the basis. Therefore, it is the choice with the smallest basis that is called the underlying Bravais lattice of a non-Bravais one.

Due to the translational symmetry required by a Bravais lattice, the smallest possible basis of a close-packed lattice is the minimum stacking repeat. A natural choice of the primitive vectors of the Bravais lattice are the two primitive vectors of the 2D close-packed lattice plus a third vector that points from the starting point of a stacking repeat to that of the next repeat. The primitive unit cells spanned by these three vectors is illustrated in Figure 2.12, in which the polytypes 10H (3322), 19H [(23)322], 15R (32), and 24R (53) are shown as general examples. For simplicity, the repeats start at A sites.

For 10H, since the second repeat in the stacking sequence starts at an A site directly above the starting site of the first repeat along the $c$-axis, the cell constructed in the abovementioned way is nothing but the conventional primitive unit cell of a hexagonal lattice. 19H is different in that the second repeat starts at a different A site, and it is not straightforward to determine the lattice type from such a skewed cell. However, a hexagonal cell of the same volume as the skewed cell can be easily constructed by pointing the third vector parallel to the $c$-axis. Therefore, the underlying Bravais lattices of both 10H and 19H are hexagonal. 10H and 19H still belong to the trigonal crystal system (because their original close-packed lattices have no more symmetry than the $3m$ point group), but their smallest repeats, if chosen as a basis, are already sufficient to hide certain asymmetry and result in a hexagonal Bravais lattice.
Figure 2.12: Construction of low-symmetry and high-symmetry primitive unit cells of SiC polytypes. Note that the $c$-dimension of the rhombohedral cells of 15R and 24R is three times as high as their minimum repeats.
containing a higher order of symmetry (6-fold). This kind of close-packed lattice belongs to the crystallographic space group $P3m1$.

15R and 24R have similarly skewed cells as 19H, but since their second repeats start at a B or C site, it is impossible to point the third vector parallel to the $c$-axis (a lattice vector has to point to an occupied site!). An alternative primitive cell has to be chosen to better reflect the symmetry. Consider 15R, since all the B sites on the layer where its second repeat starts are occupied, three lattice vectors can be chosen so that they all point from the A site where the first repeat starts to the closest B sites on the starting layer of the second repeat (see Figure 2.12). The same thing can be done for 24R. It is not difficult to prove that the rhombohedral cell determined by these three vectors has the same volume as the skewed cell and hence is also a primitive unit cell.

A rhombohedron-shaped primitive unit cell directly confirms that the close-packed lattices of 15R and 24R have an underlying rhombohedral Bravais lattice (corresponding to the crystallographic space group $R3m$). There is one exception, though — if a stacking repeat contains just one layer, the angle between the rhombohedral primitive vectors becomes 60º, and additional symmetry appears — this lattice is nothing but the fcc one, which corresponds to space group $F\bar{4}3m$ in the cubic crystal system.

The repeat of few hexagonal polytypes consists of two halves with opposite signs, like $2H (+-)$, $6H (+++++-)$, and $16H_2 (+++++---++++++)$. Such a close-packed lattice, if translated along the $c$-axis by half the stacking repeat and then rotated by 60º about the $c$-axis through certain sites (not necessarily lattice sites), will overlap itself. This is a 6-fold screw symmetry, and hence these lattices belong to the hexagonal crystal system (the space group is $P6_3mc$), but the underlying Bravais lattice is
the same hexagonal lattice as that of the trigonal space group $P3m1$. In the $h\cdot k$ notation system, the two segments become the same and hence the notation can be further simplified. However, the minimum repeat in the $h\cdot k$ notation of a $P6_3mc$ polytype does not complete a stacking repeat (a stacking repeat requires translation symmetry).

In tetrahedrally bonded binary compounds like SiC, the two different atoms in a bond are not interchangeable. Therefore, no additional symmetry is permitted, and the discussion above has exhausted all the possible lattice types and space groups of SiC polytypes. Some other polytypic materials like CdI$_2$ do have additional symmetries, but they will not be discussed in this dissertation.

Given the Hægg notation of an $\alpha$-SiC polytype, the type of the underlying Bravais lattice can be determined by the difference between the number of $+$ signs and that of $-$ signs in the notation (practically this can be calculated easily by assigning alternative $+$ and $-$ signs to the numbers in the corresponding Zhdanov notation). If the difference is an integer (including 0) multiple of 3, then every stacking repeat starts at the same type of sites in the ABC notation, and the underlying Bravais lattice is hexagonal. Otherwise, the underlying Bravais lattice is rhombohedral. In rhombohedral polytypes, two consecutive minimum repeats start at different types of sites, and hence the repeat in the ABC notation is 3 times as big as the minimum repeat. Quite a few newly reported long-period SiC polytypes are not yet well studied, and before their underlying Bravais lattices are determined, they are usually referred to in the style of nH/3nR. For example, the polytype with the biggest stacking repeat to the author’s knowledge is 474H/1422R [20].

Hexagonal and rhombohedral lattices are closely related. A non-primitive rhombohedral unit cell can be constructed in a hexagonal Bravais lattice with 3 times the
volume of the primitive cell, and *vice versa* (see Ref. [12] for details). The non-primitive hexagonal unit cell of rhombohedral SiC (constructed by choosing three consecutive minimum repeats as the basis) is often used in x-ray crystallography, and the *c*-dimension of this cell directly corresponds to the number of layers in the Ramsdell notation of the rhombohedral polytype [12]. A non-primitive hexagonal unit cell can be similarly constructed in the 3C polytype as well, with 3 layers in the *c*-dimension.

### 2.1.5 Why So Many Polytypes in SiC?

To date, there is not yet a definitive answer to this question. Many SiC polytypes have a big number of layers in one stacking repeat, and some long range force must exist so as to produce the long range order, but the nature and origin of this long range force is not yet clear. So far, theories about the origin of SiC polytypes mainly belong to two categories: one with a thermodynamic approach concerning the total entropy and/or energy of the structure, the other dealing with the role of screw dislocations in the growth of long-period polytypic crystals.

**Entropy/Energy Considerations**

The low energy needed for a SiC stacking layer (*i.e.*, a silicon-carbon bilayer bonded along the stacking direction) to “slip” from one type of site to another [21] is believed to be responsible for the formation of stacking faults, which may help produce disordered crystals. Since a completely disordered system has the lowest configurational entropy, intuition would suggest that disordered lattices be favored in the formation of close-packed crystals. However, this is exactly the opposite of the real case in SiC or any other polytypic material — disordered crystals are seldom observed.
Jagodzinski [22] proposed in 1954 that the long range force between SiC stacking layers lies in the vibrational (phonon) entropy of a close-packed structure, which causes ordering during the formation of stacking faults, because the total entropy (the sum of vibrational entropy and configurational one) favors ordered crystals. In this view, long-period SiC polytypes should rather be regarded as metastable thermodynamic phases whose existence depends on pressure and temperature conditions [12]. Qualitatively, this is consistent with the formation of different SiC polytypes under different temperature [23] and with the fact that polytypic transformations may occur in SiC crystals [24].

Starting from a parent crystal of 3C-SiC, this theory explained how stacking fault formation would result in other polytypes, and derived the sequence of the abundance of 6H-, 15R-, and 4H-SiC in commercial SiC (for abrasion purposes). Evidence of polytypic transformation induced by a periodic slip process has been observed in ZnS [25], which is structurally similar to SiC.

With the advancement in computational methods (such as the ab initio pseudopotential technique) and computing power in the recent decades, there have been a number of calculations about the energy of SiC polytypes using various methods including the axial next-nearest neighbor Ising (ANNNI) model and the density function theory. Especially, Heine and Cheng et al.’s ab initio calculation [26, 27] suggested small differences of phonon free energy may be responsible for the stability of 4H-, 6H-, 15R-, and even higher-order SiC polytypes at different temperatures.

Comprehensive reviews about the recent calculations are available in Ref. 28 and 29. Figure 2.13 summarizes the calculated total energy of some common SiC polytypes. Although different people’s results don’t quite agree due to differences in the calculation
methods and assumptions, they all found 4H- and 6H-SiC (and 15R-SiC, if calculated) have lower energy than 3C-SiC, whereas the energy 2H-SiC is higher. The energy difference between different SiC polytypes is only few meV per atom, though.

Special attention has to be paid to the ANNNI model, which is frequently used in the discussion of stacking faults and inclusions in SiC. Pioneer work of the ANNNI model’s application to polytypic materials was done by theoretical crystallographers in the 1980’s (summarized in Ref. 30), whereas Cheng et al.’s work [31] was the first to receive much attention in the physics community.

Using the ANNNI model, the energy per Si–C atom pair of a polytype is given by

\[ E = E_0 - \frac{1}{N} \sum_{i,n} J_n \sigma_i \sigma_{i+n}, \]

where \( E_0 \) is an offset energy, \( N \) is the total number of layers (Si–C bilayers), \( J_n \) is the parameter of interlayer interaction (\( n = 1 \) for the adjacent layer, \( n = 2 \) for the second nearest layer, and so forth), and \( \sigma_i \) is a “spin” parameter that is equal to +1 for a + or ↑ layer in the Hägg notation and −1 for a − or ↓ layer. The index \( i \) is summed over \( N \), while \( n \) is usually limited to no more than 3 in the calculations. The values of \( J_1 \), \( J_2 \), and \( J_3 \) calculated by different groups are all in 1 meV order of magnitude, but the particular numbers differ greatly between different calculations.

Cheng et al. [31] pointed out that if \( J_1 = -2J_2 > 0 \) and \( J_3 = 0 \), there is a multi-degeneracy point at zero temperature where an infinite number of polytypes may coexist. Their calculations indicate SiC lies very close to this multi-degeneracy point. However, other people’s calculations didn’t confirm this result. Limpijumnong et al. [29] found a \( J_1 \) value not much bigger than \( |J_2| \), but noted that the energy cost of a twin boundary in 3C-SiC [which equals \( 2(J_1 + 2J_2) \), see Ref. 27] would become negative in this case, and this is favorable to polytypic transformation.
Table 2.1: Comparison of different calculations of the interlayer interaction parameters in SiC (Ref. 21 and 29 belong to the same group).
Screw Dislocation Theory

The screw dislocation theory of polytype formation (see Ref. [12] for details) was originally proposed by Frank [33] as a direct application of the theory of crystal growth assisted by screw dislocations [34] to SiC. The screw dislocation ledge is supposed to determine the stacking repeat of polytypes. This theory was later refined by Mitchell [35] and Krishna and Verma [36] to explain the occurrence of some SiC polytypes based on the 6H, 4H, and 15R phases, such as \((33)_n32\), \((33)_n34\), \((22)_n23\), and \((23)_n22\). However, many polytypes cannot be derived from single screw dislocations. Some of these “anomalous” polytypes were later explained by Pandey and Krishna [37] using a faulted matrix (i.e., lattice) model, which takes into account the possible presence of stacking fault(s) in the screw dislocation ledge.

More work is still needed to develop a comprehensive theory explaining the formation of most observed SiC polytypes and the absence of other hypothetical ones.

2.2 Properties of SiC Polytypes

SiC exists very rarely in nature, and it is furnace-synthesized SiC that was first known and studied in the 19th century. Baumhauer [6] discovered three “types” of SiC in the 1910’s using optical methods and named the phenomenon “polytypie” (nowadays known as polytypism), but the lattice structures of these polytypes were not determined until 1925 [38]. The first found polytype, then called Type I SiC, turned out to be 15R, which is second to 6H (then Type II) in occurrence in commercial SiC as an abrasive material. The third type, 4H-SiC, is the third commonest. Recent advances in growth techniques have made possible the commercial availability of large wafers of 6H- and
4H-SiC for electrical applications (Cree, Inc. in Durham, North Carolina is a leading manufacturer of 6H- and 4H-SiC wafers). 3C-SiC’s potential application in device fabrication is also under research and development in the industry (Hoya Advanced Semiconductor Technologies, Inc. in Tokyo, Japan, a subsidiary of Hoya Corporation that is rather known for optical glass products, has announced the production of up to 6 inch diameter monocrystalline 3C-SiC wafers).

Ref. 39, *Properties of Silicon Carbide*, is a detailed handbook of this material. A comprehensive summary of the physical parameters of 3C-, 4H-, and 6H-SiC is available in Ref. 40, whereas Ref. 13 is an in-depth review of these 3 polytypes plus 2H and 15R.

### 2.2.1 Lattice Constant

In an ideal close-packed lattice, the ratio of stacking layer thickness \((c/n)\) and the basal plane lattice constant \((a)\) is equal to \(\sqrt{2/3} = 0.8165\). However, this exact number is only found in the cubic 3C structure, which is the polytype with the highest symmetry (the hexagonal parameters \(c\) and \(a\) are determined by the cubic lattice constant). In other polytypes, due to the asymmetry between the \(c\)-axis and the directions in the basal plane, the lattices “relax” slightly in order to lower the total energy (this is related to the phenomenon of spontaneous polarization in non-cubic SiC; see Section 2.2.3), and the relaxation yields a \(c/(na)\) ratio no more than 0.5% higher than ideal. Table 2.2 is adapted from Ref. [28], in which the experimental values and theoretical calculations are compared. Since the differences in the \(c/n\) and \(a\) lattice constant between different polytypes is very small, the approximate value of \(c/n = 0.25\) nm and \(a = 0.31\) nm is usually good enough in structural analyses and simple calculations.
<table>
<thead>
<tr>
<th>Polytype</th>
<th>$a$ (Å)</th>
<th>$c/n$ (Å)</th>
<th>$c/(na)$</th>
<th>% above ideal</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C</td>
<td>calculation</td>
<td>3.063</td>
<td>2.501</td>
<td>0.8165</td>
</tr>
<tr>
<td></td>
<td>experiment</td>
<td>3.083</td>
<td>2.517</td>
<td>0.8165</td>
</tr>
<tr>
<td>6H</td>
<td>calculation</td>
<td>3.062</td>
<td>2.502</td>
<td>0.8172</td>
</tr>
<tr>
<td></td>
<td>experiment</td>
<td>3.081</td>
<td>2.520</td>
<td>0.8178</td>
</tr>
<tr>
<td>4H</td>
<td>calculation</td>
<td>3.061</td>
<td>2.503</td>
<td>0.8179</td>
</tr>
<tr>
<td></td>
<td>experiment</td>
<td>3.081</td>
<td>2.521</td>
<td>0.8184</td>
</tr>
<tr>
<td>2H</td>
<td>calculation</td>
<td>3.057</td>
<td>2.508</td>
<td>0.8201</td>
</tr>
<tr>
<td></td>
<td>experiment</td>
<td>3.076</td>
<td>2.524</td>
<td>0.8205</td>
</tr>
</tbody>
</table>

Table 2.2: Comparison of calculated and experimentally measured lattice constants of several common SiC polytypes. The last column refers to the value of $c/(na)$ compared to the ideal value of 0.8165. Adapted from Ref. 28 (original references are left out).

Figure 2.14: Experimental (solid circle) and theoretical (open circle) values of the bandgap of several SiC polytypes, including 4 hypothetical ones. The solid circle between 6H and 15R corresponds to 33R. Adapted from Ref. 42.
2.2.2 Bandgap and Band Structure

Choyke, Hamilton, and Patrick experimentally characterized several common SiC polytypes in the 1960’s [14, 41] and found they all have indirect bandgaps that vary from 2.390 eV in 3C to 2.986 eV in 15R, 3.023 eV in 6H, 3.265 eV in 4H, and 3.330 eV in 2H (exciton bandgaps at 2K or 6K). A nearly linear dependence of bandgap on hexagonality [14] was found in these polytypes with the exception of 2H-SiC [41]. Backes et al. [42] calculated the energy band structures of ten SiC polytypes (including several hypothetical ones) by interface matching of electronic wave functions and confirmed the nearly linear dependence between hexagonality 15% and 50% (see Figure 2.14; note that the slight violation of the linear tendency between hexagonality 33% and 40% (6H, 33R, and 15R) is also confirmed in this calculation). Chen and Srichaikul [43] calculated the band structures of 3C-, 2H-, 6H-, and 4H-SiC using a hybrid pseudo-potential and tight-binding approach, and the bandgaps from their result better matched experimentally measured values.

The first Brillouin zone of 3C-SiC has the well known corner-chopped octahedron shape [Figure 2.15(a)] and the CBM was found at the high-symmetry X points with a 3-fold degeneracy [14]. The fact that 3C-SiC has the smallest bandgap among all SiC polytypes is a contributing factor to the stability of n-type 3C-SiC, and its importance will be further discussed in Section 2.3.

The reciprocal lattice of a hexagonal lattice is still hexagonal, and its hexagonal prism-shaped first Brillouin zone is illustrated in Figure 2.15(b). The CBM of 2H-SiC is found at the K points [41], which is 2-fold degenerate.
Figure 2.15: The first Brillouin zones of (a) fcc, (b) hexagonal, and (c) rhombohedral Bravais lattices. Adapted from Ref. 49. Note that the $\Gamma$–L direction in (a) is the $c$-axis \{[111] in the cubic lattice\} and corresponds to $k_z$ in (c).
Early measurements of the low-temperature luminescence of 4H-SiC crystals [44] suggested the CBM’s of 4H-SiC reside at low-symmetry points in the interior of the hexagonal Brillouin zone. However, recent phonon energy calculations [45] and measurements [46] indicate the CBM be located at the high-symmetry M points, which is further supported by Lambrecht and Segall’s calculation [47]. Chen and Srichaikul [43] placed the CBM at 99% along the \( \Gamma \)–M direction. In this dissertation, the CBM of 4H-SiC will be treated as residing at the M points and hence having a 3-fold degeneracy. Also, a second 4H CBM at the M points with a higher density of state at \(~0.14\) eV above the first CBM has been observed using BEEM and confirmed by calculations [48, 49].

Raman scattering results placed the CBM of 6H-SiC along the M–L line [50] (which is on the zone boundary), but didn’t determine its exact location. Theorists haven’t got any agreement in the calculated locations, either: e.g., Chen and Srichaikul [43] placed it at 73% along the M–L line from the M point, whereas Persson and Lindefelt [51] placed it at 44% from M. The difficulty in determining the 6H CBM’s location partly lies in the fact that the energy change along the M–L line is less than 50 meV, as indicated in the calculations mentioned above. States close to this CBM are 6-fold degenerate, and Lambrecht et al. [52] pointed out that the 6H conduction band has a double-well structure symmetric about the M point along the L–M–L line.

As shown in Section 2.1.4, 15R-SiC’s rhombohedral primitive unit cell is quite similar to 3C’s except that it is stretched along the \( c \)-axis (the [111] direction of a cubic cell). Consequently, its first Brillouin zone in the reciprocal lattice is similar to that of the fcc lattice except that it is squeezed along the \( c \)-axis [Figure 2.15 (c)]. An additional similarity to 3C is that 15R’s CBM is located at the X point [49]. A second 15R CBM at
the L points at ~0.5 eV above the first is observed in BEEM measurements and confirmed by calculations [53].

The valance band maximum of all SiC polytypes is located at the zone center Γ point [52], regardless of the shape of the Brillouin zone. All polytypes have a small (few meV) spin-orbit splitting of the valence band [49], whereas non-cubic polytypes also have a crystal field splitting that depends nearly linearly on the hexagonality (maximized in 2H at >130 meV), as indicated by calculations [49, 52]. Additionally, according to Backes et al.’s calculation [42], the valance band offset (VBO) between a non-cubic polytype crystal and an adjacent 3C-SiC crystal varies nearly linearly with respect to hexagonality (up to 0.10 eV between 2H and 3C; the latter has lower energy). This is very close to Qteish et al.’s calculation [54] that suggested a VBO of 0.13 eV between 2H and 3C.

