ELECTRONIC PROPERTIES OF STACKING-FAULT INDUCED HETEROSTRUCTURES IN SILICON CARBIDE STUDIED WITH BALLISTIC ELECTRON EMISSION MICROSCOPY

DISSERTATION

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* * * * *

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ABSTRACT

The electronic properties of stacking-fault (SF) induced inclusions in hexagonal silicon carbide (SiC) and the valence band structure of 3C- and 4H-SiC are studied using ultrahigh vacuum ballistic electron/hole emission microscopy (BEEM/BHEM). Our contribution to the denuded-zone formation in Si epitaxy on Si(001) is also presented.

In recent years, the SF inclusions with local 3C or 8H stacking sequence have been found to form in 4H- or 6H-SiC in various circumstances, which can be of concern in terms of device performance and reliability. We show that both 3C and 8H inclusions behave as electron quantum wells (QWs) by measuring local Schottky barrier heights (SBHs) on and away from inclusions with BEEM. The QW energy level of single SF 3C inclusions formed during 4H-SiC p-i-n diode operation is measured to be ~0.25 eV below the conduction band minimum (CBM) of 4H-SiC. In comparison, a deeper QW energy depth (~0.53 eV) was previously measured on double SF 3C inclusions formed in 4H-SiC during high-temperature processing. From the capacitance-voltage (C-V) measurements and electrostatic modeling on the 2SF sample, we show that free carrier charging of the inclusions in the bulk can reduce the C-V extracted SBH. The QW energy depth of the 8H inclusions formed during 4H-SiC epilayer growth is measured to be ~0.39 eV below 4H-SiC CBM. In addition, we observe the direct effect of the spontaneous polarization
difference between 8H- and 4H-SiC on local SBH, as well as the strong reflection of injected hot electrons from subsurface 8H inclusions.

The valence band maximum (VBM) of 3C-SiC is estimated to be \(~0.06\) eV lower than 4H-SiC using BHEM. No evidence of additional VBM in 3C-SiC supports that the second VBM observed in 4H-SiC is a crystal-field split VBM located \(~110\) meV below the highest VBM.

Our earlier study of the denuded-zone formation in Si epitaxy on Si(001) is also described. Both Monte Carlo simulation (small critical cluster) and the continuum model (large critical cluster) are used to investigate how the anisotropy of denuded zones along the fast and slow diffusion directions relates to the anisotropy of corresponding diffusion constants.
Dedicated to my family
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Now, I have come to the moment when I can look back at my graduate study at Ohio State, with a chance of expressing my deep appreciation to all good people for their tremendous help and support during the course.

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As someone says, the end of something means the start of another new thing. I am starting a new journey in the hope of better future.
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CHAPTER 1

OVERVIEW

In this work, ballistic electron/hole emission microscopy (BEEM/BHEM) is used in ultra-high vacuum (UHV) environment to study the electrical properties of stacking-fault (SF) induced heterostructures (composed of different structural polytypes) formed in the hexagonal silicon carbide (SiC) host and valence band structures of 3C- and 4H-SiC. The author’s contribution to an earlier project of the denuded-zone formation in Si epitaxy on Si(001) will be also presented.

SiC is one of the well-known wide band gap semiconductors which is particularly promising in power device application thanks to its superior electrical, thermal, and mechanical properties [1,2]. Hence there have been enormous research activities related to this material in recent years. SiC is known to crystallize in many different polytypes (more than 200) [3] due to its low stacking fault energy, and its energy band gap varies significantly depending on polytype [4-10]. This variety in crystal structure and corresponding electronic properties is very unique and interesting in fundamental science perspective, but it can raise an issue in stability and consistency of the devices based on SiC. In fact, stacking-fault-induced 3C (cubic) inclusions have been found to
spontaneously form during the operation of p-i-n diodes made from 4H- and 6H-SiC (the most common polytypes), and have been found to degrade forward-bias characteristics of the diodes [11,12]. Another type of 3C inclusions has been observed to form during high-temperature processing of heavily n-type doped 4H-SiC [13-16]. Several important steps in device fabrication are performed at high temperature and thus in this case the quality issue of device can stem from the fabrication stage. Very recently, it has been shown that SF inclusions (this time with an “8H” structure) can also form during 4H-SiC epilayer growth using chemical vapor deposition (CVD) [17,18], which can also affect the quality of devices fabricated from these epilayers.

BEEM is a variant of scanning tunneling microscopy (STM) invented by Kaiser and Bell in 1988 [19]. Hot carriers (electrons) are locally injected from the STM tip with adjustable energy and flux into the metal film, at the nanometer scale, allowing microscopic investigation of energy barriers at buried metal/semiconductor (or insulator) interfaces. BEEM can also be used to investigate conduction band structure of the underlying material system. BHEM is another version of BEEM that uses holes instead of electrons as the injected hot carriers [20]. In the similar fashion to BEEM, the energy barrier at the interface and valence band structure of the underlying semiconductor or insulator can be probed with BHEM.

Using these unique capabilities of BEEM, we characterized SF-induced 3C and 8H inclusions formed in hexagonal SiC where these inclusions are exposed on sample surface. The quantum well (QW) nature of the inclusions expected from the band structure dependence of SiC on polytype was confirmed. With BHEM, the theoretically
predicted difference of crystal-field splitting [4,7,8] in the valence band structures of 3C-
and 4H-SiC was demonstrated experimentally.

All BEEM/BHEM measurements together with macroscopic I-V and C-V measurements on the samples studied in this presented work have been performed in UHV STM/BEEM system equipped with an electron-beam evaporation subsystem developed mainly by Darrell Jones and Benjamin Kaczer, and later maintained and modified by Hseung Jai Im, Yi Ding and the author. The detailed information about the system can be found in the Ph.D theses of Darrell Jones and Benjamin Kaczer [21,22]. In our UHV system (base pressure: $\sim1\times10^{-10}$ Torr), the cleanliness of sample surface and evaporated metal films is ensured, which enables studying the samples for several months with high-quality and reliable results.

The results of our work and related background information are presented in the following way.