The electron effective mass \( m_e \) at the CBM’s of the common SiC polytypes has been measured and calculated by various groups, and a nice summary is available in Ref. 49 and 51. Except for the M–L direction in 6H, where a nearly flat conduction band edges causes a big effective mass, \( m_e \) at the first CBM of the five common polytypes is smaller than 0.8 electron mass. The hole effective mass at the valence band edge of the common SiC polytypes is also calculated in Ref. 51 and 52.

### 2.2.3 Spontaneous Polarization

There are basically two different types of layers in SiC — \( h \) and \( k \), which correspond to hexagonal turns and cubic segments, respectively (although it was pointed out in Section 2.1.3 that each layer in the \( h-k \) notation of SiC polytypes corresponds to a different type of sites that can be distinguished by different ionization energy, all the \( h \)
layers are similar, so are k layers). Qteish et al. [54] found that spontaneously charged dipole layers occur near the h layers, and for this reason, all SiC polytypes except 3C-SiC (the only polytype that doesn’t have any h layer) should have spontaneous polarization and consequently be pyroelectric.

Iwata [55] made an alternative argument about the origin of spontaneous polarization from the view of symmetry and energy. As a result of the high symmetry, all the four tetrahedral bonds of any given atom in 3C-SiC are equal and hence leave no room to spontaneous polarization (which, if exists, would violate the symmetry). In all non-cubic SiC polytypes, on the other hand, the bond along the c-axis direction (called the L-bond by Qteish et al.) is different from the other three (the T-bonds), and charge transfer occurs between the L- and T-bonds to lower the system’s Gibbs free energy, which gives rise to spontaneous polarization.

According to Qteish et al.’s calculation, the charged dipole layer resides across the T-bonds on the carbon side of an h layer, with positive charge around the silicon atoms in the h layer and negative charge around the silicon atoms on the other side of the abovementioned T-bonds (Figure 2.16). Since the c-axis direction is usually chosen to be pointing from the silicon atom to the carbon atom in an L-bond, the direction of spontaneous polarization in non-cubic SiC is against the c-axis. This finding is quite counter-intuitive (first, considerations of nearest neighbors [56] would suggest the L-bond of an h layer has more symmetry; second, since carbon has bigger electronegativity than silicon, intuition would suggest negative charge around carbon atoms instead of silicon atoms). Previously, the stacking layer of SiC has been defined as the Si–C bilayer bonded with the L-bonds; now that the T-bonds are found to be more characteristic of the
Figure 2.16: Spontaneous polarization in unrelaxed 6H-SiC, adapted from Ref. 55. In (b), the solid line is the average density of the negative valence charge in the unit of $e^{-}$/pair of Si-C atoms, and the dashed line is the average total potential. The solid and dotted shot vertical lines are the projected locations of silicon and carbon atoms, respectively.
material’s electrical properties, it would make more sense to redefine the bilayer as bonded with the $T$-bonds. However, the previous definition has its advantages in describing the lattice structure, because the silicon and carbon atoms bonded with an $L$-bond are on the same site in the basal plane. Therefore, the definition of stacking layer/bilayer will not be changed in this dissertation, and whenever the $T$-bonds are of concern, it will be explicitly emphasized.

The magnitude of spontaneous polarization in unrelaxed (i.e., with ideal lattice constant determined by the perfect tetrahedral geometry) 2H-, 6H-, and 8H-SiC are calculated by Qteish et al. to be $3.33 \times 10^{-2}$ C/m$^2$, $9.49 \times 10^{-3}$ C/m$^2$, and $6.91 \times 10^{-3}$ C/m$^2$, respectively. A plot of the polarization vs. hexagonality (Figure 2.17) reveals a nearly linear relationship from 3C to 8H and 6H, but 2H-SiC noticeably deviates from the linear tendency. This is an indication that the contribution of an individual dipole layer to the total spontaneous polarization is nearly the same if the adjacent dipole layers (or $h$ layers) are separated by two or more $k$ layers, but if the dipole layers are closer to each other, the polarization is enhanced due to the interaction between adjacent dipole layers. Lattice relaxation is also found to cause an increase in the polarization. Qteish et al. calculated the spontaneous polarization of relaxed 2H-SiC to be $4.32 \times 10^{-2}$ C/m$^2$, about 30% larger than the unrelaxed configuration.

Unfortunately, the spontaneous polarization of 4H-SiC has not been calculated so far. As a rough estimate, we interpolated Qteish et al.’s calculated values of 2H-, 6H-, and 8H-SiC (see Figure 2.17) to find $P = \sim 1.6 - 1.7 \times 10^{-2}$ C/m$^2$ for relaxed 4H-SiC. Recently, Bai et al. [57] indirectly estimated the spontaneous polarization of 4H-SiC to be $\sim 1.1 \times 10^{-2}$ C/m$^2$ through low-temperature photoluminescence measurements of 3C-SiC.
Figure 2.17: Spontaneous polarization vs. hexagonality. Solid rhombus markers: calculated polarization of unrelaxed SiC crystals. Solid circle: calculated polarization of relaxed 2H-SiC. Dotted line: projected linear tendency from 3C, 8H, and 6H. Dashed line: Estimated polarization vs. hexagonality curve of relaxed crystals. Open circle: interpolated polarization of relaxed 4H-SiC. All the calculated values come from Ref. 54. The dotted and dashed lines are estimated by the author.
inclusions in 4H-SiC (see the next section for more information about inclusions). The two estimates are in the same order of magnitude. The estimate from calculations will be used in the following discussions.

A big depolarization field created by the accumulation of surface charge and/or the redistribution of free carriers usually exists in a spontaneously polarized crystal to neutralize its macroscopic polarity (this is how the term pyroelectricity comes: fire would remove some surface charges, then the crystal would behave like a strong electric dipole). Without the depolarization field, the dipole layers would have caused a strong voltage buildup inside the crystal in a step-like pattern, as shown in Fig. 2.18 (c) for the case of 4H-SiC. The depolarization field, uniform and pointing against the polarization, contributes a linear decrease of potential along the c-axis and makes the total potential zero on average [thick line in Fig. 2.18 (c)], but the potential steps are still apparent [except for 2H-SiC, where the steps that were not obvious due to the absence of k layers would be smeared out, as illustrated in Figure 2.18 (d)].

The strength of a dipole layer can be characterized by the potential step it creates along the c-axis in the absence of the depolarization field. Given the magnitude of spontaneous polarization, this can be derived using the relationships \( P = -\varepsilon_\infty E \) and \( E = -\frac{h n V}{c} \) (assuming that all the dipole layers in the crystal are alike), where \( \varepsilon_\infty \) is the high-frequency dielectric constant (a value of 6.52 is used for all SiC polytypes in Qteish et al.’s calculation), \( E \) is the depolarization field, \( h \) is the hexagonality, \( n \) is the number of layers per repeat (\( h n \) is therefore the number of hexagonal turns per repeat), \( c \) is the width of the repeat (\( c / n \) is \( \sim 0.252 \) nm for all SiC polytypes), and \( V \) is the potential step. For 4H-SiC, whose hexagonality is 50%, the potential step \( V = \frac{P(c / n)}{h \varepsilon_0 \varepsilon_\infty} \) is \( \sim 0.14 \) eV.
Figure 2.18: (a) Dipole layers in 4H-SiC. (b) In 2H-SiC, due to the absence of cubic layers, the dipole layers are effectively connected to form a continuous polarization in the crystal. (c) Potential steps formed by dipole layers in 4H-SiC. Upper thin line: without depolarization. Lower thin line: the potential of depolarization field. Middle thick line: total potential. (d) Potential in 2H-SiC (same axes as in c). Thin line: without depolarization. Thick line: total potential. Note that the potential in (c) is a rough estimate because the charge distribution is not known. Also, the potential fluctuation in (d) is overestimated for illustration purposes. The calculated potential in 2H-SiC [see Figure 2.19 and Ref. 54] doesn’t contain any noticeable fluctuation in this scale.
Now to consider the depolarization field: since it produces a potential of $-0.14$ eV over one $h$ layer and one $k$ layer in 4H-SiC, its potential over the dipole layer is about $-0.07$ eV, so the apparent potential step (from a minimum to the next maximum) is approximately reduced to $-0.07$ eV [see Figure 2.18 (c)]. Note that the depolarization field is really huge: $\approx 2.8 \times 10^8$ V/m in 4H-SiC, according to the estimate above!

For 6H- and 8H-SiC, following the same treatment as to 4H-SiC and using the same dielectric constant [54], the potential step of a dipole layer is found to be $-0.12$ eV. After taking the depolarization field into account, the potential step becomes $-0.08$ eV for 6H and $-0.09$ eV for 8H (both are slight overestimates). This agrees well with the calculated potential of 6H and 8H in Qteish et al.’s original publication.

The same approach yields a potential “step” [which isn’t really step-like, see the thin line in Figure 2.18(d)] of $\approx 0.14$ eV in unrelaxed 2H-SiC in the absence of any depolarization field. In Qteish et al.’s original calculation of the spontaneous polarization in 2H-SiC, they used a hypothetical 3C/2H superlattice (each supercell contains three $k$ layers followed by six $h$ layers, see Ref. 54) and found an overall potential barrier of $\approx 0.25$ eV in the supercell. This divided by 6 (the number of $h$ layers) yields $-0.04$ eV, instead of 0.14 eV. However, the effect of depolarization is already included in the 0.25 eV barrier, and hence the 0.04 eV is not purely the potential step of a dipole layer. Dividing $-0.25$ eV by 3 (the number of $k$ layers in the 3C slab) actually yields the contribution of the depolarization field to the potential over the thickness of one layer. Therefore, the contribution of a dipole layer alone to the total potential is $0.25/6 - (-0.25/3) \approx 0.13$ eV, which is close to the estimate in the previous paragraph (the difference is probably because the 0.25 eV barrier is rounded at 3C/2H boundaries).
2.3 Inclusions in SiC

Inclusions in SiC are extended defects in a host polytype that resembles the structure of a different polytype. They are formed by stacking faults, but unlike stacking faults, which are 2D planar defects, inclusions are 3D defects with a finite size in the $c$-dimension and involve more than one stacking layers.

2.3.1 Stacking Faults and Partial Dislocations

If a 3D lattice is regarded as 2D planes stacked together, then a stacking fault is a disturbance to the regular stacking sequence of these planes [58]. It was previously mentioned that stacking faults can be formed by the slip of stacking layers. However, the latter does not necessarily result in the former — if the displacement of the slip is a Bravais lattice vector, then the new lattice is the same as the original one and no fault is formed. Therefore, in some lattices (such as a simple cubic one) where there are no alternative sites for a layer to reside on, stacking faults are not possible. Close-packed lattices, on the other hand, always have two (and only two, given the underlying layer) alternative sites for a layer to choose from, and the displacement between these two types of sites ($\frac{1}{3}<10\bar{1}0>$, see Figure 2.6 and 2.8) is smaller than the minimum lattice vector $\frac{1}{3}<1\bar{1}20>$, so a stacking fault will be formed if a layer (and all other layers above it) slips by $\frac{1}{3}<10\bar{1}0>$. If the displacement of a layer is bigger than this vector, it can always be decomposed into a Bravais lattice vector plus $\frac{1}{3}<10\bar{1}0>$, and it is the latter component that is of concern.

As illustrated in Figure 2.19 (a), a slip (and hence a stacking fault) in a close-packed lattice can be formed by the glide of a dislocation with Burgers vector $\frac{1}{3}[\bar{1}100]$. 

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Figure 2.19: (a) Shockley partial (and the stacking fault formed by its glide) in 3C-SiC, as viewed in a cross-sectional (11\(\overline{2}0\)) plane (only the atoms residing inside this plane are shown). To illustrate the slip, the lattice above the fault plane is not relaxed. Note that a slip twice as big in the opposite direction would also form a partial, but it is not to be considered, because its Burgers vector is bigger than the smallest Bravais lattice vector. (b) Frank partial. The lattice around the partial is relaxed to accommodate the removal of a layer to its left.
Also, the fault terminates at this dislocation (which is called a partial dislocation or “partial” because its Burgers vector is smaller than the smallest Bravais lattice vector).

There are actually two types of partial dislocations in close-packed lattices. The one described above that is associated with the slip of stacking layers is known as the Shockley partial, and a stacking fault formed by the glide of a Shockley partial is called a Shockley-type fault. Another type of partial dislocation, known as the Frank partial, is associated with the removal of part of a layer [Figure 2.19(b)]. The stacking fault created by the removal of a layer is indistinguishable from that caused by a slip, but if the fault terminates within the crystal, then the bounding partial is different. Unless specially noted, all partial dislocations discussed in this dissertation belong to the Shockley type.

Partial dislocations and stacking faults can be created by sheer stress from surfaces or grain boundaries, but in the absence of stress, they may be created by the dissociation of perfect dislocation (whose Burgers vector is a Bravais lattice vector) into two partials propagating in opposite directions.

The energy per unit length of a dislocation is proportional to the square of its Burgers vector length. Since \( \frac{1}{3} [\overline{1}1\overline{2}0] \) (corresponding to \( \frac{1}{2} [0\overline{1}1] \) in the cubic coordinates of the fcc lattice) is the smallest primitive vector of a close-packed lattice, a dislocation with this vector as the Burgers vector has the smallest energy among perfect dislocations in close-packed crystals and hence is the most likely to be formed. However, the dislocation energy may be further lowered if this perfect dislocation dissociates into two partials: \( \frac{1}{3} [\overline{1}1\overline{2}0] \rightarrow \frac{1}{3} [10\overline{1}0] + \frac{1}{3} [0\overline{1}\overline{1}0] \) (or \( \frac{1}{2} [0\overline{1}1] \rightarrow \frac{1}{6} [1\overline{2}1] + \frac{1}{6} [\overline{1}\overline{1}2] \) in cubic coordinates). Figure 2.20 (a) and (b) illustrate the dissociation of such a perfect dislocation. The two parallel partials leave a stacking fault in between when they move.
Figure 2.20: (a) A perfect dislocation; (b) dissociation into two parallel partials; (c) partials move apart and leave a stacking fault in between. Viewed against the c-axis. For simplicity, only two layers are shown (dashed circles are on the lower layer).
apart from each other [Figure 2.20(c)]. The total energy of the two partials is only 2/3 of that of the parental perfect dislocation. Consequently, a repulsive force exists between the two partials that is found to be approximately inversely proportional to the distance between them [59]. On the other hand, the creation of a stacking fault costs energy (called the stacking fault energy) that is proportional to the area of the fault. There is hence an equilibrium separation between the two partials under a given condition, and the stacking fault energy can be calculated from this separation [59, 60].

After the equilibrium separation is reached, the two partials may move together in the same direction, with a stacking fault ribbon in between. Under certain conditions (see Section 2.3.3), one of the two partials may become relatively immobile while the other moves away from it and hence leaves an expanded stacking fault behind [59, 61].

Mathematically, the dissociation of \( \frac{1}{3} <11\bar{2}0> \) may take other forms like \( \frac{1}{9} <2\bar{1}30> + \frac{1}{9} <12\bar{3}0> \) or \( \frac{1}{9} <11\bar{2}0> + \frac{2}{9} <1\bar{1}\bar{2}0> \), which, if exist, would have even lower total dislocation energy. However, these partials are actually not favored, because the stacking faults created by them would have very high energy due to the violation of close-packing (and tetrahedral bonding in SiC) throughout the entire fault. Stacking faults bounded by \( \frac{1}{3} <10\bar{1}0> \) (corresponding to a slip from one close-packing site to another) only violate the close-packing requirement near the two partials and hence have the least energy (they appear as local minima in the plot of stacking fault energy versus the fault translation vector [58]). Since \( \frac{1}{3} <10\bar{1}0> \) is the smallest vector pointing from one close-packing site to another, it is the most favored partial. The stacking fault created by the motion of \( \frac{1}{3} <10\bar{1}0> \) is parallel to the basal plane and hence also called a basal slip. Non-basal slips haven’t been observed due to the much more cost of energy.
The angle between a dislocation’s line and its Burgers vector defines its character (90º corresponds to a pure edge dislocation; 0º pure screw). The perfect dislocation illustrated in Figure 2.20(a) is of 60º character (mixed edge and screw). The dislocation line in a close-packed lattice usually follows a close-packing direction \( \frac{1}{3} < 11 \bar{2} 0 > \) due to the lower core energy in these orientations [58], and hence a perfect dislocation with Burgers vector \( \frac{1}{3} < 11 \bar{2} 0 > \) is of either 60º or 0º character [unfortunately, it is hard to visualize a 0º (pure screw) dislocation in a two-layer illustration like Figure 2.20(a)]. Since the Burgers vectors of the two partials make 30º with that of the parental perfect dislocation, the two partials must be of either 30º or 90º characters [Figure 2.20(c)].

Finally, some notes about Figure 2.19 and 2.20. First, in Figure 2.19(a), the core of the Shockley partial happens to consist of carbon atoms, but it is no problem for it to have a silicon core. In tetrahedrally bonded crystals like SiC, there is actually a very interesting relationship between the core structures of the partials and the character of the parental perfect dislocation, the discussions of which can be found in Ref. 56 and 58. Second, the two partials in Figure 2.20(b) look different, but both can be represented by Figure 2.19(a). This is because Figure 2.19(a) doesn’t care whether the dislocation is perpendicular to this plane or not. The \( \{2\bar{1}0\} \) plane [the dash-dotted line on the right in Figure 2.20(a) and (b)], if viewed against the \( \{2\bar{1}10\} \) direction (i.e., viewed from the other side of the block arrow), just look the same as \( \{1\bar{1}20\} \). Third, the Burgurs vector \( B_1 \) in Figure 2.20(b) and (c) is equal to the corresponding slip vector \( s_1 \) in Figure 2.20(a), but \( B_2 \) is the reverse of \( s_2 \). This is because the dislocations, concerned in the same context, have to have the same line sense (chosen to be pointing in the \( \{2\bar{1}10\} \) direction here) when their Burgurs vectors are determined (following the convention described in Ref. 58).
2.3.2 Cubic Inclusions in 4H-SiC

By definition, the stacking sequence across a stacking fault is different from that of the host lattice. Iwata and Lindefelt et al. [62, 63] studied all the geometrically distinguishable stacking faults in 3C-, 4H-, 6H-, and 15-SiC and found that the stacking sequence across a stacking fault in these polytypes may look like 2H, 3C, or other SiC polytypes. This dissertation will mainly deal with stacking faults in 4H-SiC.

As illustrated in Figure 2.21(a) – (c), a stacking fault in 4H-SiC can reside at two inequivalent locations, either below an \( h \) layer, or below a \( k \) layer. The stacking faults disturb the 2222… stacking (in Zhdanov notation) of 4H-SiC and result in the faulted stacking sequences of 221322… and 223122…, and hence are named SF(13) and SF(31), respectively, by Iwata et al. [62]. SF(13) and SF(31) can be transformed into each other by interchanging Si and C atoms.