First, a brief review of the material properties of SiC with the focus on structural polytype, band structure, and spontaneous polarization (SP) is given in the beginning of chapter 2. Then the experimental observation of 3C and 8H inclusions in hexagonal SiC and the earlier theoretical and experimental studies on them done by other groups are introduced. The general information about metal/semiconductor contacts including the basic model of Schottky barrier formation and $I-V/C-V$ characteristics of the contact is provided in the last part of the chapter.

In chapter 3, the basic aspects of our main experimental technique BEEM/BHEM are first reviewed, and the equipment setups for BEEM/BHEM and other measurements
in UHV are depicted. The sample preparation and experimental procedures are also described, as well as data processing methods.

The results of our work on SiC samples are presented in chapter 4. The measurement results on two types (so-called “single” and “double” SF) of 3C inclusions are first presented. Our BEEM measurements on single SF (1SF) inclusions confirm their predicted QW behavior, with the QW energy depth of ~0.25 eV below the conduction band minimum (CBM) of 4H-SiC, and this compares with the QW energy (~0.53 eV) of double SF (2SF) inclusions measured previously by Yi Ding and the author. Macroscopic C-V measurements on 2SF inclusions are then discussed, which show that the existence of QWs in semiconductors with an inclined geometry with respect to the metal/semiconductor (M/S) interface produces a reduction in the C-V extracted Schottky barrier height (SBH). It is then discussed how the QW energy in the bulk can in fact be estimated from the C-V curves in conjunction with finite-element electrostatic modeling.

The BEEM measurements on samples with in-grown 8H inclusions are then presented, which show that these are also QWs, with the QW energy of ~0.39 eV below 4H-SiC CBM. On the 8H inclusion sample, we additionally made two interesting observations. One is the increase of BEEM-measured SBH on one side of inclusions on surface where remnants of 8H inclusions exist. This is very likely the effect of the SP difference between the inclusion remnant and the 4H-SiC host. The other observation is the (apparent) strong reflection of hot electrons from subsurface inclusions, which significantly suppresses the BEEM current amplitude on one side of the inclusion close to the location where it intersects the sample surface. The valence band offset of 3C- and
4H-SiC is measured to be ~0.06 eV with the valence band maximum (VBM) of 3C-SiC lower than 4H-SiC using BHEM. The BHEM spectra on p-type 3C-SiC shows no evidence of an additional VBM, indicating that the second VBM observed on 4H-SiC is a crystal-field split band.

Chapter 5 contains the Monte Carlo simulations (small critical cluster) and continuum model (large critical cluster) describing the formation of denuded zones in Si homoepitaxy on Si(001) exhibiting adparticle diffusion anisotropy. The ratio of denuded zones along the fast and slow diffusion directions is found to scale with the ratio of corresponding diffusion constants with a power of 1/2, quite differently from the earlier prediction of the power between 1/6 and 1/4. A comparison of this modeling with experiments indicates that diffusion on Si(001) remains highly anisotropic at least up to ~700 °C.

Finally, the summary of our findings is given in chapter 6 together with a discussion of possible future directions.
CHAPTER 2

INTRODUCTION

2.1 Silicon Carbide (SiC)

The recent great increase of research efforts on wide band gap semiconductor materials such as silicon carbide (SiC), gallium nitride (GaN), and diamond (C) was initiated by their superior material properties, which makes them desirable for various advanced electronic and opto-electronic devices [1,2].

Among them, SiC is currently under extensive theoretical and experimental studies aimed at developing high voltage, high power, and high frequency electronic devices, which take advantage of its high breakdown electric field and high carrier saturation speed. SiC is particularly attractive in power device application where it is crucial to dissipate the heat generated during device operation efficiently, thanks to its excellent thermal conductivity (more than three times of Si and GaAs [23]). Additionally, the large band gap, mechanical strength, and chemical stability of SiC make it considered as a good candidate material for the electronic devices operating at very high temperature and in harsh conditions with severe radiation.
Besides its great potential in device application, the material properties of SiC are themselves very interesting in fundamental physics viewpoints. SiC can crystallize in many different structures (polytypes) [3] and its electronic properties vary substantially depending on polytype. This aspect has very recently attracted a lot of attention with relation to the formation of planar stacking fault (SF) inclusions in hexagonal SiC which were proposed to behave as *self-forming electron* quantum wells (QWs) due to the unique characteristics of SiC in energy band structure.

This subchapter is dedicated to reviewing the overall material properties of SiC. The polytypism of SiC will first be introduced, and the electronic energy band structure depending on polytype will then be presented in detail. Finally, the spontaneous polarization (SP) in the hexagonal polytypes of SiC will be addressed.

### 2.1.1 Structural Polytypes

*Polymorphism* represents the phenomenon that a substance crystallizes in more than one structure. *Polytypism* is its one-dimensional variant where only the stacking sequence of the basic structural unit (called “basis”) along one direction is different [3]. SiC is in fact the material in which *Polytypism* was first discovered and more than 200 polytypes of SiC have been reported up to now [24]. In the case of SiC, the basis is the Si-C bilayer with Si and C atoms separated by 1.89 Å [3]. The Si-C pairs in one bilayer (often referred to as the basal plane) form the hexagonal close-packed structure such as Figure 2.1(a). The crystal structure of SiC is actually found to be three-dimensional close-packing [3]. In this case, there are two equivalent ways to stack one hexagonal basal plane on top of another one. Suppose that the Si-C pairs in the first basal plane
Figure 2.1: (a) Basal plane (A) of hexagonal closed-packed structure with the possible stacking sites (B or C) of the adjacent layers and hexagonal coordinates indicated, (b) possible choices of stacking hexagonal planes along c-axis, and (c) tetrahedral bonding (solid black lines) of Si to the nearest four C atoms (black circles).
occupy the sites depicted as “A” in Figure 2.1(b) where Si atom is drawn to be larger than C atom since Si-C bond is expected to be more covalent (10 to 12 % ionic) [3]. Then, in the second basal plane, they can occupy either “B” or “C” sites to be close-packed along the stacking direction. If “B” sites are here occupied, then Si-C pairs in the third basal plane can occupy either “A” or “C” sites (A sites are occupied in the figure), etc. Accordingly, by stacking Si-C bilayers continuously by following this rule, it is possible to have an infinite number of different stacking sequences of basal planes, each resulting in a different crystal structure. In this type of three-dimensional close-packed structure, a Si atom is bonded to the nearest four C atoms tetrahedrally and vice versa [Figure 2.1(c)].