Adding one more stacking fault a layer below SF(13) or a layer above SF(31) will result in the same structure as illustrated in Figure 2.21(d). The stacking sequence is now 2622… and hence this double-stacking-fault structure is named 2SF(62) by Iwata et al. This name is a little misleading in that readers may think a different structure 2SF(26) also exists (the latter is actually indistinguishable from the former), but once clarified, there is no need to adopt a new name for this structure.

Obviously, in 2SF(62) there exists a “3C-SiC-like” slab sandwiched between perfect 4H-SiC crystals above and below it. This slab is a cubic inclusion in 4H-SiC. By adding more stacking faults [for example, the 3SF(71) and 4SF(10,2) structures in Figure 2.21(e) and (f)], the cubic inclusion can be widened.
Figure 2.21: (a) Perfect 4H stacking; (b) SF(13); (c) SF(31); (d) 2SF(62); (e) 3SF(71); (f) 4SF(10,2). Adapted from Ref. 62.

Figure 2.22: The width of a cubic inclusion in 4H-SiC. (a) SF(31); (b) 2SF(62).
A concern is where to draw the boundary between the inclusion and the 4H region. Take the double-stacking-fault cubic inclusion in the 2SF(62) structure as an example: one view is that since 7 consecutive layers extend in one direction, the inclusion should include all the 7 layers; another view is that since there are only 6 “+” layers among the 7 in the Hägg notation, the inclusion should only include these 6 layers; and a third view is that since there are only 5 $k$ layers among the 7, and since 3C-SiC only contains $k$ layers, only the 5 $k$ layers should be counted into the inclusion. The third view is essentially supported by electrical considerations: since 3C-SiC is not polarized, any spontaneoulsy polarized dipole layer should belong to the 4H-SiC region. The two dotted ovals in Figure 2.22(b) indicate the $T$-bonds where the dipole layers closest to the inclusion are located. The region sandwiched by these two ovals (marked by a dashed oval) effectively contains 5 layers (shifted by a $T$-bond from the conventionally defined bilayers). Similarly, the triple- and quadruple-stacking-fault inclusions in the 3SF(71) and 4SF(10,2) structures contain no more than 6 and 9 layers, respectively. Also, a very small inclusion containing no more than 2 $k$ layers can be defined in the SF(13) and SF(31) structures, as illustrated in Figure 2.22(a). The issue of inclusion width is important in the calculation of the quantum well states in the inclusions (see Section 2.3.4 for more information).

2.3.3 Experimental Observation of Self-Forming Inclusions

Stacking faults in SiC are not new to physicists, but recent findings of self-forming cubic inclusions in 4H- and 6H-SiC are special in that they appear to be “self-forming” under certain thermal or electrical conditions that hadn’t been thought to be
related to the formation of inclusions. Also, the driving force of stacking fault expansion to form the inclusions is quite possibly of electrical origin.

The degradation of 4H-SiC $p-i-n$ or $p^+n^+n^+$ power diodes after electrical stressing (i.e., long hours of forward voltage operation) was first reported in the 3rd European Conference on Silicon Carbide and Related Materials in 2000 [4, 5]. Stacking faults in the degraded diodes were observed using cathodeluminescence, photoluminescence, synchrotron white beam x-ray topography [64], and electroluminescence [65] methods. Further studies of the degraded diodes using cross-sectional transmission electron microscope (TEM) revealed cubic inclusions of the single-stacking-fault SF(31) type [66, 67]. Similarly degraded 6H-SiC diodes are also reported in Ref. 68 and the culprit is found to be single-stacking-fault cubic inclusions in the 6H lattice (inclusions in 6H-SiC will not be further discussed in this dissertation). Recombination of electrons and holes at partial dislocation cores is thought to provide the energy needed for the partial dislocations to glide.

Subsequently, cubic inclusions have been found in high-temperature-processed 4H-SiC samples by various groups [68 – 71]. The 4H-SiC wafers used in all these studies are purchased from Cree, Inc, have Si-face with an 8° miscut from the basal plane, and were free of large-scale inclusions before processing (there must exist very narrow ribbons of stacking faults, though, as it is the expansion of these ribbons that formed the inclusions observed after the processing). Most of the wafers investigated in these studies contains either have a heavily $n$-type substrate or a heavily $n$-type epilayer. The high-temperature processing is either thermal oxidation in dry oxygen [68 – 70] or annealing in argon [69, 71]. All the inclusions imaged with cross-sectional TEM on these
samples are of the double-stacking-fault 2SF(62) type, but if the inclusion terminates inside the crystal, the bounding partials of the two stacking faults may have a small separation in between, effectively forming a narrow ribbon of the single-stacking-fault SF(31) inclusion [72].

Brillson et al. [69] studied the temperature and doping dependence of the formation of double-stacking-fault 2SF(62) cubic inclusions in $n$-type N-doped 4H-SiC epilayers, and found that inclusions only form when the doping of the epilayers is in the range of $4 \times 10^{17}$ cm$^{-3}$ to $1.7 \times 10^{19}$ cm$^{-3}$. However, Skromme et al. [70] studied samples with heavily $n$-type N-doped substrate and only found inclusions in regions where the doping of the substrate is $> 1 \times 10^{19}$ cm$^{-3}$, while the regions with smaller doping in the substrate remained inclusion-free after thermal processing (see Section 4.1.1 for details).

Iwata et al. [62] calculated the stacking fault energy for successive faults in 4H-SiC. The energy for adding a second fault to form 2SF(62) is found to be only 26% (according to a supercell calculation) or 17% (according to an ANNNI calculation) of that for the creation of the first stacking fault, while adding one more fault to form 3SF(71) will cost more than the energy of the first fault. This finding is consistent with the fact that only 2SF(62) has been observed in high-temperature-processed 4H-SiC.

### 2.3.4 Quantum Well States of the Inclusions

Luminescence measurements on 4H-SiC samples containing cubic inclusions have revealed spectral peaks with lower energy than typical 4H-SiC peaks. Sridhara et al. [73] observed a set of peaks in the photoluminescence spectrum of an electrically stressed 4H-SiC diode [containing single-stacking-fault SF(31) inclusions] that are absent
in the spectrum of unstressed diodes. Skromme *et al.* [70] observed a photoluminescence energy of 2.42 eV in regions containing double-stacking-fault 2SF(62) inclusions measured at 1.7 K, vs. 3.164 eV in pure 4H-SiC region. Okojie *et al.* [68] analyzed 4H-SiC samples containing 2SF(62) inclusions using cathodoluminescence spectroscopy based on low-energy electron nanoluminescence and observed a 2.5 eV photon peak at 300 K, compared with the 3.22 eV peak in pure 4H-SiC. Based on these findings, people have proposed that the inclusions behave like quantum wells with a binding energy lower than the CBM of 4H-SiC [72, 73].

Miao *et al.* [21] performed first-principle calculations of the stacking fault energy of SF(31) in 4H-SiC as well as the band structure of the faulted crystal. A localized band with maximum depth of 0.2 – 0.3 eV below the CBM of 4H-SiC was found at the single-stacking-fault inclusions.

Iwata *et al.* performed *ab initio* supercell calculations of the band structures of various inclusions in SiC polytypes. For cubic inclusions in 4H-SiC, they found that the two single-stacking-fault inclusions SF(31) and SF(13) have localized 2D band at 0.22 eV and 0.18 eV, respectively, below the 4H-SiC CBM at the M point [62]. The localized band of 2SF(62), 3SF(71), and 4SF(10,2) inclusions is found at 0.597 eV, 0.709 eV, and 0.747 eV below the 4H-SiC CBM, respectively [75] (all at the M point). A second split-off band is also found at 0.110 eV and 0.345 eV below the 4H-SiC CBM for 3SF(71) and 4SF(10,2), but this doesn’t exist in single- and double-stacking-fault inclusions.

The localized 2D band in the inclusions below the 4H-SiC CBM can be interpreted as the electronic states in a quantum well where electrons are only confined in one direction and are free to travel in the other two dimensions (further constraints will
reduce the structure to quantum wires or quantum dots). Therefore, an alternative view of the electronic structure of the inclusions is to consider the potential of a 3C-SiC slab sandwiched between 4H-SiC crystals, which forms a quantum well structure in the direction parallel to the $c$-axis. Iwata et al. [62] calculated the binding energy of this simple quantum well problem assuming the inclusion width as discussed in Section 2.3.2 [2, 5, 6, 9 layers for SF(31), 2SF(62), 3SF(71), and 4SF(10,2), respectively], and the results agree very well with the *ab initio* calculation.

The quantum well nature of cubic inclusions in 4H-SiC has been proposed to be the reason for the formation of inclusions in $n$-type materials [21, 62, 72], because the energy lowering achieved by electrons entering the quantum wells may outweigh the energy cost of stacking fault expansion. Liu et al. [71] pointed out that at the high temperature under which the double-stacking-fault 2SF(62) inclusions are created in heavily $n$-type 4H-SiC, the Fermi level is lower than the localized state in single-stacking-fault inclusion, and hence the latter is not favored.

Our BEEM study of 2SF(62) inclusions [74] in high-temperature-processed 4H-SiC (see Chapter 4 for details) directly confirmed the quantum well behavior of these inclusions and the quantum well energy is estimated to be $\sim0.53$ eV below the 4H-SiC CBM, which agrees well with Iwata et al.’s calculations.
CHAPTER 3

Experimental Methods

The BEEM technique is the principal tool in our study of cubic inclusions in 4H-SiC and threading dislocations in GaN, and it is the variations in Schottky barrier heights measured with BEEM that provided information about the electrical properties of the buried semiconductor structures.

3.1 Schottky Barrier

Details about the Schottky barrier [76], a rectifying barrier at M/S interfaces, can be found Ref. 77 – 79. Two issues will be briefly reviewed in this section: the barrier height’s dependence on metal work function, and the inhomogeneity of the barrier.

The conventional Schottky theory [76] of the barrier after his name ignores any interface states, and the Schottky barrier height of metal/n-type semiconductor contact is equal to the metal work function minus the electron affinity of the semiconductor [Figure 3.1(a)]. According to this model, the difference in the Schottky barrier heights of metal contacts on the same semiconductor should equal the difference in the metal work function. However, experimental measurements of the Schottky barrier heights of
different M/S contacts have revealed that Schottky barrier heights usually have a rather weak dependence on the metal work function. To explain this discrepancy, Bardeen [80] in 1947 proposed a Schottky barrier theory in which the previously ignored interface states are taken into account. The Bardeen model assumes a thin insulating interfacial layer (possibly an oxide layer) between the metal and the semiconductor, but electrons are assumed to easily tunnel through the potential barrier formed by the interfacial layer (in reality, this layer is present in most M/S contacts prepared under non-ideal conditions, such as an exposure of the semiconductor surface to air before metal deposition). There are localized states at the interface between the semiconductor and the interfacial layer, which are filled to the Fermi level of the M/S contact system. If the interface state density is very big, the Fermi level at the interface will effectively be pinned at the charge neutrality level (when the interface states are filled up to this level, the total charge in these states equals zero), and the barrier height is completely independent of the metal work function. This is known as Fermi level pinning, and the large-interface-state-density limit of the Bardeen model is also known as the Bardeen limit [Figure 3.1(b)].

The voltage drop across the interfacial layer accounts for the discrepancy of the barrier height at the Schottky-limit vs. in the Bardeen model. Experimentally determined barrier height dependence on metal work function varies between 0 (the Bardeen limit) and 1 (the Schottky limit) for M/S systems with different interface state density.

During the decades following the advent of Schottky barrier theories, analysis and modeling were mainly focused on the macroscopic properties of Schottky contacts. However, the picture of a homogeneous barrier across the entire Schottky diode is of course an oversimplification, since many factors including defects in the semiconductor,
Figure 3.1: (a) Schematic illustration of a Schottky contact at the Schottky limit; (b) in the Bardeen model. Small bars across the semiconductor surface in (b) represent interface states. $\phi_m$ is the metal work function, $\chi_s$ the semiconductor electron affinity, $\phi_b$ the barrier height, and $E_F$ the Fermi level. Only the case of $n$-type semiconductor is shown (the depletion potential of a $p$-type contact would have a positive slope vs. the negative slope as shown for $n$-type), and the effect of image force lowering (see Section 4.2.3) is ignored. The voltage drop across the interfacial layer is determined by the interface state density and the metal work function.
spatial variations of the properties of the interfacial layer, and impurity accumulations at the M/S interface will result in spatial variations of the local barrier height that might greatly influence the macroscopic “average” properties of Schottky contacts, which are often observed to be far from the “ideal” behavior predicted under the assumption of interface homogeneity. In fact, an “ideality factor” (usually noticeably bigger than 1, the ideal case) is needed in the thermionic emission theory of Schottky diodes [81] to account for various non-ideal effects including the inhomogeneity of barrier heights.

Tung’s theory of Schottky barrier height inhomogeneity [82] assumes a nm-scale distribution of microscopic patches of reduced local barrier height at the M/S interface in an attempt to explain some of the non-ideal behavior of Schottky diodes. In one of our prior projects [83], direct measurements of local Schottky barrier heights on Pt/6H-SiC diodes using BEEM indicated that the Tung model could explain the behavior of near-ideal diodes very well, while some “gross defects” other than low-Schottky barrier height patches are probably responsible for the badly non-ideal behavior of some other diodes.

It should be noted that the low-barrier stripes (see Section 4.1 for details) we observed in the studies of cubic inclusions in 4H-SiC are not related to the Tung model, which only deals with interfacial patches that do not extend into the semiconductor bulk.

### 3.2 Ballistic Electron Emission Microscopy

BEEM [1], a variant of STM, has been used in the studies of the sub-surface electronic properties of various material systems, including simple Schottky contacts (which is the main application of BEEM), metal/insulator/semiconductor structures [84], buried resonance tunneling heterostructures [85], and in our case, quantum well
structures in SiC. One thing in common with these material systems is that there is a thin
and clean metal film on the very top of the structure (the metal and the substrate must be
separated by non-leaky energy barrier). Traditional STM imaging is done over the metal
surface. What distinguishes BEEM from STM is an extra terminal at the substrate, where
the BEEM signal is collected. Comprehensive reviews of the BEEM technique are
available in Ref. 86 – 89.

3.2.1 Schematics of BEEM

BEEM is a three-terminal modification of STM. In the most common setup
(involving the study of a metal/n-type semiconductor Schottky contact) as illustrated in
Figure 3.2, the metal film is grounded, the STM tip is biased at a voltage \(-V_T\), and the
semiconductor substrate is held at virtual ground via a high-gain (usually \(10^{10} \text{ V/A}\))
current amplifier. Analogous to a bipolar transistor, the STM tip is the emitter, the metal
film is the base, and the semiconductor substrate is the collector.

When the STM tip is very close to the metal surface, electrons may tunnel
through the vacuum barrier and enter the metal as hot electrons (whose energy is higher
than the metal Fermi level) with a momentum distribution determined by the tip bias \(V_T\).
If the metal film is thin compared to the mean free path of hot electrons in the metal, a
fraction of the injected hot electrons may travel through the metal film ballistically or
quasi-ballistically (\(i.e., \) only undergoing elastic or quasi-elastic collisions) and reach the
M/S interface without significantly losing energy. Among them, those with higher
energy than the \textit{local} Schottky barrier may surmount the barrier, enter the semiconductor,
and be collected as the collector current (or BEEM current) \(I_c\) [Figure 3.2(b)].
Figure 3.2: (a) Schematic illustration of BEEM; (b) energy diagram of BEEM; (c) energy diagram of “hole BEEM”. $I_T$ is the tunnel current. Adapted from Ref. 88 with modifications.
For the case of a metal/p-type semiconductor contact [90], the STM tip is biased at a positive voltage $V_T$ and ballistic holes are effectively injected into the metal [Figure 3.2(c)]. Strictly speaking, the term “BEEM” is no longer valid in this case, but once clarified, it is usually no problem to call it “hole BEEM” as the counterpart of the normal “electron BEEM”.

3.2.2 BEEM Spectrum

One of the most important applications of BEEM is the determination of local Schottky barrier height. This is achieved by using the STM tip as a local hot electron emitter and varying the tip bias $-V_T$ while measuring the corresponding BEEM current $I_c$ (Figure 3.3). At low temperatures, the obtained $I_c - V_T$ curve (i.e., a BEEM spectrum) shows only a small noise current below a threshold voltage $V_{th}$, which directly corresponds to the local Schottky barrier height (at room temperature, due to the thermal tail of the Fermi distribution of electrons in the STM tip, few hot electrons may have higher energy than $V_{th}$ when the tip voltage $V_T$ is still below $V_{th}$, and hence a small sub-threshold BEEM current is present near $V_{th}$). As the bias voltage $V_T$ increases beyond $V_{th}$, many hot electrons start to enter the semiconductor substrate, resulting in a rapid increase of the BEEM current. A relationship $I_c \propto (V_T - V_{th})^2$ or $I_c \propto (V_T - V_{th})^{5/2}$ often well fits the BEEM spectrum close to the threshold at low temperatures [91]; however, in order to take into account the non-negligible thermal tail of the Fermi distribution at room temperature, a comprehensive model such as the Bell-Kaiser model [92] is usually needed for a better estimate of the local Schottky barrier height (see Section 3.2.4 for details).
Additional information about the semiconductor conduction band structure may also be obtained through BEEM spectral measurements. For example, the BEEM spectra on Au/GaAs(100) has the regular shape predicted by the BK theory near the threshold region (corresponding to the Schottky barrier), but as the tip bias $V_T$ increases, a rapid increase of BEEM current is observed that can be explained by additional BEEM transmission channels into the second and third CBM’s of GaAs. By fitting the BEEM spectra on Au/GaAs(100) as the superposition of three independent transmission channels, Bell and Kaiser [92] obtained three threshold voltages, the second and the third at 0.29 eV and 0.47 eV above the first, corresponding to the higher CBM’s. Using BEEM, a second CBM has been found in 4H-SiC [48] (see Figure 3.3) and 15R-SiC [53].

3.2.3 BEEM Imaging

BEEM may also be used in an imaging mode. While an STM image of the metal film topography is acquired (usually under a fixed tip bias $V_T$ and a constant tunnel current $I_T$), a simultaneous “BEEM image” (a plot of the BEEM current $I_c$ vs. location on a gray scale) can be obtained (Figure 3.4). The comparison of an STM image and the simultaneous BEEM image may reveal certain relationships between structural features of the metal (or the semiconductor) and variations in the amplitude of BEEM current.

For a simple M/S system consisting of the same metal over a uniform semiconductor bulk, BEEM spectra over most locations with different BEEM current amplitude usually yield essentially the same Schottky barrier height. This indicates variations of BEEM current are mostly due to the non-uniformity of the thin metal film, which, in most cases, is thermally deposited non-epitaxial metal that typically has nm-
Figure 3.3: Sample BEEM spectrum (average of 9 measurements over the same location) on 4H-SiC. The Bell-Kaiser fitting curve is shown but is nearly completely overlapped by the raw data.

![Figure 3.3: Sample BEEM spectrum](image)

Figure 3.4: (a) Sample STM Image (80 nm)$^2$ over a Pt/4H-SiC contact, taken at $V_T = 1.5$ V, $I_T = 5$ nA; (b) simultaneous BEEM image.

![Figure 3.4: Sample STM Image](image)
scale polycrystalline structures [Figure 3.4(a)]. The transmission of hot electrons in the metal film depends on many factors including the film thickness, the inclination of the local metal surface where tunnel electrons enter the metal, and the orientation of lattice planes in the nanocrystals. As seen in Figure 3.4(b), there are usually variations of BEEM current within a same metal grain (i.e., a nanocrystal), and some metal grains have a generally bigger BEEM current than others while some have very small BEEM current.