One extreme case in the basal plane (Si-C bilayer) stacking is the one where the stacking sequence is …(ABC)(ABC)… in the classical ABC notation, such as in Figure 2.2(a). The triangle in stacking sequence shown in the figure represent the projection of the tetrahedron composed of one Si atom (centered, black open circle) and four nearest-neighbor C atoms (black closed circle) on the (0211) plane. The central Si atom and two C atoms [the upper and right sides of the Si atom in Figure 2.2(a)] are in fact in the (0211) plane. The other two C atoms are located away from the (0211) plane on both sides by the half of the smallest lattice vector in the hexagonal basal plane [see Figure 2.1(a)], and the black closed circle depicted with a shorter bond (solid black line) length to the Si atom [the left side from the Si atom in Figure 2.2(a)] represent the projection of these two C atoms on the plane. The crystal structure with this …(ABC)… stacking sequence is found to be pure cubic, i.e., a zinc-blende structure consisting of two interpenetrating face-centered (fcc) cubic lattices. This polytype is usually named 3C.
Figure 2.2: Stacking sequences of Si-C bilayers and unit cells with atom distribution indicated of (a) 3C- and (b) 2H-SiC. The triangles in stacking sequence represent the projection of tetrahedra on $\{11\overline{2}0\}$ plane. The figures on lower right corner in (a) and (b) show the bond orientation seen in the c-axis direction for both polytypes.
following the Ramsdell notation [25] where the front number represent the number of layers in the unit cell and the following letter specifies the lattice type (C: cubic, H: hexagonal, R: rhombohedral). It is sometimes called $\beta$-SiC because of its similarity with $\beta$-ZnS (zinc sulfide) that originated the name of “zinc-blende”. This 3C polytype can also be denoted as $+++$ in the Hägg notation [26] describing a polytype by specifying the relationship between successive layers, \textit{i.e.}, cyclic stackings (AB, BC, and CA) denoted with the $+$ sign and anticyclic stackings (AC, CB, and BA) with the $-$ sign. The unit cell of 3C-SiC is shown with the distribution of the Si and C atoms inside it in Figure 2.2(a). The stacking direction of the basal planes perpendicular to the planes is in fact [111] direction of the cubic unit cell of 3C-SiC as indicated in the figure.

Another extreme case in the stacking is when the stacking sequence is …(AB)(AB)… illustrated in Figure 2.2(b), inducing a pure hexagonal wurtzite structure. This polytype is labeled 2H in the Ramsdell notation and $+-+$ in the Hägg notation. Its unit cell and the distribution of the base atoms are represented in Figure 2.2(b). One difference of pure cubic (3C) and hexagonal (2H) stackings is the relative orientation of the respective bonds of Si and C atoms in a bilayer to C and Si atoms in the adjacent layers. In the cubic stacking, the bonds are staggered when they are seen from the stacking direction while the bonds in the hexagonal stacking are eclipsed, as illustrated in Figure 2.2(a) and 2.2(b) [5].

Other polytypes are essentially combinations of the cubic and hexagonal stackings. Except completely disordered stackings, they have either hexagonal or rhombohedral symmetries with \textit{n} number of Si-C bilayers in the unit cells. All these polytypes have
Figure 2.3: The stacking sequences of several polytypes. 4H and 6H are most common polytypes.
higher periodicity (more Si-C bilayers) along the c-axis than 2H-SiC and they are in general called \( \alpha \)-SiC together with 2H-SiC. Figure 2.3 shows the stacking sequences of several ones among these polytypes projected in the \((1\bar{1}20)\) plane. 4H- and 6H-SiC are the most common polytypes, and single crystal wafers of these polytypes are currently available and hence all recent research for making commercial devices out of SiC are focused on these polytypes. The stacking sequence of 4H-SiC is written as …(ABCB)(ABCB)… and that of 6H-SiC is …(ABCACB)(ABCACB)…. The corresponding Hägg notations are \(+ + - -\) for 4H and \(+ + + - - -\) for 6H respectively. 15R-SiC is also fairly common and has the stacking sequence of …(ABCBACABACBCACB)…. A substantial amount of information about its material properties has been investigated. The Hägg notation for 15R is written as \((+ + - - -)\), in which the subscript is used to represent that the basic unit, \(+ + - - -\) has to be repeated three times to complete the unit cell.

Since the SiC polytypes are mixtures of cubic and hexagonal stackings, a quantity defined as the hexagonality \( H \) representing the fraction of hexagonal stackings out of all the stackings (cubic + hexagonal) in a polytype is used frequently to describe how much the polytype is cubic-like or hexagonal-like in structural sense [5]. For instance, 4H-SiC has the hexagonality of 50 % and 6H-SiC has 33%. As is obvious from the definition, the hexagonality of 2H-SiC is 100 % and that of 3C-SiC is 0 %. It is naturally expected that a polytype with a smaller \( H \) should be closer to 3C, i.e., more cubic-like than one with a larger \( H \) in other material properties as well as in structure, and this is generally true for most of the polytypes.
2.1.2 Electronic Band Structure of Polytypes

The material characteristics of SiC in structural, mechanical, thermal, and electrical aspects have been described in great detail and compared well with other materials in several references [27-32]. In this section, the electronic band structures of the SiC polytypes will be mainly discussed since they are the key physical substances together with the polytypism of SiC itself underlying the experimental observations and measurements for the SiC sample systems addressed in this work.

The band gaps of several common polytypes of SiC have been measured carefully by Choyke et al. from the optical absorption or luminescence spectra of the polytypes [9,10]. The measured band gaps range widely from 2.390 eV for 3C-SiC to 3.330 eV for 2H-SiC. Those for 4H- and 6H-SiC which are in between the two extreme cases in structure are measured to be 3.265 eV and 3.023 eV respectively. The first-principle calculations of band structures of several polytypes of SiC also have been carried out by many groups [4-8]. The calculated band gaps in fact vary somewhat considerably depending on the calculation method (For instance, density functional theory with the local density approximation is known to underestimate band gaps.). But the overall band structures are very similar from all the calculations. According to the calculations and the experimental supports, the band gaps of SiC polytypes are indirect. This means that the conduction band minimum (CBM) of each polytype occurs at non-zero crystal momentum, shifted with respect to the valence band maximum (VBM) that occurs at the Brillouin zone (BZ) center.
Figure 2.4: First Brillouin zones of (a) fcc (cubic), (b) hexagonal, and (c) rhombohedral lattices with high symmetry points marked.
Figure 2.4 shows the BZs of cubic, hexagonal, and rhombohedral polytypes with high symmetry points marked. The global CBM of 3C-SiC is found to occur at the $X$ point [Figure 2.4(a)], implying that the number of equivalent CBMs is three [9,33]. In the case of 2H-SiC, the CBM is at the $K$ point with two equivalent CBMs [8,10], while 4H-SiC has its CBM at the $M$ point giving three equivalent CBMs [8,34-36] [Figure 2.4(b)]. For 6H-SiC, the theoretical calculations predict the conduction band supplying the global CBM to be very flat along the $ML$ line and the CBM resides at some place on the line, resulting in six equivalent CBMs [8,37]. This has been confirmed experimentally from the Raman scattering measurement by Colwell et al. [38]. However, the exact location of the CBM and the detailed shape of conduction band affecting the determination of effective electron mass are not yet well-established, either experimentally or theoretically. In 15R-SiC, the CBM is located at the $X$ point [Figure 2.4(c)] and the number of equivalent CBMs is six as in 6H-SiC [39].

Another interesting point to note in the conduction band structures of SiC polytypes is the location of second CBM. According to the calculation done by Persson et al. [8], the second CBM of 3C-SiC is at the same symmetry point ($X$) as the first one with 2.92 eV higher energy and this was confirmed experimentally from optical absorption measurements with slightly larger energy difference (~3.1 eV) between the two minima [40]. Persson et al.’s calculations also show that the three hexagonal polytypes (2H, 4H, 6H) have their second CBMs located at the $M$ point and the energy difference between the first and second CBMs is 0.60 eV for 2H, 0.122 eV for 4H, and 1.16 eV for 6H respectively. The energy position of the second CBM in 4H-SiC has been probed
experimentally by BEEM [41-43] and optical phonon spectra measurements [27,44], with measured energy that ranges 0.10 – 0.14 eV above the first CBM. In the case of 15R-SiC, the second CBM is calculated to be located at the $L$ point, at ~0.50 eV higher than the first, and its existence and separation from the first CBM were confirmed experimentally with BEEM measurements [43].

The valence band maximum (VBM) is located at the BZ center (the $\Gamma$ point) for all polytypes. Interestingly, it is predicted theoretically that the offsets of VBMs among different polytypes are quite small, at most 0.10-0.13 eV for the case of 2H and 3C [6,7]. In other words, the VBMs of all polytypes are similarly located in energy. This means that the considerable variation of band gap for different polytypes is mainly due to the difference of CBM location. The previous n-type SBH measurements on 4H-, 6H-, and 15R-SiC with BEEM support this aspect [41-43], as will be discussed in more detail in subchapter 4.5. The spin-orbit splitting in valence band structure is calculated to be small, for example, 14.5 meV for 3C and around 9 meV for 2H, 4H, and 6H by Persson et al. [8]. In fact, the spin-orbit splitting of 3C has been measured experimentally to be even smaller (10 meV) [45,46]. For hexagonal polytypes, there is additional energy splitting caused by the crystal field and it has been calculated by several groups [4,7,8]. The crystal-field splitting is largest for 2H-SiC with the calculated range of 97-160 meV and it decreases somewhat linearly as the hexagonality decreases (56-130 meV for 4H-SiC and 21-53 meV for 6H-SiC). The existence and location of crystal-field split band of 4H-SiC were confirmed by BHEM measurements [47] (see subchapter 4.5), however there has been no experimental evidence for the hexagonality dependence of the crystal-field
### (a)

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\( a \sqrt{m_{\parallel MG} m_{\parallel MK} = 0.42 \text{ (Geometric average is measured experimentally.)}} \) [49]}

### (b)

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<td>1.54</td>
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<tr>
<td>( m_{\perp} )</td>
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<td>15R-SiC</td>
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</tr>
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<td>1.56</td>
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</tr>
<tr>
<td>( m_{\perp} )</td>
<td>0.61</td>
<td>0.61</td>
<td>1.59</td>
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</table>

Table 2.1: Effective (a) electron and (b) hole masses of several SiC polytypes in units of the free electron mass \( m_0 \). Both theoretically calculated and experimentally measured values are listed with the corresponding references. In (b), the second VBM is the spin-orbit split band and the third one the crystal-field split band.
splitting.

The effective electron masses of 3C- and 4H-SiC have been measured experimentally and reported by several groups, and they agree quite well with the theoretically calculated values [33,48]. For 6H-SiC, only the longitudinal effective mass along the c-axis has been measured [49], but due to the peculiar band shape along the direction there is still a large inconsistency between the measured value and the calculated ones, even among the values calculated theoretically by different groups [8,36,50,51]. The effective electron masses of 2H-SiC also have been calculated theoretically [8,36] but no experimental measurements have been reported yet. The effective hole masses of several representative SiC polytypes have been calculated theoretically [5,8]. However, only the hole effective masses of 4H-SiC have been measured experimentally and reported by Son et al. recently [52]. Table 2.1 lists the calculated and measured effective electron/hole masses of 3C-, 2H-, 4H-, 6H-, and 15R-SiC. For the calculated values, the effective electron masses at the second CBM and the effective hole masses at the spin-orbit and crystal field split VBM are also listed.