On the other hand, a difference in the Schottky barrier height may result in a quite noticeable change in the BEEM current amplitude under the same tip bias $V_T$: assuming different locations have a similar BEEM spectral shape, a bigger separation between $V_T$ and the threshold voltage $V_{th}$ will cause a bigger BEEM current (see Figure 3.3).

During a scan of a pair of STM/BEEM images, the STM tip may stop at a certain location for a few seconds to measure a BEEM spectrum and resume the scan after the spectrum acquisition is finished. This mode is often used to investigate the variations of local Schottky barrier height with respect to location.

### 3.2.4 Bell-Kaiser Model

An important assumption in the Bell-Kaiser model is the conservation of the transverse momentum of electrons across the M/S interface [92]. Under this assumption, if the semiconductor CBM in the momentum space has no momentum parallel to the M/S interface [such as Au/Si(100), see Figure 3.5(b)], then the transverse momentum of states near the CBM must be small, and only hot electrons with small transverse momentum in the metal may be able to enter the semiconductor. The tunnel electrons should be strongly forward-focused (i.e., with small transverse momentum) when entering the metal.
Figure 3.5: (a) Six CBM’s of Si in the first Brillouin zone; (b) their projections on the (100) plane; (c) on the (111) plane. Illustrated using a constant-energy pocket near the actual CBM points. The dark dot in (b) and (c) indicates where the transverse momentum is zero.
film (because the tunneling probability is the biggest in the direction normal to the metal surface, along which the distance in the vacuum barrier is the smallest). However, elastic scattering of hot electrons inside the metal film may smear the forward-focused distribution, and fewer electrons will have small transverse momentum when they arrive at the M/S interface. The Bell-Kaiser model deals this issue by using a scaling factor as a free parameter in the fitting, and only the spectral shape instead of the absolute amplitude of BEEM current is of concern in the determination of local Schottky barrier heights [92].

For M/S contacts in which the semiconductor CBM has a large transverse momentum, such as Au/Si(111) [Figure 3.5(c)], the situation is different. If the forward-focused distribution of hot electrons is mostly preserved in the metal film till the M/S interface, then only a very small number of hot electrons will have sufficient transverse momentum to enter the semiconductor, and the spectral shape will be supposedly quite different from the case of zero transverse momentum at the semiconductor CBM.

However, BEEM spectra on Au/Si(111) measured at room temperature were found to have almost identical shape to that on Au/Si(100). It was proposed that strong scattering of hot electrons in the metal film at room temperature may explain this effect by randomizing the direction of hot electrons before they reach the M/S interface [93], and BEEM measurements at 77 K on the contact of thick Au films to Si(111) did produce a different spectral shape as predicted in the Bell-Kaiser model [94] (this is evidence that transverse momentum is conserved at the Au/Si(111) interface in this particular study, but there hasn’t been any agreement about whether it is conserved in general cases [89]).

Since the BEEM spectral shape measured at room temperature doesn’t depend much on the momentum of states around the semiconductor CBM, the Bell-Kaiser fitting
equations [92] developed for M/S contacts whose semiconductor CBM has no transverse momentum generally work for any room temperature BEEM spectrum regardless of the semiconductor conduction band structure, as far as the determination of Schottky barrier height is concerned [94]. Moreover, the fitting of room temperature hole BEEM spectra using the Bell-Kaiser equations for electron BEEM is also found to work well near the threshold region [86], even though there is a major difference in the distribution of ballistic carriers between these two cases [see Figure 3.2(b) and (c)]. The reason behind the wider-than-expected applicable range of the Bell-Kaiser fitting is that it mainly takes care of the thermal tail of the Fermi distribution at finite temperature, and the threshold voltage (\( i.e., \) the Schottky barrier height) extracted from this fitting is extremely insensitive to other parameters such as the effective mass of electrons or holes. In other words, when the Bell-Kaiser fitting equations for M/S contacts with no transverse component are applied to other M/S systems, they are rather an empirical tool of barrier height determination than a physical model of the transport of ballistic carriers.

3.3 Equipment Setup

Sample cleanliness is of great importance to the validity of an experiment and the quality of the measured data, as is the reason why the experiments described in this dissertation were performed in a custom-built UHV system at a base pressure of \( \sim 1 - 2 \times 10^{-10} \) Torr sustained by ion pumps. The UHV system consists of two chambers (one for sample preparation, the other for STM/BEEM measurements) and various attachment apparatuses. It was initially assembled by Darrel Jones and subsequently updated and maintained by Benjamin Kaczer, Hsung Jai Im, Kibog Park, and the author. Details
about its construction and major updates are available in the dissertations of Jones [95] and Kaczer [88].

### 3.3.1 Sample Preparation

The as-received SiC and GaN samples in our studies are bare semiconductor wafers without metal overlayers. Each sample is cleaned (specific cleaning procedures for different samples will be described in Chapter 4) and mounted on a sample block before being introduced into the sample preparation chamber via an airlock. Ohmic contact can usually be achieved between SiC and the tantalum clips on the sample block just by the clip pressure. For GaN, indium solder is applied to two small areas of the sample to make Ohmic contacts.

A tungsten filament on the sample block enables mild outgassing of the samples (usually at <230 °C) inside the preparation chamber. Resistive heating of the samples is also possible when necessary, and a pyrometer can be used to monitor the sample temperature through a viewport.

The preparation chamber is capable of *in situ* metal deposition using an e-beam evaporation system, which has three e-guns and allows for three metal sources to stay inside the vacuum chamber. If a different metal is needed, the preparation chamber will have to be vented to replace the metal source. Pt, Pd, Au, Ni, and Al have been used in this evaporation system, and Pt has been the choice of metal for the study of SiC and GaN due to its excellent stability and the high-quality Schottky contact it makes with these semiconductors. Evaporated metal is deposited on sample surfaces via a shadow mask with 0.5 mm diameter circular holes arranged in a honeycomb pattern, and the
thickness of the metal films is measured using calibrated quartz monitors during the deposition. A mechanical shutter actuated by a rotational feedthrough on the chamber is used to control the deposition, and the deposition rate is usually adjusted to less than 0.05 nm per second before the shutter is opened.

Due to the intense heat generated by the e-gun during the metal deposition, the pressure in the preparation chamber can go up to $10^{-6}$ Torr range momentarily when the metal source starts to melt, as measured by an ion gauge mounted on the chamber wall (typically, the sustained pressure during a deposition is $10^{-8} – 10^{-7}$ Torr. This may pose a threat to sample cleanliness and the integrity of the deposited metal film, but the high quality and durability of the Schottky contact formed in our system (see Chapter 4 for details) indicates this is not of a major concern.

### 3.3.2 Measurements in the STM/BEEM Chamber

After metal deposition, the sample is transported in UHV into the STM/BEEM chamber for characterization. A 1-mil diameter gold wire, electrically connected to a BNC feedthrough and mechanically attached to the sample manipulator via a coated copper wire (see Figure 3.4), is used to ground the metal film when the wire is connected to the grounded chamber chassis through a grounding cap on the BNC connector. The semiconductor substrate is connected to a computer-controlled Keithley 428 Current Amplifier, which may be used to apply a DC bias voltage to the substrate and measure the macroscopic $IV$ curve of a Schottky diode. For macroscopic $CV$ characterizations, the Keithley 428 can also be used to measure the AC current response of the diode while a low-frequency ($< 10$ KHz) AC voltage is applied to the metal film via the gold wire.
Figure 3.6: Gold wire for grounding the metal film. Inset: close-up view of the gold wire, which is in contact with a metal dot on the sample (metal dots are barely visible), and the STM tip, which appears to be contacting the sample but is actually separated by a several nm wide vacuum barrier. Mirror images of the gold wire and the tip are formed on the highly reflective sample surface. See Ref. 88 and 95 for information about components not described in this dissertation.

Figure 3.7: Outer electrodes of the STM scanner tube (cross-sectional view along the direction toward the sample, in the actual orientation with respect to horizontal).
The STM, home-built in 1993 [95], is still in good working condition after minor maintenance including re-poling the piezoceramic scanner and reconnecting broken electrical contacts. The scanner is made of a piezoceramic tube coated with gold on the inner and outer walls, and the outer coating is divided into 4 quadrants (Figure 3.7). When opposite voltages are applied to opposite quadrants, the scanner tilts toward the positively biased quadrant, which enables two-dimensional scanning in the plane perpendicular to the scanner tube. A voltage applied to the inner electrode will result in a longitudinal expansion (under positive bias) or contraction (negative bias) of the tube.

The STM is exclusively operated under a constant-current mode in all our experiments. As the tip (attached to the scanner) scans across different locations on the sample, an analog feedback loop adjusts the bias voltage on the inner electrode in order to maintain the same tunneling current between the STM tip and the sample surface (i.e., a negative feedback). If the density of surface states on the sample is the same, the tip-sample distance will be maintained, and the corresponding voltage on the inner electrode can be converted to an STM image showing the morphology of the sample surface.

The BEEM functionality of the STM is engaged when tunneling occurs between the STM tip and the metal film above an energy barrier (the latter grounded by the gold wire). Most of the tunnel current (usually maintained at 4 or 5 nA) is drained to ground through the gold wire, and a very small fraction (typically in the scale of 1 pA) may go into the semiconductor substrate and be measured by the Keithley 428 with up to $10^{10}$ V/A amplification (the semiconductor substrate is held at virtual ground by the Keithley 428). Due to the finite conductivity of the metal overlayer and the contact resistance between the gold wire and the metal film, there is a small voltage drop between the
location below the STM tip and the contact point of the gold wire, which is effectively an applied voltage across the diode and may cause a non-negligible macroscopic diode current flowing through the substrate if the zero-bias resistance of the Schottky contact is in the scale of 10 MΩ or smaller. This diode current has to be subtracted from the measured substrate current in order to find the BEEM current due to the hot carriers crossing the local Schottky barrier. A small fluctuation in the contact resistance between the gold wire and the metal film may cause a big fluctuation in the voltage drop across the diode. If the zero-bias resistance of the diode is smaller than few MΩ, the diode current usually fluctuates in a scale much larger than the actual BEEM current and makes it virtually impossible to determine the BEEM current even after averaging a big number of BEEM measurements. In our experiments on SiC and GaN, the zero-bias resistance of the investigated diodes is usually in GΩ range or beyond, and hence the diode current is not a concern.

3.3.3 STM Tip Preparation and Modification

Three types of STM tips have been used in the experiments: tungsten tips made by electrically etching 5 mil tungsten wire in NaOH [95]; controlled-geometry platinum/iridium (Pt/Ir) tips purchased from Materials Analytical Services; and Pt/Ir tips made by cutting a 5 mil Pt/Ir wire using scissors. At times, when one particular STM tip doesn’t work well, we usually try other tips of different types, but no real differences attributed to the tip material/preparation have been found so far.

An STM tip is mounted on a tip holder (see Figure 3.6) and introduced into the UHV system via the airlock. In the preparation chamber, the tip first undergoes electron
bombardment to remove any contaminants or oxide [95]. The same bombardment procedure can be used to clean a used tip.

If a tip works poorly \([i.e., \text{producing low-quality STM/BEEM images lacking resolution, or unstable images with line-to-line or pixel-to-pixel changes, or other pathological images against what may be (re)produced using good tips}]\), the reason is usually one of the following: first, the tip may be too blunt without a sharp apex (tunneling has to occur at a well defined location on the tip in order to have reasonable resolution in STM/BEEM imaging); second, the tip apex may be loosely attached to the bulk of the tip (tunneling is usually unstable in this situation); and third, there may be more than one sharp apexes on the tip that simultaneously have tunneling with the sample and hence causing a “double” or “multiple” STM image. In addition, some tips may yield BEEM spectra with abnormally high threshold, suggesting the existence of an insulating layer over these tips. Since it is very time-consuming to move the tip to the preparation chamber to do the bombardment for cleaning purposes once a tip is mounted on the scanner in the STM chamber, several procedures can be used inside the STM chamber in an attempt to improve a poorly working tip.

**Tip Crashing**

First, the tip can be intentionally crashed into the metal film on the sample surface either by applying a “controlled crash” ramp voltage on the scanner inner electrode [88] or by manually adjusting the voltage on the electrode until the tip runs into the metal. After such a crash, the tip may lose some loose atoms to the sample and/or pick up some metal atoms from the metal film. The newly picked atoms may form a sharp apex, and if they are solidly attached to the tip \((i.e., \text{if they don’t move relative to the tip while the tip})\)
scans across the sample surface), then the tip may come to a good working condition for STM/BEEM data acquisition.

Tip crashing have proven to be an effective method for tip improvement on Pt/SiC samples. Pt and SiC usually form very stable Schottky contact with zero-bias resistance in GΩ range, and tip crashing doesn’t seem to hurt the integrity of the diode. Therefore, it is usually no problem to crash the tip many times on a Pt/SiC diode. The most violent procedure is to manually crash the tip into the metal film and then sweep it sideway by adjusting the voltages on the outer electrodes of the scanner while the apex of the tip is still buried inside the metal.

However, metal/GaN contacts are much more vulnerable to damage during tip crashing. In several instances, metal/GaN diodes were seriously degraded after tip crashing. Therefore, this method is to be used with extreme caution on GaN samples.

**Tip Brushing**

The gold wire used for grounding the metal film during BEEM measurements can also serve as a “tip brush”. Once the tip is retreated away from the sample surface, the gold wire, which is attached to the manipulator block, can be used to rub against the apex of the tip. This procedure may remove sloppy attachment atoms on the tip and hence is often used in conjunction with tip crashing — if the apex of the tip appear to be sloppy after a crash, it may be brushed and crashed again until nice tunneling is achieved.

**Tip Scratching**

If crashing and brushing fails to improve a tip, the tip may be picked up by the grabber (together with the holder) and scratched against a tungsten wire mounted on a transporter arm. The scratch is forceful and may significantly change the shape of the tip
As observed under an optical microscope, a formerly “sharp” tip may become “blunt” after scratching; however, since tunneling actually occurs at the atomic scale apex, the apparent shape of the tip under the optical microscope is usually not correlated to its quality. However, if the sample surface is very rough, tunneling at different locations over the sample may occur between the sample and different locations on a blunt tip. Therefore, a nm-scale apex on a very blunt tip may be OK over a very flat sample surface but may not be able to handle a relatively rougher sample.

After some attempts of tip modification using different methods above, a former poor tip may be improved to a good condition so that it may be repeatedly used over several hours or days to produce stable and reproducible STM/BEEM images and BEEM spectra. Another criterion of a good tip is the tunnel current as monitored on an oscilloscope should have a pattern of regular oscillation as determined by the finite gain of the feedback loop (see Ref. 88 for details).

3.3.4 Micro Inchworm

Significant tunneling between the tip and the sample won’t occur until their separation is within nm range. Every time after they are separated by a big distance, a piezoceramic micro inchworm (see Figure 3.6) has to be used for coarse approach of the tip/scanner assembly toward the sample. The inchworm has two piezoceramic clamps, a piezoceramic center element, and a reference electrode. A higher or lower voltage on a clamp relative to the reference electrode means the clamp is tightened onto or released from an alumina shaft. During the operation of the inchworm, the bias applied on the clamps sweeps between 0 V and 600 - 700 V, and the reference electrode is usually held
at ~200 V. A voltage drop between the center element and the reference electrode results in the expansion and contraction of the center element, which drives the motion of the alumina shaft relative to the inchworm (for detailed description of the operation mechanism of the inchworm, see Ref. 95). A control program may direct the inchworm to move the tip forward (toward the sample) or backward (away from the sample) by a certain number of steps. Under an “auto approach” mode of the inchworm control program, before the inchworm moves one step, the STM scanner is extended by a distance greater than a step of the inchworm motion in order to reach out for the sample; and the detection of a tunnel current terminates the auto approach.

During the expansion and contraction of the center element, it is preferable that the two clamps should NOT both be clamped onto the alumina shaft, otherwise there would be stress buildup in the center element, which might cause damage and reduce the lifetime of the inchworm. The previous version of the inchworm control program contained a small bug: the center element started to contract or expand at the same time when one of the two clamps started to loosen. The control program has been modified so that one of the two clamps has to be completely loosened before the voltage on the center element starts to change.

In addition to the inchworm for tip approach, there is another inchworm to move the sample laterally relative to the tip. Both are controlled by the same program.

3.4 Data Acquisition and Processing

The STM/BEEE equipment is controlled using an old computer with a 133 MHz Intel Pentium CPU, and STM/BEEM images are displayed real-time (line by line, as the
scanning proceeds) during the data acquisition. The binary raw data may subsequently be processed to extract needed information in other formats.

3.4.1 STM/BEEM Software

An MS-DOS program written in BASIC that has been frequently updated by various people since it was initially compiled over a decade ago is used to control the STM and acquire STM/BEEM data. More information about this program can be found in Ref. 88 and 95. Updates by the author mainly involve the implementation of a “tip locking” algorithm when BEEM spectra are to be repeatedly measured over nominally the same location.

The need of a tip-locking functionality is due to the non-ideal behaviors of the scanner assembly. There is always some “creep” in the piezoceramic scanner’s response to different voltages applied to the electrodes — ideally the tip should instantly be moved to a new location and stop there, but in reality it will continue to move a little bit in the same direction as the tip displacement after the new voltages are already established, due to the slow relaxation of the lattice in the piezoelectric material. A bigger adjustment of the tip position causes bigger creep, and the speed of creep is usually in the range of several nm per minute initially and decreases over time. Additionally, slight fluctuations in the temperature may result in small changes of the positions of the tip/scanner assembly and the sample, which appears as “drift” of the tip relative to the sample. The speed of drift is usually in the range of several nm per hour.

Both creep and drift may cause a distortion of the STM/BEEM images. Concerning BEEM spectral measurements, when the tip nominally stays at the same
location (i.e., when the voltages on the outer electrodes of scanner don’t change), its actual location relative to the sample is actually changing over time. If the creep is severe, the tip may move over several nm during the acquisition of a BEEM spectrum (which usually takes 10 – 30 seconds), and hence the resulting spectrum is no longer a local measurement. Drift is usually not much of a concern in the measurement of one spectrum, but if a number of BEEM spectra are to be taken over a particular location so that the results can be averaged to reduce noise, it will be preferable to “lock” the tip over a particular location on the sample in order for the average to be a true local measurement instead of a spatial average over the path of creep and/or drift (from now on, both creep and drift will be referred to as “drift” because they have essentially the same effect).

One way to achieve this goal is to take STM images around a small region before and after one or more BEEM spectra are taken, and compare the STM images to make sure there is negligible drift — if noticeable drift is present, an offset on the tip location can be manually inputted into the control program to compensate the drift.

Since the approach above is time-consuming and labor-intensive, an automated mechanism to compensate the drift is very helpful when taking a large number of spectra over a same location. Previously, following the algorithm proposed by Swartzentruber [96], a tip locking command that allows the tip to track a certain topographic feature on the metal film had been implemented in the program by Ben Kaczer [88], but this command only works when no STM/BEEM data are taken. In the updated program (Appendix A), automatic tip locking becomes an option for the case of repeated BEEM spectra measurement — after each spectrum is taken, the tip looks for the local topographic maximum/minimum or the maximum BEEM current, depending on an input
parameter. Unless the drift is so big that the tip comes to the vicinity of another local
maximum/minimum over the course of one BEEM spectrum acquisition, the algorithm
will be able to bring the tip back to the selected local feature, and then the subsequent
BEEM spectrum is measured. The comparison of STM images taken before and after a
batch of BEEM spectra usually confirms that the tip locking mechanism effectively keeps
the tip with few nm from the selected feature.