2.1.3 Spontaneous Polarization in Hexagonal SiC

Due to the crystal symmetry, it is known that the four tetrahedral bonds of any given atom (Si or C) in 3C-SiC (zinc blende) are equivalent and hence there is no “pile-up” of valence electrons inside the crystal, resulting in no spontaneous polarization [54,55]. However, other polytypes with hexagonal turns in stacking sequence do not have cubic symmetry. For these polytypes, the longitudinal bond along the c-axis (L-bond) can be different from the other three transverse bonds (T-bonds), and bond-to-bond charge
transfer is allowed between the two types of bonds, giving rise to structural relaxation and spontaneous polarization (SP) [54,55]. The spontaneous polarization of a material in fact results from both charge density redistribution and ionic relaxation.

Qteish *et al.* have performed self-consistent pseudopotential calculations of the charge density redistribution of 2H-, 6H-, and 8H-SiC, and have shown that there is a flow of electrons from the $L$-bond to the $T$-bonds at an isolated hexagonal stacking, which causes the pile-up of holes on one side and electrons on the other side from the $T$-bonds and creates an electric dipole layer localized across the $T$-bonds as illustrated in Figure 2.5 [54]. We note in the figure that the direction of the electric dipole layer, which produces the SP of a hexagonal polytype, is opposite to the c-axis. According to their calculations, the SP of 2H-, 6H-, and 8H-SiC is $3.33 \times 10^{-2}$, $9.49 \times 10^{-3}$, and $6.91 \times 10^{-3}$ C/m$^2$ respectively without considering the ionic relaxation, and it varies almost linearly with hexagonality. For the SP of 2H-SiC, the calculated value is a bit larger than the one ($2.80 \times 10^{-2}$ C/m$^2$) extrapolated from the values of 6H- and 8H-SiC assuming the linear dependence on hexagonality and this is believed to be due to the dipole-dipole interaction between adjacent dipole layers which will be strongest in 2H-SiC. Qteish *et al.* have also calculated the SP of 2H-SiC when the ionic relaxation is considered and the calculated value is $4.32 \times 10^{-2}$ C/m$^2$, about 30% larger than in the unrelaxed configuration.

To date, there has been no theoretical calculation of the SP of 4H-SiC and hence only the value interpolated based on the calculations for 2H-, 6H-, and 8H-SiC can be used as an estimate. For the relaxed 4H-SiC, the estimated value is $\sim 1.6-1.7 \times 10^{-2}$ C/m$^2$ (see Ref. 32). Recently, Bai *et al.* have reported the SP of 4H-SiC to be $\sim 1.1 \times 10^{-2}$ C/m$^2$,
based on their low-temperature photoluminescence measurements of 4H-SiC with thin 3C (thirteen bilayers) inclusions embedded, and by considering the SP difference between 3C- and 4H-SiC [56]. This measured value will be used in the following analysis of experimental data and modeling.

Figure 2.5: The dipole layer across the $T$-bond resulting from the electron transfer between $L$- and $T$-bond at a hexagonal turn in Si-C bilayer stacking. For simplicity, only the Si-C bond chains along the stacking direction are shown.

2.2 Stacking Fault (SF) Inclusion Quantum Wells (QWs) in SiC

The enormous structural variety of SiC (polytypes) is mainly the consequence of the very low energy necessary to locally change the stacking sequence in any of its polytypes. For example, the stacking fault (SF) formation energies in 4H- and 6H-SiC are measured to be 15 and 3 mJ/m$^2$, respectively, which is significantly lower compared with the corresponding SF formation energies of Si (55 mJ/m$^2$) and GaAs (45 mJ/m$^2$) [57,58]. Recently, it has been found that thin planar inclusions can be formed and propagated through the material spontaneously in 4H- and 6H-SiC polytypes where the planar inclusions have a local stacking sequence along the c-axis that is different from the host
materials. These SF inclusions can be driven by electrical stressing (high-current device operation) [11,12], thermal stressing (high-temperature annealing) [13-16], or can form during epilayer growth [17,18], with a particular stacking sequence for each process. Their formation is believed to be possible due to the low stacking fault energy of SiC.

In addition to the interests in the structural sense, these SF inclusions are also very interesting in terms of electronic properties since they are expected to behave as conduction band electron quantum wells due to the unique polytype-dependence of the electronic band structure of SiC. This expected behavior of the SF inclusions is indeed confirmed experimentally in this work.

2.2.1 3C inclusions in 4H- and 6H-SiC

The first discovery of the spontaneous development of basal plane SF inclusions was made during high forward-current operation of the p-i-n diodes fabricated with 4H-SiC for high-voltage switching applications. The SF development was revealed as so-called “forward voltage drift”, i.e., the voltage required for flowing a given forward-bias current increases during device operation. This voltage drift is very undesirable in terms of device reliability, as it represents degradation of the diode device quality. The initial notion of this phenomenon was given by Konstantinov and Bleichner in 1997 who reported the observation of “bright line defects” in their electroluminescence measurements of 4H- and 6H-SiC p-i-n diodes [11], and it came into everyone’s attention by the presentation given by Lendenmann et al. at the European Conference of Silicon Carbide and Related Materials in 2000 which showed the effect of these defects on the long term stability of 4H-SiC p-i-n diodes [12].
The SF inclusions formed this way are found to reside in the basal plane and have local cubic (3C) stacking sequences along the c-axis that is different from the surrounding hexagonal stacking. It was argued/demonstrated that these SF inclusions are created by the glide of single Schockley type partial dislocations, in which the part of the crystal above the shear plane is rigidly shifted with respect to the part below the shear plane. Accordingly, these SF inclusions are commonly named “single” SF (1SF) 3C inclusions. As indicated in Figure 2.6(a), a perfect basal plane dislocation with Burgers vector \( \vec{b} = (1/3)(1\bar{2}0) \) can dissociate into two partial dislocations with Burgers vectors of \((1/3)(0\bar{1}0)\) and \((1/3)(0\bar{1}0)\) respectively, and the propagation (glide) of these partials can induce the planar SF inclusions [60]. The schematic drawing illustrating this mechanism well can be found in Ref. 32. In the 4H-SiC case, such a process can produce two different types of stacking sequences by a single shear, which can be denoted as \((22) \rightarrow (13)\) and \((22) \rightarrow (31)\) in Zhdanov’s notation [61] [see Figure 2.6(b)]. However, all 1SF inclusions that have been experimentally observed in electrically stressed 4H-SiC p-i-n diodes were found to be induced by the (31) transformation by analyzing the actual stacking sequence of atoms with high-resolution transmission electron microscopy (TEM) [62,63]. The theoretical calculations of SF formation energy performed by Iwata et al. showed that the fault formation energy of (31) transformation \( E_{(31)}^{4H} = 17.7 \text{ mJ/m}^2 \) is slightly smaller than (13) transformation \( E_{(13)}^{4H} = 18.1 \text{ mJ/m}^2 \) [64], and this is thought to explain the experimentally observed preference of (31) transformation. In the 6H-SiC case, there are three possible Shockley-type faulted stacking sequences which can be
Figure 2.6: (a) The dissociation of a perfect basal plane dislocation into two partial dislocations. (b) The configuration of single [(13), (31)] and double [(62)] Schockley type stacking faults in 4H-SiC. The red-dotted lines represent the slip planes.
Figure 2.7: The configuration of three single Schockley type stacking faults in 6H-SiC. The red-dotted lines represent the slip planes.
denoted as (24), (42), and (1113) (Figure 2.7). Similarly to 4H-SiC case, all SF inclusions observed experimentally in degraded 6H-SiC p-i-n diodes show only the (42) type of stacking sequence. Consistently with the 4H-SiC case, this observation can also be understood based on the differences in the calculated SF formation energies of the three types of transformation, i.e., \( E_{(42)}^{6H} = 3.1 \text{ mJ/m}^2 \), \( E_{(24)}^{6H} = 3.4 \text{ mJ/m}^2 \), and \( E_{(1113)}^{6H} = 40.1 \text{ mJ/m}^2 \) [64].

Soon after the 1SF 3C inclusions were discovered, similar (Schockley type) SF 3C inclusions were also found in heavily n-type doped 4H-SiC substrates or epilayer films during high temperature processing (either thermal oxidation in dry oxygen or annealing in argon ambient [13-16]). In this case, the 3C inclusions were induced by double SFs (2SFs) with an additional shear occurring on the plane right next to the faulted plane of the (31) transformation in the single SF case [Figure 2.6(b)]. This is denoted as a (62) transformation in Zhdanov’s notation and results in wider inclusions with local cubic stacking. Brillson et al. showed that the formation of these 2SF 3C inclusions is strongly doping- and temperature-dependent, appearing only in highly n-type doped 4H-SiC with a doping range of \( 4 \times 10^{17} \text{ cm}^{-3} \) to \( 1.7 \times 10^{19} \text{ cm}^{-3} \) and at temperatures larger than 800 °C [14]. They showed this by measuring the cathodoluminescence of n- (N) and p-type (Al) 4H-SiC epilayers that were dry-oxidized or annealed in argon ambient [14]. The doping dependence of the 2SF formation was also shown by Skromme et al. but they observed that the faults formed in the regions where the substrate doping was greater than \( 1.9 \times 10^{19} \text{ cm}^{-3} \), while the regions with smaller substrate doping remained SF-free after thermal dry-oxidation [15]. Interestingly, the
fault formation energy necessary to shear a second layer inducing the double SF (62) in 4H-SiC is calculated to be much smaller (4.5 mJ/m²) than for shearing the first layer (17.7 mJ/m²) [64]. Similarly to the single SF case, this low fault energy for the additional SF could explain the preference for the formation of double SFs in heavily n-type doped 4H-SiC.

**Stacking Fault Growth Mechanism**

Together with the structural analysis of the single and double SFs, the mechanism of the spontaneous growth of these SFs is another important issue to be addressed. This issue is composed of two main questions. The first is what activates the motion of the partial dislocations bounding the faulted area. The second is what kind of driving force actually leads the expansion of the faulted area by lowering the total system energy.

According to the mechanical deformation rate study by P. Pirouz et al., the activation energy for partial dislocation glide in SiC is of the order of 2.5 eV [65]. As described previously, the double SFs are found to be formed at high temperatures and thus it is quite likely that the much enhanced lattice vibrations (phonons) compared with room temperature may be the source of motion of the bounding partial dislocations in this case. On the other hand, the single SFs are formed at room temperature and hence it is unlikely that the partial dislocation motion can be activated directly by thermal lattice vibrations. Also very interestingly the activation barrier for partial dislocation glide under electrical stress of 4H-SiC p-i-n diodes was measured to be ~0.27 eV [66], which is about 2.2 eV lower than the pure thermal activation energy [65]. Blumenau et al. have calculated the energy states associated with Si- and C-terminated partials in 3C- and 2H-SiC using
density functional tight-binding methods [67,68], and they have found that only Si-terminated partials should be electrically active by inducing states in the gap at an energy 0.4 eV above the top of the valence band. Accordingly it has been proposed that the excess energy from the non-radiative part of electron transition from the allowed energy states (QW states) in the SF inclusion to the gap states of the Si-core partials (recombination) are converted into phonons and these phonons can serve to activate the dislocation motion. It is therefore expected that the partial dislocations leading the growth of faulted area are the Si-terminated partials in the 1SF case. The part of the activation energy provided by electron-hole recombination process is estimated to be ~2.2 eV based on the measured pure thermal activation energy (~2.5 eV) and activation energy under electrical stress (~0.27 eV).