3.4.2 Raw Data Processing

The raw data are stored in little-endian binary format in two files, one with .dat
extension for STM/BEEM images, the other with .i extension for BEEM spectra [88].
The data acquisition software is capable of reading raw data and export STM/BEEM
images in bitmap format and BEEM spectra in MS Excel spreadsheets. However, it is
sometimes desirable to convert the binary raw data into space-delimited text files that can
be easily and more flexibly processed using MS Excel. Several MS-DOS programs have
been written by the author for this purpose (see Appendix B).

In the study of cubic inclusions in 4H-SiC, there is the need to “average” an STM
or BEEM image along the direction of the inclusion in order to get a line profile showing
the dependence of metal surface morphology or BEEM current on the distance to the
inclusions. However, in most STM/BEEM images the inclusions are at a small angle to
the vertical axis of the images, and the image has to be rotated or skewed before the
averaging is made. Therefore, MS-DOS programs have also been written to “skew” the
text files of STM images so that the inclusion center on every horizontal scan line is
aligned in the same column of the spreadsheet.
CHAPTER 4

RESULTS

BEEM studies of double-stacking-fault cubic inclusions in 4H-SiC are the highlight of our recent research. The inclusions are found to support 2D propagating quantum well states, and the CBM of the 2D quantum well is measured. Our attempt to investigate single-stacking-fault cubic inclusions in 4H-SiC hasn’t been successful due to the very low density of inclusions in the samples we studied, but in the process we characterized the Schottky contact between Pt and $p$-type 4H-SiC using BEEM. An earlier study of dislocation charge in GaN will also be presented in this chapter.

4.1 Quantum Well State of Cubic Inclusions in 4H-SiC

As discussed in Section 2.3, self-forming cubic inclusions in 4H-SiC have been observed in electrically stressed power diodes and high-temperature-processed $n$-type materials using cross-sectional TEM, and luminescence studies of the inclusions (single-stacking-fault type in the former case and double-stacking-fault type in the latter) have suggested the inclusions may behave like quantum wells. If true, they would be a very unique physical system in that there is no change in composition, density, or nearest-
neighbor stacking across the quantum well boundaries, yet they have highly localized quantum well states. Our BEEM studies of high-temperature-processed n-type 4H-SiC samples directly confirmed the quantum well nature of the double-stacking-fault cubic inclusions. BEEM images of Pt/SiC interfaces show parallel stripes with significantly reduced Schottky barrier height, corresponding to the intersections of cubic inclusions with the Pt/SiC interface. The difference in barrier height between the cubic inclusion openings and the bulk 4H-SiC regions represents a direct measurement of the lowest quantum well state in the inclusions.

4.1.1 Sample Processing and Characterization by Collaborators

The SiC samples investigated in this study were provided by Dr. Brian J. Skromme at Arizona State University (ASU), where the inclusions were formed through high-temperature processing and studied using electrical, optical, and structural methods. Some of these initial studies are summarized below and in Section 2.3.3.

The starting materials were several identical 35 mm diameter 4H-SiC wafers purchased from Cree, Inc. The wafers have a 2 µm lightly n-type nitrogen-doped (1 – 1.5×10^{17} \text{ cm}^{-3}) epilayer on a heavily n-type nitrogen-doped (~3×10^{19} \text{ cm}^{-3}) Si-face substrate. There is an 8º surface miscut from the (1000) basal plane, with the c-axis tilting toward the minor flat of the wafers.

After a 90 minute dry oxidation at 1150 ºC, the central region of the wafers appeared to be “dimpled” with small surface depressions clearly visible to bare eyes when viewed from certain angles, while the peripheral region appeared unchanged (Figure 4.1). The difference is believed to be due to the higher doping level of the
Figure 4.1: 4H-SiC wafer after oxidation at 1150 °C. Photo from ASU.

Figure 4.2: Cross-sectional TEM image of a double-stacking-fault cubic inclusion in 4H-SiC. From ASU.
substrate in the central region (it is well known that dopants tend to have a higher concentration on the center facet of the ingot during crystal growth). High-resolution cross-sectional TEM images (Figs. 4.2) revealed many cubic inclusions (all of the double-stacking-fault type) with an average $c$-axis spacing of $\sim 77$ nm in the 4H-SiC matrix in the central region, while no inclusions were found in the peripheral region. TEM and secondary electron imaging of the central transformed region also revealed that many of the inclusions extend all the way from the substrate to the epilayer surface.

Titanium, nickel, platinum films were deposited on oxide-stripped wafer surface to form Schottky contacts. Macroscopic $I-V$ and $C-V$ measurements on Shottky diodes revealed a Schottky barrier height reduction of $\sim 0.41-0.47$ eV on the transformed central region compared to the untransformed peripheral region, but on the two regions the barrier height has the same dependence on metal work function (Figure 4.3). This indicates a similar interface state density (as discussed in Section 3.1) for the transformed and untransformed SiC materials. The importance of this finding will be readdressed later in Section 4.1.3. Also, it should be noted that the Schottky barrier heights from macroscopic $I-V$ measurements as shown in Figure 4.3 are extrapolated to unity ideality factor, because Schottky diodes with low barrier heights tend to have a large ideality factor, thought to be due to discrete patches of low barrier height that are commonly present even in the absence of cubic inclusions [83, 97].

4.1.2 **Identifying the Cubic Inclusions Using BEEM**

Cleaved and oxide-stripped pieces from the transformed region of a 4H-SiC wafer were studied with BEEM. The samples were degreased using trichloroethylene/acetone/
Figure 4.3: Dependence of macroscopic Schottky barrier height (extrapolated to unity ideality factor) on metal work function, from macroscopic diode $I$-$V$ measurements. Upper line: untransformed region, slope = 0.625; lower line: transformed region, slope = 0.605. From ASU.

Figure 4.4: Macroscopic $I$-$V$ curves of a typical Pt/4H-SiC diode on a sample containing cubic inclusions. Inset: the same curve zoomed in around the zero-bias region. The zero-bias resistance of this diode is about 4 GΩ.
methanol ultrasonic bath (10 minutes each), further cleaned with two cycles of 30
minutes ultraviolet ozone oxidation and 2 min etching in 1:10 HF:H₂O, and introduced
into the preparation chamber where they were outgassed overnight at <230 °C. Two sets
of Pt films (~8 nm and ~4 nm thick, respectively) were deposited in situ to form Schottky
diodes, most of which showed nice rectification behavior with a large zero-bias resistance
ranging from several GΩ to several hundred GΩ (Figure 4.4).

BEEM measurements were performed in the STM/BEEM chamber. At random
locations on the transformed SiC samples, BEEM measurements showed a local Schottky
barrier height of 1.54±0.02 eV and a second CBM at ~0.13 eV above the first one (see
Figure 3.3). This is essentially the same as the results of our earlier study of the contact
between Pt and normal 4H-SiC, in which we found a 1.58±0.03 eV Schottky barrier
height and a second CBM at ~0.14 eV higher. The slight difference in the barrier height
is probably due to lower signal-to-noise in our earlier study [48].

However, when we searched for BEEM current at a \( V_T = 1.5 \) V (just below the
Schottky barrier height of bulk 4H-SiC), we could easily locate where the inclusions
intersect the Pt/SiC interface. Fig. 4.5(a) is a (150 nm)² STM topographic image of the
top metal surface of a diode made with a 8 nm-thick Pt film, and shows no particularly
distinctive features other than ~6 nm diameter Pt crystallites, which are normal for
polycrystalline thin metal films. Fig. 4.5(b) is a simultaneously measured BEEM image
(a plot of local BEEM current vs. tip location) at \( V_T = 1.5 \) V, and shows a straight “stripe”
of strongly enhanced BEEM current, but essentially no BEEM current elsewhere.

Since electrons must have higher energy than the local Schottky barrier height in
order to enter the semiconductor, the enhanced BEEM current indicates significant
Figure 4.5: (a) $(100 \text{ nm})^2$ STM image of 8 nm thick Pt film on transformed 4H-SiC, taken at $V_T = 1.5 \text{ V}$ and $I_T = 1.5 \text{ V}$. Gray scale: 4 nm. (b) Simultaneous BEEM image. Gray scale: 1 pA (the gray areas have zero BEEM current). (c) 1500 nm × 125 nm STM image of the same metal film. (d) Simultaneous BEEM image. White circles in (d) indicate small “glitches” in the BEEM current due to the capacitive coupling between the STM tip/scanner and the sample.

Figure 4.6: Schematic illustration of the orientation of cubic inclusions in our samples. The dashed lines represent the intersection of the inclusions with (a) wafer surface; (b) cross-section parallel to the major flat. (a) and (b) are not to the same scale.
lowering of the Schottky barrier height over the stripes. BEEM spectra measurements confirmed that the barrier height lowering between the stripes and bulk 4H-SiC is > 0.5 eV (see Section 4.1.4 for details). A lowering of over 1/3 of the original is too big to be attributed to surface/interface effects such as atomic layer steps or interface (on our previous survey of Pd/6H-SiC Schottky barrier inhomogeneity using BEEM [83], we never observed variations > 0.2 eV).

Many similar stripes were observed on the sample. They were all straight, parallel to each other (as shown in Fig. 4.5(d)), and longer than our largest BEEM images of ~1.6 µm. We carefully measured the density of high BEEM stripes on two different Pt contacts by sampling ~5% of the 0.5 mm contact diameter along a line perpendicular to the high-BEEM stripes. The average density was found to be ~1.8/µm and ~1.5/µm for the two contacts, although the total number of stripes observed in this survey was not big enough to be sure that the difference in measured density between the two contacts is statistically significant. The separation between adjacent inclusions was highly non-uniform, ranging from > 2 µm down to ~60 nm (note that cubic inclusions originate from pre-existing dislocations randomly located in the samples). The average spacing (~520 nm) of these stripes agrees well with the result of TEM measurements that the average spacing of inclusions in the bulk is 77 nm along the c-axis – due to the 8° surface miscut, the expected spacing along the wafer surface is ~77 nm / sin 8° ≈ 550 nm.

The orientation of the enhanced BEEM stripes is found to be perpendicular to the wafer major flat [Figure 4.6(a)], which matches that of the bright stripes observed in secondary electron images of the transformed region of the bare wafer [70]. This is exactly the expected orientation of the intersection of cubic inclusions with the wafer
surface, as illustrated in Figure 4.6(b) (recall that the $c$-axis of the wafer tilts by $8^\circ$ toward the minor flat). Additionally, the inclusions are expected to tilt to the right into the 4H-SiC bulk, which is consistent with the observed asymmetry of BEEM current amplitude on the two sides of inclusions (see Section 4.1.5 for details).

Based on all the evidence above, we are confident to conclude that the enhanced BEEM stripes in BEEM images directly correspond to individual cubic inclusions in the transformed 4H-SiC material. Also, essentially the same Schottky barrier height is found using BEEM over all inclusions we studied (with only one exception), as will be discussed in details in subsequent sections. Since only the double-stacking-fault cubic inclusions were observed in the transformed 4H-SiC samples using cross-sectional TEM, we believe the inclusions we observed are all of this type with the one noted exception.

On a related note, a small ($< 0.5$ nm) topographic depression was often observed to coincide with the bright stripes in BEEM (see Figure 4.13 in Section 4.1.6). However, similar depressions were also observed at locations with no extra BEEM current or reduced barrier height, and are probably due to atomic steps that existed on the vicinal wafer surface before metal deposition.

A comment on the quality of the BEEM image in Figure 4.5(d): “glitches” of BEEM current are sometimes observed in parts of BEEM images where we expect no BEEM current to exist. These glitches typically have a dark “head” on the left and a bright “tail” on the right in the same scan line. They are displacement current due to the capacitive coupling between the tip and the sample. If there is a sudden change in the tip position, the tip/sample capacitance will change, and some displacement current can flow as a result. But this displacement current must time-integrate to zero, and hence every
such glitch has both a positive (bright) and negative (dark) part. We have noticed a very stable tip seldom produces such glitches, whereas a relatively unstable tip may produce many glitches in BEEM images as well as protrusion-like artifacts at corresponding locations in the simultaneous STM images. A speculative explanation is that the unstable part of a tip may suddenly “swing” toward to the metal surface (or loose atoms may jump onto the tip apex) due to the large electric field between the tip and the sample, causing a sudden reduction of the tip/sample separation and hence a huge increase in the tunnel current. When the feedback loop (see Section 3.3.2) senses the tunnel current increase, it will try to compensate this “error signal” by moving the tip very rapidly away from the sample. As the tip/sample separation becomes bigger, the tip/sample capacitance becomes smaller, and hence a displacement current flows into the semiconductor, causing an apparent reduction in the measured BEEM current (the dark “head” of a glitch). Since the rapid retreat of the tip is an over-reaction, the tip will have to be moved toward the sample subsequently, causing a displacement in the opposite direction (the bright “tail” of a glitch). On the other hand, the initial reduction of the tip/sample separation due to tip instability is generally not big enough to result in a significant displacement current. Therefore, most glitches begin with a dark head on the left (note that a scan line goes from left to right), and few have the form of a white head, a dark middle, and a white tail.

A same tip usually produces more glitches in a faster scan than in a slower scan, possibility because the electric field at the tip apex changes as the tip moves quickly across the nodular metal surface, which causes the unstable part (or loose atoms) of the tip to be more mobile. In a fast survey scan of a large area it is usually no problem to tolerate a few glitches as long as they do not overwhelm the real signal.
4.1.3 Quantum Well State of the Inclusions

Now to consider the issue of Schottky barrier height variations. BEEM spectra measured away from the high-BEEM stripes are always like those of normal Pt/4H-SiC contacts with a local Schottky barrier height of 1.54±0.02 eV (right-most curve in Figure 4.7), confirming that >95% of the sample surface looks just like untransformed, bulk 4H-SiC. However, directly over the stripes, BEEM spectra yield a local Schottky barrier height of 1.01±0.03 eV (left-most curve in Figure 4.7), which we found over all but one location on the > 100 stripes on which BEEM spectra were measured (the sole exception will be discussed later).

Around the stripe boundaries (middle curve in Figure 4.7), BEEM data appear to be a superposition of the two spectral types above, due to the finite spatial resolution of the BEEM technique caused by multiple elastic scattering of hot BEEM electrons in the metal film [94]. If we fit a boundary spectrum as a superposition of two spectra, we obtain essentially the same two Schottky barrier heights (~1.54 eV and ~1.01 eV) as found far from the inclusions and directly over them, respectively. As expected, we’ve found that the relative weight of the inclusion component as compared with the 4H-SiC component decreases as the tip moves farther away from the center of the stripe.

We believe that our measured ~0.53 eV local reduction in Schottky barrier height over the cubic inclusions represents a direct local estimate of the lowest quantum well state energy, with respect to the bulk 4H-SiC CBM.

First, we note that to measure a BEEM current over the inclusions, the hot BEEM electrons must enter a propagating state in order to reach the substrate interior and be collected as BEEM current. No localized interface effects (such as the low barrier-height
Figure 4.7: Typical averaged BEEM $I_c-V_T$ curves (average of 53 to 95 individual curves at the same location). The left most curve is scaled by a factor of 0.25. The fitted curves are not shows as they are completely overlapped by the raw data.

Figure 4.8: Calculated energy profile (relative to the metal Fermi level) near a Pt Schottky contact on 4H-SiC with double-stacking-fault inclusions. (a) Close-up view of a quantum well opening at the M/S interface. (b) Larger-scale view of the depletion region. Note that the quantum wells are partly filled deep in the bulk.
“patches” on an otherwise homogeneous substrate in the Tung model) could produce a potential reduction as big as \( \sim 0.53 \) eV (over 1/3 of the 4H-SiC barrier height) cutting through the near-interface depletion potential of 4H-SiC. In the Tung model, there is also a potential “pinch-off” effect [82] that causes a potential rise inside the semiconductor bulk beneath a low-barrier patch and raises the effective local barrier height to a value closer to the normal barrier height in the surrounding regions. Consequently, if a low-barrier patch caused a 0.53 eV reduction in the measured barrier height, the actual potential in the patch at the M/S interface would have to be even lower, which is essentially impossible. But the \( \sim 0.53 \) eV barrier lowering is easily explained by a thin planar inclusion with a lower-energy 2D conduction band (of propagating states) that intersects the M/S interface, creating a lower-energy channel for BEEM electrons to conduct through the depletion region and into the substrate. This is illustrated in Figure 4.8, which shows our calculated conduction band potential energy profiles for a double-stacking-fault cubic inclusion intersecting an M/S interface, assuming the quantum wells support a 2D conduction band with its CBM at 0.53 eV below the 4H-SiC bulk CBM.

Second, the inclusions and surrounding 4H-SiC regions are both entirely in depletion close to the M/S interface. Hence there is negligible screening by free carriers near the interface that would affect the local interface potential (this is not true deep in the bulk beyond the depletion region, where the quantum wells should be filled [72]).

An important third issue is whether the M/S interface near the inclusions has a different interface state density (which determines the “strength” of the Fermi level pinning) and/or charge neutrality level than the rest of the M/S interface, because this could cause the measured Schottky barrier height reduction at the inclusions to differ
from the actual difference between the quantum well 2D CBM and the bulk 4H-SiC CBM. As discussed earlier, however, the data in Figure 4.3 indicate that interface pinning is essentially the same (and rather weak) on both the transformed and untransformed parts of the sample. Since diode $I-V$ measurements are dominated by low barrier-height regions of a sample [82], Figure 4.3 gives strong evidence that any interface-state pinning is about the same near the inclusions as it is over the rest of the M/S interface. Theoretical calculations also indicate that stacking-fault-induced inclusions (and polytypism in general) affect almost only the conduction band (and not the valence band) energy relative to the vacuum level [62], suggesting that changes in the Schottky barrier heights should track changes in the lowest conduction band energy. This conclusion is consistent with our earlier BEEM measurements [53] that the Schottky barrier of palladium contacts to 4H-, 6H-, and 15R-SiC (with bandgaps of 3.265 eV, 3.023 eV, and 2.986 eV, respectively) are 1.54 eV, 1.27 eV, and 1.22 eV, respectively, which indicate the Schottky barrier heights on different SiC polytypes indeed track their bandgaps to within ~0.05 eV (as a conservative estimate). Unfortunately, there hasn’t been any reliable BEEM measurement of the Schottky barrier height on 3C-SiC due to the lack of high-quality samples, although theoretical calculations suggest the valence band offset between 3C- and 4H-SiC is ~0.05 eV (4H is higher) [28]. Therefore, we use the barrier height’s tracking of bandgap in 4H-, 6H-, and 15R-SiC and our uncertainties in Schottky barrier heights measured with BEEM to roughly estimate an ~0.06 eV uncertainty in our extracted lowest quantum well energy.