Dislocation motion is usually related to mechanical stress and thus the shear stress due to the doping difference between the substrate and the epilayer was naturally considered initially as the driving force of the fault expansion for both single and double SFs [11,62,69,70]. However, Ha et al. explicitly showed that the mechanical stress is not a possible driving force in the case of single SFs formed in p-i-n diodes, based on their observation that the faults form in the diodes fabricated on (1120)-oriented wafers as easily as on (0001)-oriented wafers [63]. The shear stress resolved in the basal plane is proportional to \( \sin(2\alpha) \) where \( \alpha \) is the sample miscut angle and it should then be very small (approaching zero) in (1120) orientation as compared with the (0001) orientation. Chung et al. reported that the dislocations observed at the epilayer/substrate interface in their annealed (in argon ambient) 4H-SiC samples with a large doping difference between
the epilayer and substrate (>10 times) have the opposite signs of Burgers vectors, sometimes only in 80 nm. If the shear stress is the driving force, this observation indicates that the shear stress reverses its direction over such a small distance, which is very unlikely to happen. Therefore, this is another experimental evidence that excludes the mechanical stress as a possible driving force for SF expansion [71]. Besides mechanical stress, the other possibility to be considered as the driving force is electronic stress, the main idea of which is that the energy provided by conduction electrons falling into the (lower-energy) QW states in the SF inclusions can lower the system energy by more than the energy cost to extend the SF [72]. Kuhr et al. have calculated the energy gain obtained from adding a SF to the system, including the consideration of the repulsive potential in the space-charge region built up by the electrons trapped inside the inclusion QWs, which limits further trapping of electrons in the QWs [73]. According to their calculations, the system energy is indeed lowered with a SF added in the double SF case, mainly due to the deep QW energy level. However, their calculations indicated that no energy gain resulted from SF formation in the single SF case, since the QW energy level in this case is expected to be much shallower than in the 2SF inclusions. On the other hand, the very recent first-principle calculation done by Lambrecht et al. showed that the repulsive potential adjacent to the QWs is strongly reduced by self-consistent screening by the trapped electrons themselves, resulting in a small net energy gain of a few meV per SiC unit for the single SF case [74]. The energy gain for the double SFs was calculated to be an order of magnitude larger than the single SFs. Although the net energy gain for the single SFs is quite small, Lambrecht et al. pointed out that it may be
enhanced by a dynamic quasi Fermi level in a nonequilibrium situation with current flow (the actual environment for 1SF formation), which may exceed the equilibrium Fermi level. This calculation indicates that the electronic stress is still a possible driving force for single SFs.

**QW Behavior and QW Width of SF 3C Inclusions**

As pointed out earlier in this subchapter, these single and double SF inclusions with local 3C stackings are expected to behave as electron QWs due to the large conduction band offset (CBO) between 3C and the surrounding 4H (or 6H) polytypes. Hereafter we will focus on the 3C inclusions in 4H-SiC since most of the experimental characterizations for 3C inclusions up to now have been on the material systems with 4H-SiC as the host. The QW nature of the 3C inclusions has indeed been indicated experimentally by luminescence measurements on faulted materials, which showed spectral peaks with a binding energy lower than the 4H-SiC band gap. Sridhara et al. observed a set of peaks in their photoluminescence spectrum of an electrically stressed 4H-SiC $p$-$i$-$n$ diode containing the 1SF 3C inclusions, which are absent in the spectrum of unstressed diodes [75]. They assumed these peaks to be due to recombination in QWs, and using the temperature dependence of the peak amplitude, they estimated the QW energy depth in the inclusion to be $\sim 0.282$ eV below 4H-SiC CBM. Skromme et al. observed a photoluminescence peak at 2.42 eV on a 4H-SiC sample with 2SF 3C inclusions [15] and Okojie et al. observed a 2.5 eV peak in the cathodoluminescence spectrum on the same type of 4H sample [13], both of which are lower in energy.
compared with the band edge peak of 4H-SiC (3.22 eV). These authors also argued that these red-shifted peaks were evidence that 2SF 3C inclusions behaved as electron QWs.

The QW behavior of the 3C inclusions was also predicted by first-principle band structure calculations. Miao et al. calculated a split-off conduction band ~0.2-0.3 eV below the 4H-SiC CBM that is quite localized in the 1SF 3C inclusions [72]. Iwata et al. have also found in their calculations similar localized split-off bands in both single and double SF 3C inclusions [76]. The split-off band energy of the 1SF (31) was calculated to be 0.22 eV and that of the 2SF (62) to be 0.597 eV below the 4H-SiC CBM.

Figure 2.8: The width of single and double SF cubic (3C) inclusions based on the SP difference of 3C- and 4H-SiC. The green-dotted ellipses represent the electric dipole layers at hexagonal turns in stacking.
In order to consider the SF 3C inclusions as QW systems embedded in the 4H-SiC host, and to use simple particle-in-a-box quantum-mechanical calculations to estimate the QW energy sub-bands in the inclusions, we need to define the width of the 3C inclusions properly since the quantum confinement effect determining the QW energy levels are very sensitive to the assumed well width. In a purely structural sense, 1SF 3C inclusions appear to have three successive cubic stackings of a Si-C bilayer (+++ in the Hägg notation) and thus would appear to have a thickness of ~7.5 Å. In the same fashion, the width of 2SF 3C inclusions would appear to consist of six Si-C bilayers, and hence to be 15 Å thick. However, if we follow the proposal of Qteish et al. and Iwata et al. [54,64] and use the difference in spontaneous polarization between 3C- and 4H-SiC to determine the boundary of the QWs, then 1SF inclusions appear to have a thickness of ~5.0 Å corresponding to two consecutive cubic stackings of a Si-C bilayer, which are bounded by a hexagonal turn on both sides (see Figure 2.8). Using similar reasoning, 2SF inclusions would appear to have a thickness of ~12.5 Å (five bilayers – see Figure 2.8). Since the QW energy levels in the inclusions are determined by the potential energy profile which is in this case conduction band profile, it seems more plausible to define the boundary of the 3C portion and the 4H host based on their electrical properties rather than just their structural properties. Therefore, in this work, the definition of the QW width based on the difference of spontaneous polarization will be adopted.
2.2.2 8H Inclusions in 4H-SiC

Very recently (in 2005), another Schockley type of SF inclusions has been reported to form in the 4H-SiC epilayer grown on 8º off-cut 4H-SiC (0001) substrates using chemical vapor deposition (CVD) by Izumi et al. [17]. They showed that these SFs reside in the basal plane and have right-triangle shapes based on the molten KOH etched features on the sample surface [17]. The molten KOH etching decorates dislocations intersecting the surface. The right-triangle shape of the SF was also shown in the PL mapping image which represents the enhanced luminescence from the SF at a photon wavelength of 467 nm. According to their high-resolution TEM measurements, these SFs are found to be composed of one complete unit of 8H (44) structure (Figure 2.9). By considering the size of the triangle observed on the surface and the 8º sample off-cut, the SFs were found to be formed initially near the interface between the substrate and epilayer and grow during epilayer growth. In this sense, these SFs are termed “in-grown” SFs. Immediately following the Izumi et al. report, Fujiwara et al. have reported that the same type of SFs were formed on their 4H-SiC (0001) homoepitaxial layers also grown using CVD [18].