A related fourth issue is that a large local variation in any fixed charge inside the semiconductor (such as a difference in the dopant concentration) could also shift the local
Schottky barrier height relative to the rest of the M/S interface. To check for local fixed charge, we measured systematic profiles of the 4H-SiC Schottky barrier height as a function of distance from an inclusion (Figure 4.9) by locking the tip at different locations to measure local BEEM spectra. These profiles show no significant systematic lateral variation in the 4H-SiC Schottky barrier height as the inclusion is approached, even for BEEM spectra measured over the boundary region where the 4H-SiC and quantum well Schottky barrier height can be measured simultaneously. We also note that no significant accumulation of dopant atoms at inclusions is expected during the 1150 °C oxidation step, because the diffusion of nitrogen atoms in SiC is known to be extremely slow even up to 1700 °C [98].

The fifth issue is related to the potential difference across the quantum well: it has been calculated [55] and indirectly confirmed [57] that a strong spontaneous polarization exists in non-cubic SiC polytypes, and the estimated depolarization field in 4H-SiC is \( \sim 2.8 \times 10^8 \) V/m (see Section 2.2.3), an order of magnitude higher than the maximum depletion field (estimated to be \( \sim 2.3 \times 10^7 \) V/m in the 4H-SiC region based on the known barrier height and dopant concentration of our samples). Such a huge depolarization field should produce a potential difference of \( \sim 0.35 \) eV across a 1.25 nm wide inclusion as shown in Figure 4.10(a), where the 3C-SiC CBM is significantly tilted, the 4H-SiC CBM is at different levels on the two sides of an inclusion, and the quantum well is effectively a triangular well [57, 99]. However, this depolarization field exists both deep in the bulk and near the M/S interface, and hence the quantum well energy relative to the local 4H CBM [the CBM on the right side in Figure 4.10(a), which is lower than that on the left side] should be the same at different depths from the M/S interface.
Figure 4.9: Schottky barrier height measured at different distances from enhanced-BEEM stripe center. Dashed lines indicate the measurements at the stripe boundaries where BEEM spectra have both 4H and inclusion components.

Figure 4.10: Effects of spontaneous polarization and image force lowering. (a) upper diagram: conduction band edge of the 4H/3C/4H quantum well structure of a 2SF(62) inclusion shown in the lower illustration. (b) Schematic illustration of a Pt/SiC contact. The shaded area is a cubic inclusion, and the thinner slabs parallel to it are 4H-SiC layers of one stacking repeat. The depolarization field pushes electrons to one side of the quantum well, indicated by the circles in (a) and (b).
Sixth, since the inclusion terminates at the M/S interface, would this alter our measured quantum well energy? We don’t have sufficient information to determine the possible structures of the inclusion “opening” at the M/S interface (see Figure 4.14 in Section 4.1.6). However, due to the effect of image force lowering (produced by induced charges in the metal film, which means the lowering should be the same for 4H-SiC as for the inclusion — see Figure 4.20 in Section 4.2.3), the true location of the potential barrier is estimated to be at ~1.5 nm below the M/S interface in our samples, as shown in Figure 4.10(b) (note that our measured barrier height is at this true barrier after the lowering). Due to the 8° surface miscut of our samples, the quantum well CBM at this depth is already several nm away from the opening, and at least one stacking repeat of 4H-SiC should be present between the inclusion and the metal film. Therefore, the 2D quantum well conduction band as shown in Figure 4.10(a) is already well established at the depth of the true barrier. The existence of a thin interfacial layer may reduce the effect of image force lowering and hence bring the true barrier closer to the M/S interface, but our latter study of Pt/p-type 4H-SiC contacts indicates such an interfacial layer is thinner than 1 nm (see Section 4.2.3) and hence shouldn’t significantly alter the analysis above.

Finally, we note that our measured quantum well energy of ~0.53±0.06 eV below the CBM of 4H-SiC is fairly close to the quantum well energy of ~0.60 eV below the 4H CBM calculated recently by Iwata et al. [75] for the same type of inclusions. Also, our unpublished recent calculation of the macroscopic C-V curve on an inclusion sample assuming the measured quantum well energy agrees very well with experimentally measured C-V curves.
With all the considerations above, we are confident about our estimate of the lowest quantum well state of double-stacking-fault cubic inclusion in 4H-SiC at 0.53±0.06 eV below the 4H-SiC CBM.

### 4.1.4 Electron Scattering in the Metal Film

As mentioned earlier, BEEM spectra taken around the boundaries of a low-barrier-height stripe are observed to be a mixture of a cubic inclusion spectrum and a bulk 4H-SiC spectrum, with relative weights of the two spectra dependent on the distance of the tip from the inclusion. This is explained by the broadening of electron distribution (which is highly localized and strongly forward-focused when the tunnel electrons enter the metal film, see Section 3.2.4) due to the scattering of BEEM electrons in the metal film and the elastic reflection of electrons back and forth between the metal surface and the M/S interface [94].

Such a spreading of BEEM electrons is consistent with the dependence of the high BEEM stripes’ width on the thickness of the metal film. Fig. 4.11 shows two typical profiles of BEEM current averaged in the direction perpendicular to the inclusions. With the same tip bias voltage $V_T = 1.5$ V, the width (full width at half maximum) of a stripe is ~8 nm for a 4 nm-thick Pt film and ~10 nm for an 8 nm-thick film. As established in Ref. [94], the scattering of electrons inside the metal film is the dominant process responsible for the “smearing” of electron distribution when they arrive at the M/S interface if the film is thick, but for thin films there will be more contribution from the back-and-forth reflections of electrons between the two surfaces of the metal film (but this contribution doesn’t reverse the general tendency of more smearing in a thick film than in a thin film.)
Figure 4.11: Averaged BEEM current profiles at $V_T = 1.5$V across typical high-BEEM stripes for (a) 8 nm thick Pt film (stripe full width at half maximum = 9.3 nm), and (b) 4 nm thick Pt film (stripe width = 7.9 nm). In general, the width is ~10 nm for an 8 nm-thick Pt film and ~8 nm for a 4 nm-thick film.

Figure 4.12: (a) (150 nm)$^2$ STM image of an 8 nm thick Pt film on transformed 4H-SiC, taken at $V_T = 1.5$ V and $I_T = 5$ nA. Gray scale: 4 nm. (b) Simultaneous BEEM image. The gray areas have zero BEEM current. (c) BEEM image over the same area taken at $V_T = 2.0$ V and tunnel current of 5 nA. (b) and (c) have different gray scales, and BEEM current exists everywhere in (c) from dark to bright areas.
Also, an ~8 nm width of the high-BEEM stripe suggests the true width of the quantum well “opening” at the M/S interface is significantly smaller than 8 nm — an actual 8-nm-wide opening would produce a wider stripe, because electrons entering the metal not directly above the inclusion may be scattered in the metal film and finally manage to enter the inclusion.

4.1.5 Electron Scattering at the Inclusion/4H-SiC Interface

We have found that the measured Schottky barrier height over the 4H-SiC host is essentially the same (~1.54 eV) on either side of an inclusion, within our ~0.02 eV measurement uncertainty. However, there is a clear asymmetry in the amplitude of the BEEM current into the 4H-SiC on one side of the inclusion compared to the other side. Figure 4.12(c) shows a BEEM image measured over the same area as in Figure 4.12(a) and (b), but here with a tip bias $V_T = 2.0$ V, which is well above the Schottky barrier height for the host 4H-SiC. The enhanced-BEEM stripe over the inclusion is still clearly identifiable, but the BEEM current over the host 4H-SiC is clearly smaller on the right side on an inclusion as compared to the left side, for a distance up to ~40 nm from the inclusion. We have observed a similar asymmetry in BEEM images around all inclusions whenever the tip bias is larger than the 4H-SiC Schottky barrier height.

Recall that the bright lines in BEEM images are located where the planar inclusion intersects the metal interface. We suspect that this asymmetry in BEEM amplitude is due to the asymmetric geometry of the inclusion under the surface, which is inclined at a shallow ~8° angle down and to the right of the intersection line, as illustrated in Figure 4.10(b). When the tip is to the left side of an inclusion, hot BEEM electrons
injected into the 4H-SiC host do not encounter any sub-surface inclusions close to the metal interface. In contrast, BEEM electrons injected to the right of the intersection line will encounter the planar inclusion immediately below the surface. It is likely that this quantum well inclusion enhances scattering of BEEM electrons back into the metal due to an unmatched impedance between bulk 4H-SiC and the inclusion, hence reducing the magnitude of the BEEM current to the immediate right side of all inclusion intersection lines. Additionally, a higher 4H-SiC potential on the other side of the inclusion due to spontaneous polarization [see Figure 4.10(a)] may also be responsible for some BEEM electrons being bounced back into the metal.

4.1.6 Geometry of the Inclusion Opening at the M/S Interface

Figure 4.13(a) and (b) show a region where two inclusions happen to be only ~60 nm apart from each other (this corresponds to a ~8 nm separation along the $c$-axis). Figure 4.13(c) and (d) are the averaged STM topographic and BEEM profiles over these the two inclusions, respectively. The topographic profile shows small topographic depressions (<0.5 nm deep), centered at ~5 to 10 nm to the left of the center of the corresponding bright stripes in the BEEM image. We find cubic inclusions are often associated with this kind of small topographic depressions, which are always found slightly to the left of the bright BEEM stripes. However, similar depressions were also observed at locations with no extra BEEM current or reduced barrier height. We suggest that these small topographic depressions are due to details of the local step structure of the vicinal SiC surface under the polycrystalline Pt film, as shown schematically in Figure 4.14(a) and (b) for two possible step arrangements. These figures assumes ~1.25
Figure 4.13: (a) $(150 \text{ nm})^2$ STM image, taken at $V_T = 1.5 \text{ V}$ and tunnel current of 5 nA. Gray scale: 4 nm. (b) Simultaneous BEEM image. The gray areas have zero BEEM current. (c) Averaged STM topographic profile from (a). (d) Averaged BEEM current profile from (b).

Figure 4.14: Schematic illustration of the step structure on the vicinal SiC surface near the opening of a cubic inclusion (shaded bar), with two configurations in (a) and (b).
nm width for the inclusion, and an ~1 nm atomic step height on the surrounding 4H-SiC vicinal basal plane surface [100], which is the stacking repeat length along the c-axis. Note that the quantum well state of the inclusion is not well defined until the inclusion is sandwiched between 4H-SiC layers.

Also, some BEEM electrons may tunnel through the potential barrier of a 1 nm wide 4H-SiC slab and enter the quantum well, which is consistent with the fact that the bright BEEM stripes are always located to the right of the topographic depressions.

Interestingly, the inclusion on the left side in Figure 4.13 has an obviously smaller BEEM current amplitude, but corresponds to a deeper topographic depression, as compared with the inclusion on the right side. With reference to Figure 4.14, it is easy to rationalize this behavior. If an inclusion happens to terminate close to the adjacent “uphill” 4H-SiC step [Figure 4.14(a)], then one would expect a somewhat deeper-than-average topographic depression, as well as a smaller-than-average “opening” for electrons to enter the quantum well, resulting in a smaller BEEM current amplitude. Note that the topographic depression should be centered to the left of the quantum well opening, consistent with our observations.

Additionally, we note that the measured Schottky barrier height for the inclusion on the left side is 1.01±0.02 eV, compared with 0.99±0.02 eV over the other inclusion. This small but systematic difference in Schottky barrier height is possibly related to the different geometry of the two inclusions’ openings at the M/S interface, although at this time we do not yet understand the reason. This ~0.03 eV difference is well within our estimated ~0.06 eV uncertainty in the determination of quantum well energy and hence doesn’t influence our conclusions.
4.1.7 Possible Evidence of a Wider Inclusion and Deeper Well

As discussed above, all inclusions we studied with BEEM had a measured Schottky barrier height of 1.01±0.03 eV, with one notable exception. Around a particular location on one enhanced BEEM stripe, we measured a Schottky barrier height of ~0.86 eV, or ~0.15 eV lower than everywhere else on this stripe or any other stripes (a second threshold at ~1.08 eV is also observed in the BEEM spectrum; see Figure 4.15).

We note first that it is difficult to think of a tip artifact that could cause such a lowering in measured Schottky barrier height, since tip-related artifacts should cause an *increase* in measure Schottky barrier height (such as a tip with an insulating particle at its end) or a simple spatial smearing (such as a blunt or double tip). Energy conservation makes it difficult to imagine how a tip artifact could allow BEEM electrons to cross a Schottky barrier if the tip voltage is significantly less than the barrier height.

Instead, we suggest that this anomalously low Schottky barrier height could be a real effect, resulting from a cubic inclusion that is slightly wider than the predominant double-stacking-fault inclusion. It is well established theoretically that wider cubic inclusions could exist (resulting from 3, 4 or more closely spaced stacking faults), and such wider cubic inclusions have been observed [57] (and sometimes intentionally produced) [99] in as-grown 4H-SiC. They are expected to be very rare in processed material because the formation energy is significantly larger than for single-and double-stacking-fault-inclusions [75]. However, if one did exist, it should have a significantly lower quantum well energy, due to reduced electron confinement. For example, Iwata *et al.* [75] have calculated that the quantum well energy of a triple- or quadruple-stacking-fault inclusion should be ~0.11 eV and ~0.15 eV lower than that of a
Figure 4.15: BEEM spectrum (average of 8 measurements) over an “abnormal” location on an enhanced BEEM stripe. A two-threshold fitting (smooth line) well fits the data.

Figure 4.16: Schematic illustration of a small segment of 3SF(71) inclusion (dotted box). Dashed lines are the boundaries of the normal 2SF(62) inclusion.
double-stacking-fault inclusion, respectively (see Section 2.3.4). This is very similar to the \(~0.15\) eV lower Schottky barrier height we measured over this particular location.

Iwata et al.’s calculations also indicate there is a second quantum well state in the triple- or quadruple-stacking-fault inclusions at \(~0.60\) eV and \(~0.40\) eV above the ground state. The second threshold in Figure 4.15 (at \(~0.22\) eV above the first threshold) may possibly be related to the second quantum well state. However, we are not sure what may cause a second threshold in the spectra measured over inclusions (see the next section).

The fact that BEEM measurements over other locations on the enhanced-BEEM stripe that contains this patch of particularly low Schottky barrier height yielded the “normal” Schottky barrier height of \(~1.01\) eV suggests that only a small segment of this inclusion contains one or more additional stacking faults other than the two faults found throughout the inclusion. This is illustrated in Figure 4.16. As of now, the existence of this kind of “abnormal” inclusions is still speculative, as it was only observed once.

### 4.1.8 Second Transmission Channel in Some Inclusion Spectra

With regard to BEEM spectra measured over a double-stacking-fault inclusion, we have found that two BEEM thresholds in the Bell-Kaiser model are needed to get a good fit for many (but not all) of the BEEM spectra measured over inclusions. The lowest threshold (which is the only threshold for some spectra) was always found to be \(~1.01\pm0.03\) eV (with the one exception discussed below). However, the second threshold varied greatly in energy (from \(~1.05\) eV to \~1.3\) eV), and the relative magnitude of BEEM current into this second transmission channel also varied greatly from one position to another. This is in contrast to the BEEM measurements over the 4H-SiC regions away
from the inclusions, where a second threshold is always found at 1.67±0.02 eV, with approximately the same relative weight (usually about three times as big as that of the first threshold). A second threshold is generally thought to be an indication of a higher energy CBM. We do not yet understand why a second threshold exists for some, but not all, areas over an inclusion. This unexplained effect doesn’t affect our estimate of the quantum well state in the inclusions, because the Schottky barrier height determined from the lowest threshold is not altered by the second threshold.

4.2 BEEM Study of p-type 4H-SiC

The original purpose of our “Hole BEEM” measurements on Pt/p-type 4H-SiC contacts was to look for single-stacking-fault 1SF(31) inclusions that have been observed to exist in some of the pn junction 4H-SiC samples we received. However, due to their extremely low number density (< 1 / 100 µm on the exposed surface), we failed to locate any inclusion. Nevertheless, we found the p-type Schottky barrier height to be ~1.45 eV with a second threshold at ~1.56 eV, which suggest a split-off valence band at ~0.11 eV below the valence band maximum. In order to compare the p- and n-type Schottky barrier heights of contacts prepared under identical sample cleaning and metal deposition conditions, we removed the p-type layer on half of a particular pn junction sample. The results presented in this section came from this well-studied sample.

4.2.1 Sample Preparation

The 4H-SiC sample studied in this project was provided by Dr. Michael Mazzola at Mississippi State University, where epitaxial p and n 4H-SiC layers were grown using chemical vapour deposition (CVD) on conducting substrate purchased from Cree, Inc. A
3.5 µm N-doped n-layer was first grown on the substrate, and a 0.35 µm p-layer doped with Al (using trimethylaluminum as a doping source) was subsequently grown in the same CVD process to form a pn junction structure. The atomic concentration of Al in the p-layer, as determined by secondary ion mass spectroscopy, is equal to $5 \times 10^{18}$ cm$^{-3}$. The free electron concentration in the n-layer is about $3 \times 10^{16}$ cm$^{-3}$.

Both the p-layer and the n-layer were studied with BEEM for comparison purposes. To expose the n-layer for investigation, half of the sample was etched in NF$_3$ inductively coupled plasma, while the p-layer on the other half was protected with photoresist. After the photoresist was stripped off, the sample was degreased by three successive 10 min ultrasonic agitation with trichloroethylene/aceton/methanol, and further cleaned by two cycles of 30 min ultraviolet ozone oxidation, 30 sec HF (49% aqueous) dip, and anhydrous methanol rinse.

The sample was then introduced into the preparation chamber and mildly outgassed for 5 hours at $< 230$ ºC. Approximately 3 nm thick Pt films were deposited on the sample to form several Schottky diodes (some on the exposed n-layer, others on the p-layer). By this means, both n- and p-Schottky contacts were prepared and formed under identical conditions. Figure 4.17 illustrates the sample structure and the energy level of the p- and n-type Schottky contacts.

After the Pt deposition, the sample was transported in UHV into the STM/BEEM chamber where diode characterization (including BEEM measurements) was performed at room temperature. The macroscopic $I-V$ curves of the Schottky diodes on the p- and n-regions revealed that they all have very high (> 100 GΩ) zero-bias resistance and good rectification behaviour (see Figure 4.18). However, the forward-bias current of the p-
Figure 4.17: (a) Structure of the half-\(n\)/half-\(p\) sample (different parts not to scale). (b) Energy diagram of the \(p\)-type schottky contact and the leaky \(pn\) junction below it.

Figure 4.18: Macroscopic \(I-V\) curves of a typical Pt/\(p\)-type 4H-SiC diode on the half-\(n\)/half-\(p\) sample. Inset: the same curve zoomed in around the zero-bias region. The zero-bias resistance of this diode is about 750 G\(\Omega\).
type diodes is several orders of magnitude smaller than that on the \( n \)-type diodes (nA vs. \( \mu \)A at 1 V). We believe this is because the somewhat leaky (10 – 100 MΩ) sub-surface \( pn \) junction, which is in series with the \( p \)-type Schottky diodes and hence limits their forward current. On the other hand, if the \( pn \) junction was not leaky, we would not have been able to observe the \( p \)-type Schottky barrier as it is back-to-back with the \( pn \) junction, as shown in Figure 4.17.

### 4.2.2 Valence Band Structure of 4H-SiC

The \( n \)-type Schottky barrier height measured with BEEM on the \( n \) region of the sample is 1.55±0.03 eV, with a second CBM at ~0.14 eV above the first. This agrees very well with our BEEM measurements on the bulk 4H-SiC region of the samples containing cubic inclusions (see Section 4.1.2).

On the \( p \)-type region, we also find that two thresholds, at \( V_T = -1.45\pm0.03 \) eV and \(-1.56\pm0.01 \) eV, respectively, are needed to fit the measured hole-BEEM spectrum (see Fig. 4.19, where the inset shows the deviation if one threshold is assumed under the same fitting range). The first threshold directly corresponds to a \( p \)-type Schottky barrier height at about 1.45 eV, \textit{i.e.} the highest valence band maximum. The second threshold suggests an additional valence band maximum at ~0.11 eV below the first. Calculations of the 4H-SiC valence band structure [51, 52] have suggested that the spin-orbit splitting of the valence band at the \( \Gamma \) point is less than 0.01 eV, smaller than the energy resolution of BEEM. The valence band crystal-field splitting (due to the spontaneous polarization and depolarization field) is calculated to be ~0.07 eV at the \( \Gamma \) point in 4H-SiC [51, 52], and BEEM is expected to be able to resolve such a split-off band as a second threshold.
Figure 4.19: BEEM spectrum on (a) Pt/n-type 4H-SiC and (b) Pt/p-type 4H-SiC. Arrows indicate the locations of fitted thresholds. Insets: comparison of one- and two-threshold Bell-Kaiser fitting curves. The two-threshold curves (straddling the measured spectrum) are much better fits than the one-threshold curves under the same fitting range (thin solid lines away from the measured data).
Therefore, the second threshold ~0.11 eV below the valence band maximum is possibly a direct measurement of the crystal-field splitting. However, Sridhara et al. [101] used differential absorption spectra measurements to determine a crystal-field splitting of 0.060 eV in 4H-SiC, which is closer to the theoretical value. Further analysis is needed for more insight about the discrepancy between our measured separation of the two thresholds and the calculated crystal-field splitting.

4.2.3 Interfacial Layer at the Pt/4H-SiC Interface

We now turn to the issue of what may be happening at the M/S interface with regard to interface states and Fermi level pinning. In either the Schottky limit or the strong-pinning Bardeen limit of the theories of Schottky barrier, the \( p \)-type and \( n \)-type barrier heights of the same semiconductor should add up to its bandgap, if image force lowering is neglected [78] (this is evident in Figure 3.1). However, the sum of our measured \( p \)-type and \( n \)-type Schottky barrier heights is ~3.00 eV, smaller than the 4H-SiC bandgap of 3.265 eV. Possible reasons of this difference include image force lowering, and weak Fermi level pinning related to the existence of an interfacial layer.

As already mentioned in Section 4.1.3, image force lowering of the Schottky barrier is due to the induced charge in the metal by charge inside the semiconductor (there is an attractive force between the original charge and the image charge, and hence the additional potential is negative for electrons and positive for holes, causing a lowering of the barrier in both cases). Figure 4.20 illustrates the case of a metal/\( n \)-type semiconductor contact, neglecting any interfacial layer. Since the maximum potential barrier occurs where the depletion field balances the field caused by the image charge,
the relationship between the lowering $\Delta \phi$, the depth of the maximum potential $x_m$, and the maximum depletion field $E_{\text{max}}$ is [78]

$$E_{\text{max}} = \frac{q}{16 \pi \varepsilon' x_m^2}$$

(1)

and

$$\Delta \phi = 2x_m E_{\text{max}},$$

(2)

where $q$ is the magnitude of electronic charge, $\varepsilon'$ is the high-frequency permittivity of the semiconductor (assumed to be 6.52 for all SiC polytypes [54]) because there is not enough time for the semiconductor to be fully polarized as a carrier in it approaches the M/S interface at the thermal velocity under room temperature. $E_{\text{max}}$ can be calculated based on the known donor concentration $N_d$ and measured barrier height $\phi_b$ [78]:

$$E_{\text{max}} = (2qN_d / \varepsilon_x)^{1/2} \left( \phi_b - V - \xi - \frac{kT}{q} \right)$$

(3)

where $\varepsilon_x$ is the static permittivity of the semiconductor (~9.7 for 4H-SiC [40]), $V$ is the applied bias between the metal and the semiconductor (0 in our BEEM measurements), and $\xi$ is the location of the Fermi level relative to the semiconductor CBM in the bulk (beyond the depletion region) that can be calculated based on $N_d$.

After finding $E_{\text{max}}$ using Eq. 3, it is straightforward to find $x_m$ using Eq. 1 and $\Delta \phi$ using Eq. 2. However, since the measured barrier height is already after image force lowering, several iteration of adding the newly derived $\Delta \phi$ to the measured barrier height will improve the accuracy of the estimate above.

Our calculated image force lowering in the absence of any interfacial layer is ~0.16 eV for Pt/p-type 4H-SiC and ~0.05 eV for Pt/n-type 4H-SiC interfaces. Therefore, image force lowering by itself (0.05 eV + 0.16 eV) cannot account for the ~0.26 eV difference in the sum of Schottky barrier heights and the bandgap. Since the sample
Figure 4.20: Image force lowering of an $n$-type Schottky barrier. Adapted from Ref. 78.

Figure 4.21: Schottky contact under flatband condition, with the interfacial layer considered. $E_F^s$ is the semiconductor Fermi level. See text for the meanings of other symbols. Note that the difference between the neutrality level $\phi_0$ and the metal Fermi level $E_F^m$ is equal to $\phi_{bn}^0 - (E_g - \phi_0)$. 
surface was cleaned \textit{ex situ}, it is quite possible that a thin SiO$_2$ layer exists between the metal and the semiconductor. We calculated the effect of an interfacial layer based on equations in Ref. 78 assuming weak Fermi level pinning and found that the assumption of a thin SiO$_2$ layer and SiC/SiO$_2$ interface states may explain the difference in the sum of Schottky barrier heights and the bandgap.

Figure 4.21 is the energy diagram of an \textit{n}-type Schottky contact in the flatband condition (\textit{i.e.}, the bands of the semiconductor near the M/S interface is flattened by a bias voltage $V$ between across the Schottky contact that balances the depletion potential). The flatband Schottky barrier height $\phi_{bn}^0$ satisfies the following equation:

$$
\phi_m = V_i' + \chi_s + \phi_{bn}^0,
$$

(4)

where $\phi_m$ is the metal work function, $\chi_s$ is the electron affinity of the semiconductor, $V_i'$, the voltage drop across the interfacial layer, is determined by the interface charge (per unit area) $Q_{ss}'$ and the interfacial layer thickness $\delta$ (by applying Gauss’s law across the interface):

$$
V_i' = \delta Q_{ss}' / \varepsilon_i,
$$

(5)

where $\varepsilon_i$ is the permittivity of the interfacial layer.

If the interfacial layer is very thin (< 1 nm), electrons and holes in the metal can easily tunnel through it and occupy the interface states at the semiconductor surface. As an approximation, we may assume the interface states are filled up to the metal Fermi level $E_F^m$ (at the zero-temperature limit) [78], then $Q_{ss}'$ is determined by the position of the charge neutrality level $\phi_0$ (see Section 3.1) relative to $E_F^m$ (Figure 4.21):

$$
Q_{ss}' = qD_s (\phi_{bn}^0 + \phi_0 - E_g),
$$

(6)

where $E_g$ is the bandgap, and $D_s$ is the density of interface states per unit area per eV.
From Eqs. 4 – 6, it can now be determined that
\[ \phi_{bn}^0 = \gamma(\phi_m - \chi_s) + (1 - \gamma)(E_g - \phi_0), \] (7)
where the factor \( \gamma \) is given by
\[ \gamma = \epsilon_i / (\epsilon_i + q \delta D_s). \] (8)

Similarly, the flatband barrier height of \( p \)-type Schottky contacts is determined as
\[ \phi_{bp}^0 = \gamma(E_g + \chi_s - \phi_m) + (1 - \gamma)\phi_0. \] (9)

Apparenty, the sum of the \( n \)- and \( p \)-type flatband barrier heights equals the bandgap:
\[ \phi_{bn}^0 + \phi_{bp}^0 = E_g. \] (10)

As \( \delta \) or \( D_s \) approaches 0, \( \gamma \) will approach 1, which is the Schottky limit. A large \( D_s \) approaching infinity will result in the Bardeen limit (\( \gamma = 0 \)). As shown in Figure 4.3, \( \gamma \) as the dependence of the barrier height on metal work function (see Eqs. 12 – 14 below to confirm that the actual barrier height has the same dependence) is \( \sim 0.62 \) from macroscopic diode \( I-V \) measurements for Ti, Ni, and Pt diodes on \( n \)-type 4H-SiC [70] prepared in a similar way to our sample in this study.

Now to consider the actual (non-flatband) Schottky barrier heights of \( p \)- and \( n \)-type diodes (under zero bias and ignoring image force lowering). The situation is quite similar to the flatband case: removing the prime marks and all the superscript 0 in Eq. 4 and 6, and they will apply to the actual barrier. However, Eq. 5 will have to be modified in order to include the depletion field inside the semiconductor:
\[ V_i = \delta(Q_{ss} + \epsilon_s E_{max}) / \epsilon_i. \] (11)

With the new equations, it can be derived (see Ref. 78 for details) that
\[ \phi_{bn} = \phi_{bn}^0 - \alpha E_{max}^n \] (12)

\[ \text{and} \]
\[ \phi_{bp} = \phi_{bp}^0 - \alpha |E_{max}'|, \]  

where \( E_{max}' \) can be calculated from Eq. 3, and there is a similar equation for \( E_{max}'' \). The factor \( \alpha \) is given by

\[ \alpha = \frac{\delta\varepsilon_s}{(\varepsilon_i + qD_s)}. \]  

(14)

It can be calculated from Eq. 11 and 12 that

\[ \alpha = \frac{E_g - (\phi_{bp} + \phi_{bn})}{|E_{max}'| + E_{max}''}. \]  

(15)

Comparing Eq. 8 and 15, the relationship between \( \gamma \) and \( \alpha \) is obvious:

\[ \alpha = \frac{\delta\varepsilon_s}{\varepsilon_i} \cdot \delta\gamma. \]  

(16)

With \( \gamma \) and \( \alpha \) determined from experiments, \( \delta \) and \( D_s \) can be derived from Eq. 8 and 16.

If the measured Schottky barrier heights \( \phi_{bp} \) and \( \phi_{bn} \) are adjusted to take into account the image force lowering calculated with the assumption of no interfacial layer (~0.16 eV for Pt/p-type 4H-SiC and ~0.05 eV for Pt/n-type 4H-SiC), which has often been assumed [102], then we get \( \delta \sim 3 \text{ Å} \) and \( D_s \sim 5.3 \times 10^{13} \text{ cm}^{-2} \). The permittivity of bulk SiO\(_2\) (\( \varepsilon_i = 3.9\varepsilon_0 \)) is used in the calculation. Since the interfacial layer is very thin and not intentionally grown, its permittivity may be smaller than the bulk value, corresponding to a smaller thickness \( \delta \) (see Eq. 16). The density of states \( D_s \) doesn’t depend on \( \varepsilon_i \).

On the other hand, the effect of image force lowering in the presence of an insulating interfacial layer is complicated [78, 103] and is still an open question for future studies. If image force lowering is neglected in the calculation above, the results are then \( \delta \sim 13 \text{ Å} \) and \( D_s \sim 9.9 \times 10^{12} \text{ cm}^{-2} \). The real levels of \( \delta \) and \( D_s \) are probably between these two extreme cases. This range of values for \( \delta \) and \( D_s \) appears to be quite reasonable.
and, as discussed above, would explain both the weak Fermi level pinning in 4H-SiC reported in Ref. 104 and our measured difference between the bandgap of 4H-SiC and the sum of $p$-type and $n$-type Schottky barrier heights.

### 4.3 Threading Dislocations in GaN

Finally, we present the results of an earlier project: BEEM study of threading dislocations in GaN, to which the author made key contributions.

GaN and its alloys are very important materials in optoelectronic and high power/frequency device applications. Similar to SiC, GaN is also tetravalent with close-packed lattice and hence may form different polytypes. However, GaN and its alloys as grown using metal-organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE) techniques are exclusively of the 2H (wurtzite) polytype, and other polytypes like 3C (zincblend), which may be metastable and only produced under very special conditions, are not of interest in this dissertation.

Since lattice-matched substrates are not easily available for GaN, GaN is usually grown on sapphire or SiC with >10% mismatch, and hence often contains a high density of threading dislocations and other defects. These threading dislocations in III-nitride films have been thought to be electrically active and of major concern for electronic and optical device applications. Calculations [105] and modeling of measured electron mobility [106, 107] in GaN films grown by MOCVD have suggested that threading dislocations in the III-nitrides might develop a significant trapped negative charge density $l$ (up to $1 \text{ e}^-/\text{c}$, where $\text{e}^-$ is the electronic charge and $\text{c} = 0.52 \text{ nm}$ is the $c$-axis lattice constant), due to defect levels located along or close to the dislocation core.
However, we performed BEEM measurements around dislocation cores over the contacts of Pt and MBE-grown GaN samples [108], and did not see evident of significant negative charge along the threading dislocations near the interface. Our results put an upper limit of $1/4$ electron/c-lattic constant ($e^-/c$) on the charge density of shallow dislocation levels that is charged all the way to the interface in our samples. Taking into account of the depletion potential of the Schottky contact, it is determined a dislocation level with a charge density of $1 e^-/c$ has to be at $\geq 1.3$ eV below the CBM of GaN.

### 4.3.1 Sample Preparation and Barrier Height Determination

The GaN samples were grown at the University of California, Santa Barbara (courtesy Professor James S. Speck). There is a 0.5 $\mu$m thick Ga-face GaN(0001) epilayer grown using MBE under Ga-rich condition, over a $1 – 2$ $\mu$m thick GaN buffer layer grown using MOCVD on a sapphire substrate. The MBE epilayer was $n$-doped using Si with a concentration of $N_D = 1\times10^{17}$ cm$^{-3}$ (corresponding Debye length $L_D$ is $\sim 11$ nm), while the MOCVD buffer layer was unintentionally $n$-doped. Prior to the BEEM studies, the samples were successively cleaned in successive trichloroethylene/acetone/methanol ultrasonic bath of 10 minutes each, followed by ammonium hydroxide etching of 2 minutes, and blown-dry with nitrogen. Ohmic contacts were made using In solder on two corners of the approximately square-shaped ($\sim 5 \times 5$ mm$^2$) samples. The samples were then introduced into the preparation chamber, mildly outgassed at $\sim 230$ °C overnight, and $\sim 6$ nm thick Pt films were deposited to form Schottky diodes.

Macroscopic diode $I-V$ measurements were then made in the STM/BEEM chamber. The diodes with the best rectification behavior, which have typically $\sim 0.8$ eV
Schottky barrier height and ideality factor of ~1.4 as determined by the diode $I-V$ curves, were selected for further studies using STM/BEEM.

In contrast, the average local Schottky barrier height as determined using BEEM is ~1.13 eV. The discrepancy with the macroscopically determined barrier height can be explained as the effect of few gross defects of abnormally low local barrier heights [83], which degrade the diode quality and cause a lowering of the overall barrier height. Since most of the contact areas are “healthy”, the likelihood for the STM tip to land over a gross defect is extremely small. In our study BEEM measurements were performed over random locations on the Pt/GaN diodes, and all the locations showed similar Schottky barrier height around 1.13 eV, which indicates they are all on the healthy areas. Hence the Schottky barrier height obtained from BEEM measurements better represents the property of the Pt/GaN contact, while that from macroscopic $I-V$ measurements only represents the overall strasport behavior of the diode instead of the contact property.

### 4.3.2 Identifying the Threading Dislocations

As shown in Figure 4.22, STM images of the Pt film surface revealed many “wing-shaped” structures (decorated by polycrystalline Pt nodules) as the pinning sites of GaN surface step flow during growth. The number density of these wing structures (~$10^8$ – $10^9$ cm$^2$) agrees with the reported threading dislocation density on similarly grown samples [109]. About 30% of the wing structures bound two more steps on one side than the other – walking around the core of such a structure, one will end up with a Burgers vector that is two steps high and perpendicular to the sample surface. This indicates a threading dislocation with a screw component (as any component of the Burgers vector
Figure 4.22: (750 nm)$^2$ STM image of GaN surface decorated with metal overlayer; showing surface steps and “wing” structures.

Figure 4.23: 1.25 µm × 2 µm AFM image of the bare surface of our GaN sample.
parallel to the surface can not be identified in this view). Therefore, these structures are related to threading dislocations with either pure screw or mixed (screw + edge) characters. The remaining 70% of the wing structures with equal number of steps on two sides have zero Burgers vector perpendicular to the surface and are most likely produced by step pinning at pure edge dislocations (where the difference in the local surface energy compared to that at dislocation-free areas may be responsible for the step pinning). The reason why the difference in the number of steps on the two sides is either 0 or 2 is that the Wurtzite GaN we studied have ABAB… stacking.

Spiral hillock structures as shown in Figure 4.23 are very common on some reported Ga-face GaN samples grown under similar conditions (MBE, Ga-rich) but are rarely observed with STM on our GaN samples. Interestingly, the rare hillocks we observed tend to cluster close to each other (Figure 4.23), suggesting their formation may be favored around particular areas like domain boundaries. They are evidently formed around threading dislocations with a screw component (again, the reason why there are two spiral arms lies in the ABAB… stacking of the wurtzite lattice).

Other rare features possibly related to threading dislocations include deep “pits” and large “cliffs” of step-bunching (not shown; see Ref. 111).

4.3.3 Expected Effect of Significant Dislocation Charge

Before the results of our BEEM measurements are presented, it helps to explain what is expected if the threading dislocations are significantly charged with negative charges all the way to the Pt/GaN interface. In this situation, the negative charge would produce a potential rise in the depletion region and effectively raise the Schottky barrier
Figure 4.24: Expected potential change due to negative charge along a dislocation.

Figure 4.25: Expected BEEM image and barrier height due to dislocation charge.
height around the threading dislocations (Figure 4.24). Consequently, a dark spot should be observed in BEEM images around a dislocation core (Figure 4.25), since the BEEM current would be small or zero if the local barrier height is close to or higher than the tip bias voltage.

4.3.4 BEEM Measurements Across the Threading Dislocations

Figure 4.26 shows the STM and BEEM images of a spiral hillock structure. There is a slight increase of the BEEM current in the vicinity of GaN surface steps, possibly due to the piezoelectric effect caused by the strain around step boundaries (GaN is well known to be piezoelectric [110], and the relaxation of surface stress around step boundaries may result in a piezoelectric field that alters the local barrier height and hence the BEEM current, but we haven’t done any detailed modeling of this effect). However, no dark spot is observed at the dislocation core (see the close-up scan in Figure 4.27), contrary to the prediction based on the assumption of significant negative charge along the dislocations.

To further verify this observation, we carefully measured the profile of BEEM current and Schottky barrier height across the dislocation core. The area in Figure 4.27 was scanned 22 times, with the scan center adjusted after each scan to compensate for the ~1 nm drift between images. During each scan, the STM tip was stopped for ~20 s at each of the positions marked by a “×” symbol in Figure 4.27(a) and (b), where an individual BEEM spectrum was measured in order to extract the local Schottky barrier height. The spectra from the corresponding locations in the 22 scans were then averaged together to yield a low noise (<~10 meV) high spatial resolution (<~3 nm) profile of Schottky barrier height across the dislocation core. This Schottky barrier height profile is
Figure 4.26: (350 nm)$^2$ STM image and simultaneous BEEM image of a “growth spiral”. The line in the center indicates where a detailed BEEM cross-section was done to quantify local potential profile at metal/GaN interface (see Figure 4.22).
Figure 4.27: (a) and (b) (50 nm)$^2$ close-up STM and BEEM images (measured at $V_T = 1.4$ V) of the dislocation core region in Figure 4.21. Crosses are where 21 different BEEM spectra were measured. (c) and (d) Profiles of the local barrier height and BEEM current across the dislocation core.
Figure 4.28: (a) (50 nm)$^2$ STM image. (b) and (c) (50 nm)$^2$ close-up STM and BEEM images (measured at $V_T = 1.4$ V) of the dislocation core region indicated in (a). Crosses are where 21 different BEEM spectra were measured. (d) and (e) Profiles of the local barrier height and BEEM current across the dislocation core.
shown in Figure 4.27(c), while the corresponding profile of BEEM current is shown in Figure 4.27(d). The Schottky barrier height profile shows only a small variation (~100 meV) that is roughly anticorrelated with the BEEM current profile. Also, the Schottky barrier height is decreased near the dislocation core and the profile is not symmetric with respect to the core. This is the opposite of what we expected from negative charge along the dislocations. But a lower barrier height is indeed supposed to produce enhanced BEEM current (see Section 3.2.3).

The clear asymmetry of the BEEM current and barrier height across the dislocation core as shown in Figure 4.27 also has an interesting implication: according to Shi et al.’s calculation [110], the screw component of a threading dislocation does not generate electric fields, whereas the edge component produces polarization fields at the interface parallel to the interface. Therefore, although we can only tell from the STM topography the spiral hillock has a screw component, BEEM measurements suggest it may also have a screw component and hence is of mixed character.

Since the wing structures are more common in our samples than the growth spirals, we have also performed similar high-resolution studies across the core region of several wing structures. Figure 4.28 shows the results of one such study, measured in a similar way as Figure 4.27. Our observations are essentially the same as for the growth spiral: a modest decrease in the Schottky barrier height at the dislocation core area at the wing apex, roughly anticorrelated with an increased local BEEM current. Contrary to the hillock, there is no obvious asymmetry in BEEM current or barrier height across the wing apex, possibly because the polarization fields of the edge dislocation is overwhelmed by the piezoelectric fields caused by the many steps bunched in the wing structure.

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Figure 4.29: (a) and (b) (350 nm)$^2$ close-up STM and BEEM images (measured at $V_T = 1.4$ V) of a “cliff” of step bunching. (c) and (d) Profiles of the local barrier height and BEEM current across “cliff”, measured along the three lines shown in (a) and (b).
We also performed a similar high-resolution profile across a 5-layer-high cliff structure (Figure 4.29) and observed similar local decrease in Schottky barrier height and increase in BEEM current. In general, threading structures imaged in large-area (~1 µm²) BEEM images often show somewhat increased BEEM current, but never any significant reduction as would be expected from negative charge at a dislocation core. Most step edges also showed a similar local increase in BEEM current, which suggest the stress origin of this effect.

4.3.5 Upper limit of Dislocation Charge Density Near the Interface

The non-existence of any dark spot around dislocation cores in our measured BEEM images indicates there is NOT significant negative charge along the threading dislocation near the interface in our samples. To estimate the upper limit of dislocation charge, we considered a model assuming a constant density of fixed charge along a dislocation in the depletion region (which is about 100 nm wide), starting from the M/S interface. Other assumptions include Fermi level pinning at 1.13 eV below the conduction band edge at the interface, and unscreened (due to the depletion of free carrier) Coulomb potential with the GaN dielectric constant. The potential “bump” (Figure 4.30) produced by such a charged dislocation can subsequently be calculated, which will cause an apparent increase in barrier height as seen from the M/S interface [upper line in Figure 4.31(a)].

However, if the electron is injected at a small distance from the dislocation core, when it travels toward the potential bump, it may be initially bounced back but then travels sideway and eventually enters the semiconductor bulk. Therefore, the effective
Figure 4.30: Potential around a negatively charged dislocation.

Figure 4.31: (a) Effective barrier height caused by dislocation charge. (b) Trajectories of an injected hot electron at different energy.
barrier height caused by the dislocation charge should actually be smaller than the
apparent barrier “as seen” from the metal side. We performed semi-classic modeling of
the trajectory of an injected hot electron by numerically solving Newton’s equation using
the conduction band effective mass of an electron in GaN and the force from the
calculated potential gradient, and determined the dependence of the electron’s trajectory
on its energy and distance from the dislocation core [Figure 4.31(b)] and the effective
barrier height around the dislocation [lower line in Figure 4.31(a)].

The estimated diameter of the “complete blackout” (i.e., the spot with no BEEM
current) around a dislocation core charged with 1/3 e⁻/c is ~2 nm in a BEEM image taken
at $V_T = 1.4$ V. Although this is smaller than the special resolution of BEEM, the extended
region with reduced BEEM current should have a much bigger size and hence may be
resolved by BEEM. A charge density of 1/4 e⁻/c would produce a dark spot barely
resolvable in BEEM images, and hence we put our estimated upper limit of dislocation
line charge near the M/S interface as 1/4 e⁻/c.

4.3.6 Upper Limit of Acceptor Level Depth

Another possible explanation of the non-existence of dark spots around
dislocation cores is, if the acceptor level along the dislocation core is shallow, it may be
depleted close to the M/S interface (Figure 4.32) and hence not able to produce any
significant barrier height difference detectable using BEEM. Assuming the Fermi level is
pinned at 1.13 eV below the GaN CBM at the interface, an acceptor level shallower than
~1.2 eV (taking image force lowering into account) below the CBM may come into
depletion near the interface.
A detailed calculation by us [112] indicates any acceptor level with 1 e⁻/c charge density and deeper than 1.3 eV below the CBM should be visible to BEEM. Therefore, the lower limit of the energy of a dislocation level with 1 e⁻/c charge density is determined to be at 1.3 eV below the CBM of GaN.

In summary, we didn’t find evidence of significant dislocation charge near the M/S interface on the MBE-grown GaN samples we studied. Although this conclusion cannot be directly applied to the material of GaN in general, our study indicates negative dislocation charge cannot be assumed to be present in all GaN materials.
Figure 4.32: Charged dislocation becomes depleted near the M/S interface.
CHAPTER 5

CONCLUSIONS

5.1 Major Findings

In this work, we used BEEM to study SiC samples containing double-stacking-fault 3C-SiC inclusions in a 4H-SiC matrix, where the inclusions intersect the sample surfaces in an as-grown cross-sectional geometry. We identified individual inclusions using BEEM imaging and characterized their electric properties using BEEM spectral measurements, which determine the local Schottky barrier heights over the inclusions and over bulk 4H-SiC. The inclusions were found to support 2D propagating quantum well states, and the 2D CBM estimated to be ~0.53±0.06 eV below the CBM of bulk 4H-SiC. This is consistent with prior speculations that cubic inclusions in 4H-SiC may behave like quantum wells due to the lower bandgap of 3C-SiC, and agrees with Iwata et al.’s calculation of the quantum well energy of this type of inclusions. Our survey of several hundred inclusions in the samples confirmed the finding through TEM measurements that inclusions in high-temperature-processed $n$-type 4H-SiC are all of this same double-stacking type ($i.e.$, all have the same quantum well energy of ~0.53±0.06 eV below 4H
CBM) except at one particular location where evidence of a lower quantum well energy was found, suggesting a wider inclusion. Also, our measurements of the apparent width of the enhanced BEEM stripes at the inclusion openings suggest the broadening of electron momentum distribution due to electron scattering in the metal film and at the metal film surfaces, which causes some electrons entering the metal away from directly above the inclusion openings to be able to enter the quantum well conduction band after scattering.

We have further surveyed Pt contact to electrically stressed 4H-SiC $pn$ diode using BEEM but were unable to locate any cubic inclusions due to their extremely low density in this type of samples. In the process of this attempt, we used BEEM to study the Schottky contact between Pt and $p$-type 4H-SiC, and observed a second transmission channel in the “hole BEEM” spectrum that suggests a split-off valence band at ~0.11 eV below the valence band maximum, which is larger than the calculated crystal-field splitting of 0.07 eV in 4H-SiC. Additionally, we compared the Schottky barrier height of Pt/$p$-type 4H-SiC contact to that of Pt/$n$-type 4H-SiC contact prepared under identical conditions, and considered the effect of image force lowering and the existence of an interfacial layer at Pt/4H-SiC contacts in order to explain the observed relationship between the $p$-type and $n$-type barrier heights and the bandgap of 4H-SiC.

We also performed BEEM measurements on Pt/GaN contacts (the GaN samples were Ga-face, grown using molecular beam epitaxy under Ga-rich condition) in order to look for evidence of negative charge along threading dislocations, as suggested by some prior measurements and calculations. However, we find no evidence of significant charge along the threading dislocations near the Pt/GaN interface. Our measurements
suggest an upper limit of $1/4 \, e^-/c$ on the density of dislocation charge near the interface in our samples. Considering the effect of depletion potential in the semiconductor, an electron acceptor level of $1 \, e^-/c$ along the dislocations in our samples should be no deeper than $1.3 \, \text{eV}$ below the CBM of GaN.

### 5.2 Future Directions

First, a few aspects of our results in the study of cubic inclusions in hexagonal SiC remain unanswered, as discussed in Chapter 4. There is sometimes (but not always) a second transmission channel in the BEEM spectra over the inclusions, which we do not understand why. The geometry of the inclusion opening may also have a small influence on the measured Schottky barrier height. Also, the effect of spontaneous polarization at the inclusion opening is also not yet known (further investigation of this issue may possibly lead to a direct measurement of the spontaneous polarization). These are open questions for future theoretical and experimental studies.

In our BEEM study of $p$-type Schottky contact on 4H-SiC, the measured second threshold does not completely agree with the theoretical value of crystal-field splitting of valence band in 4H-SiC. More considerations are needed in this issue.

On GaN, we observed possible evidence of piezoelectric effect around surface step boundaries. This is an interesting topic of further measurements and modeling.

The success of our BEEM measurements on a semiconductor quantum well heterostructure with an as-grown cross-sectional geometry suggests BEEM may be used to characterize manually cross-sectioned heterostructures. This is currently an on-going project in our group (the study of cleaved AlGaAs/GaAs/AlGaAs heterostructures).
Another on-going study in our group is the modeling of macroscopic $C-V$ curves on 4H-SiC samples containing cubic inclusions. $C-V$ measurements are known to generally reflect the overall properties of an M/S contact instead of being dominated by few low-barrier patches at the M/S interface, but $C-V$ data on our inclusion samples yielded similar barrier height as measured by BEEM or macroscopic diode $I-V$, suggesting the inclusions dominate the $C-V$ behavior of the Schottky contacts. This effect is explained in our modeling (to be published soon).
APPENDIX A

TIP-LOCKING ALGORITHM

Below we list the tip locking subroutine of the beem.bas program (see Ref. 88 for the main blocks of this program).

43000
' Measure an I-V curve ------------------------------------------
--
' check if the scan is local BEEM IV
IF xsize > 2 AND ysize > 2 THEN GOTO 43030
' Lock tip onto feature for BEEM IV
totalstep = 50 ' About 9 sec on P-133
xstep = 1
ystep = xstep
IF ysize = 2 THEN
  sign = -1
ELSE
  sign = 1
END IF
END IF
GOSUB 43050
extremez& = presentz&
extremex = xtipp
extremey = ytipp
DO
  lastz& = presentz&
xip = xtipp + xstep
  xvolt = XAtoV(xip)
  xvolt% = xvolt * 204.8
  xpiezv% = xvolt%: GOSUB 53100 ' x DAC update
  CALL dtwait(4,18932)
  IF escpress% = 1 THEN EXIT DO
xtipp = xip
GOSUB 43050
xflag = 1
IF (sign*lastz&) > (sign*presentz&) THEN
  xflag = -1

ELSE
    IF (sign*extremez&) < (sign*presentz&) THEN
        extremez& = presentz&
        extremex = xtipp
        extremey = ytipp
    END IF
END IF

xstep = xstep*xflag
lastz& = presentz&
yip = ytipp + ystep
yvolt = YAtoV(yip)
yvolt% = yvolt * 204.8
ypiezv% = yvolt%: GOSUB 53200 ' y DAC update
CALL dtwait(4,18932)
    IF escpress% = 1 THEN EXIT DO
ytipp = yip
GOSUB 43050
yflag = 1
    IF (sign*lastz&) > (sign*presentz&) THEN
        yflag = -1
    ELSE
        IF (sign*extremez&) < (sign*presentz&) THEN
            extremez& = presentz&
            extremex = xtipp
            extremey = ytipp
        END IF
    END IF
END IF

ystep = ystep*yflag
LOCATE 22, 11: PRINT SPACE$(50)
LOCATE 22, 11: PRINT "Tip @(";CINT(xtipp);",";CINT(ytipp);") A"
totalstep = totalstep - 1
    IF totalstep = 0 AND xflag + yflag <> 2 THEN totalstep = 1
LOOP WHILE totalstep > 0 AND escpress% = 0
escpress% = 0
    IF 0.95*(sign*extremez&) > (sign*presentz&) THEN
        xip = extremex
        xvolt = XAtoV(xip)
        xvolt% = xvolt * 204.8
        xpiezv% = xvolt%: GOSUB 53100 ' x DAC update
        CALL dtwait(4,18932)
        xtipp = xip
        yip = extremey
        yvolt = YAtoV(yip)
        yvolt% = yvolt * 204.8
        ypiezv% = yvolt%: GOSUB 53200 ' y DAC update
        CALL dtwait(4,18932)
        ytipp = maxy
        GOSUB 43050
        IF 0.95*(sign*extremez&) > (sign*presentz&) THEN GOSUB 43000
    END IF

update tip position table entries
xang = XVtoA(xvolt): yang = YVtoA(yvolt)
a$ = NFmt$(xang, 9, 2)
MID$(table$(2), 40, 9) = a$
\texttt{a$ = NFmt$(yang, 9, 2)} \\
\texttt{MID$(table$(2), 52, 9) = a$} \\
\texttt{LOCATE 2, 1: PRINT table$(2);} \\
\texttt{\ ' update scan center table entries} \\
\texttt{xscen = xang: yscen = yang} \\
\texttt{a$ = NFmt$(xscen, 9, 2)} \\
\texttt{MID$(table$(3), 40, 9) = a$} \\
\texttt{a$ = NFmt$(yscen, 9, 2)} \\
\texttt{MID$(table$(3), 52, 9) = a$} \\
\texttt{LOCATE 3, 1: PRINT table$(3);} \\
\texttt{CALL dtwait(4, 18932)} \\
\texttt{43030} \\
\texttt{CALL fdti(cpgrid%, ncurr\%)} \\
\texttt{\ ' write I-V curve data into file} \\
\texttt{CALL FSETLOC(ihandle%, 13\% + CLNG(curr\% \* 2 \* \(cpgrid\% + 2\))} \\
\texttt{CALL FWRITE(ihandle\%, VARPTR(ix\%), 2, byteswritten\%, ecode\%)} \\
\texttt{CALL FWRITE(ihandle\%, VARPTR(iy\%), 2, byteswritten\%, ecode\%)} \\
\texttt{CALL FWRITE(ihandle\%, VARPTR(ipgrid%(1)), 2 \* cpgrid\%, byteswritten\%, ecode\%)} \\
\texttt{CALL FSETLOC(ihandle%, 13\% + CLNG(curr\% + gridpts\%) \* 2 \* (cpgrid\% + 2))} \\
\texttt{CALL FWRITE(ihandle\%, VARPTR(ix\%), 2, byteswritten\%, ecode\%)} \\
\texttt{CALL FWRITE(ihandle\%, VARPTR(iy\%), 2, byteswritten\%, ecode\%)} \\
\texttt{CALL FWRITE(ihandle\%, VARPTR(ipgrid2%(1)), 2 \* cpgrid\%, byteswritten\%, ecode\%)} \\
\texttt{curr\% = curr\% + 1} \\
\texttt{GOSUB 52500 \ 'Display I-V if required.} \\
\texttt{RETURN} \\
\texttt{43050} \\
\texttt{SETTRG 0, 0} \\
\texttt{SETCLK 0, tDrate0\%, tDratel\%, 1} \\
\texttt{presentz\& = 0} \\
\texttt{IF xsize = 2 THEN} \\
\texttt{SETMUX chanmap\%(ichan\%)} \\
\texttt{FOR i\% = 1 TO nsamples\%} \\
\texttt{\ \ CALL dtwait(0,5)} \\
\texttt{\ \ ADCIN curr\%, 1} \\
\texttt{\ \ presentz\& = presentz\& + curr\%} \\
\texttt{\ \ NEXT i\%} \\
\texttt{ELSE} \\
\texttt{SETMUX chanmap\%(zchan\%)} \\
\texttt{FOR i\% = 1 TO nsamples\%} \\
\texttt{\ \ CALL dtwait(0,5)} \\
\texttt{\ \ ADCIN topo\%, 1} \\
\texttt{\ \ presentz\& = presentz\& - topo\%} \\
\texttt{\ \ NEXT i\%} \\
\texttt{END IF} \\
\texttt{RETURN}
APPENDIX B

CONVERSION OF BINARY DATA INTO TEXT FILE

Below we list the `getbeem.c` program as an example of STM/BEEM data conversion from binary to text.

```c
#define version "GETBEEM v1"
#include <stdio.h>
#include <stdlib.h>
#include <string.h>
#include <stddef.h>
#include <ctype.h>

int pixels, pagain, linecompt;
long ptnumber;
double factor=32768;
char infname[80], outfname[80];

int getword(FILE *fptr)
{
    unsigned int c;
    c=getc(fptr);
    c+=256*getc(fptr);
    return (c<32768)?c:c-65536;
}

void main()
{
    FILE *fi, *fo;
    int i, j;
```
printf("Input file name (w/o .dat): ");
scanf("%s", infname);
strcpy(outfname, infname);

strcat(infname, ".dat");

if((fi=fopen(infname,"rb"))==NULL)
{
    printf("\nREAD: Can't open file %s!\n\n",infname);
    return;
}
else
{
    strcat(outfname, ".beem");
    fo=fopen(outfname,"w");

    pixels=getword(fi);
    fseek(fi,10L,SEEK_CUR);
    pagain=getword(fi);
    factor/=pagain;
    linecompt=getword(fi);

    ptnumber=pixels*linecompt;
    fseek(fi,2L*ptnumber,SEEK_CUR);

    for(i=0; i<linecompt; i++)
    {
        for(j=1; j<pixels; j++)
            fprintf(fo, "\t", getword(fi)/factor);
        fprintf(fo, \n", getword(fi)/factor);
    }
    fclose(fi);
    fclose(fo);
    printf("BEEM data extracted successfully.");
}

LIST OF REFERENCES


[8] This can be calculated using the electronegativity of Si (1.8) and C (2.5) and Pauling’s empirical relationship: percent ionic character = 100% × (1 − e^−Δχ^2/4), where Δχ is the difference in electronegativity.


[38] H. Ott, Zeit. Krist. 61, 515 (1925); ibid. 62, 201 (1925); ibid. 63, 1 (1926).


D. E. Jones, *Ph. D. Thesis* (The Ohio State University, Columbus, 1997).


[111] H.-J. Im, Ph. D. Thesis (The Ohio State University, Columbus, 2001).