In photoluminescence spectra measured by both Izumi et al. and Fujiwara et al., peaks corresponding to phonon replicas with a band gap of ~2.7 eV (lower than the band edge emission of 4H-SiC) were observed, indicating that these SF 8H inclusions also behave as QWs similar to the 3C inclusions.

Interestingly, the faulted area with in-grown SF 8H inclusions was not observed to expand after long-time laser irradiation or forward p-i-n diode operation, differently
Figure 2.9: The stacking sequence of the in-grown SF embedded in 4H-SiC, shown to have one complete unit of 8H stacking.
from the 1SF 3C inclusions.

The formation mechanism of the in-grown SFs is not clear at present but it is considered as a possibility that some kind of disturbance in step flow growth causes an error in stacking at the point where epitaxial growth starts, and subsequently the SFs are created. It was experimentally shown that the density of in-grown SFs becomes larger as the growth rate increases and for the same growth rate it can be reduced by increasing the growth temperature. Also the density of in-grown SFs was found to be further reduced with the improvement of substrate surface before growth by polishing effectively. These experimental results seem to support the proposed idea for the formation mechanism of these in-grown SFs.

2.3 Metal/Semiconductor (M/S) Contact

It has been of long-term interest and importance to understand, characterize, and further control M/S contacts during the recent period of great advances in modern semiconductor device technology. For various types of semiconductor devices developed with different structures/materials and for different purposes, M/S contacts have always been needed as fundamental gateways through which charge carriers are delivered into and out of those devices.

In many technologically important cases, the Fermi level in the metal is positioned somewhere in the semiconductor band gap when the contact is made. Thus it is naturally expected that an energy barrier (the Schottky barrier) would be formed that would affect carrier (electron or hole) conduction through the contact. Fundamental interests in M/S contacts include how the barrier forms and what would be the resultant
carrier conduction properties depending on the bias voltage between the metal and the semiconductor. Despite its long history, the understanding of Schottky barrier formation at M/S contact is not yet complete, mainly due to the complexity related to interface electronic states. Accordingly, the control of properties of M/S contacts still remains as a major challenge in semiconductor device technology.

Here two basic models of Schottky barrier formation that have been commonly used will be briefly reviewed, followed by a discussion about barrier lowering due to the image force. Then current-voltage ($I-V$) and capacitance-voltage ($C-V$) characteristics of M/S contacts based on the thermionic-emission theory and the depletion approximation respectively will be introduced. These are conventionally used to measure the Schottky barrier height (SBH) at contacts. More comprehensive and detailed discussions about M/S contacts are available in many references [77-79].

### 2.3.1 Basic Models of Schottky Barrier Formation

The simplest model of energy barrier formation at M/S interface was proposed by Schottky in 1938, which did not consider the existence of possible interface states [80]. The basic idea of this model is illustrated in Figure 2.10 (here we consider only the n-type semiconductor case and the same basic idea is applied also for the p-type case). Figure 2.10(a) shows the energy band diagram when the metal and semiconductor (n-type) are both electrically neutral and separated from each other. If the metal and semiconductor are connected electrically by either a wire or direct electron tunneling through a thin vacuum gap between them when they are brought close enough to each other, electrons will move from the semiconductor to the metal until the two Fermi levels
Figure 2.10: The formation of a Schottky barrier in the basic Schottky theory without considering interface states. Figure adopted from Ref. 79: (a) electrically neutral and isolated, (b) electrically connected and separated by a narrow gap, and (c) perfect contact.
become coincident. Here the Fermi level of the semiconductor is assumed to be higher than that of the metal. The energies of electrons at rest just outside the surfaces of metal and semiconductor can be no longer the same and there will be an electric field in the gap induced by the positive charge in the semiconductor (uncompensated donor charges left in depletion region after electrons move to the metal) and the resulting negative charge on the metal surface compensating the semiconductor positive charge [Figure 2.10(b)]. When the metal and semiconductor finally touch, the potential drop ($V_i$) across the gap (from metal to semiconductor) due to the electric field in the gap becomes zero and the vacuum barrier disappears altogether. We then end up with an ideal metal-semiconductor contact with the barrier height, $\phi_B = W_m - \chi_s$, where $W_m$ is the metal work function and $\chi_s$ is the electron affinity of the semiconductor [Figure 2.10(c)]. According to the Schottky theory, the SBH at the M/S interface is linearly proportional to the metal work function. However, it is experimentally found that the barrier height often has a weaker
dependence on $W_m$ than expected, and for some semiconductors (such as Si and GaAs) turns out to be almost independent of the choice of metal.

To handle this discrepancy, Bardeen (1947) proposed another model that takes into account the effect of interface states [81]. This model assumes that there exists a thin insulating layer separating the metal and semiconductor (this insulating layer is assumed to be thin enough for electrons to easily tunnel through it), and also assumes that a continuous distribution of interface states is present at the semiconductor/insulator interface (Figure 2.11). These interface states are characterized by a charge-neutrality level $\phi_0$ referenced from the valence band maximum, meaning that the interface will have a net positive charge when the interface states are filled up to a level below $\phi_0$ and a net negative charge when they are filled above $\phi_0$. In this case, it can be shown that the interface states will behave like a negative-feedback loop that tries to keep the Fermi level near the neutrality level, and also that the deviation of $\phi_0$ from the Fermi level is determined by the density of interface states per unit energy. If the density of interface states is very large, $\phi_0$ becomes coincident with the Fermi level and the barrier height will be $\phi_B \approx E_g - \phi_0$ ($E_g$ is the band gap of the semiconductor), and hence is almost insensitive to $W_m$. This limit is the so-called Bardeen limit and the Fermi level is said to be “pinned” at the neutrality level. The other extreme case where no interface state exists and thus there would be no pinning of the Fermi level at the interface is usually called the Schottky limit. As pointed out previously, $\phi_B$ increases linearly with $W_m$ in this limit.
2.3.2 Image-Force Lowering of the Schottky Barrier

When an electron approaches the M/S interface from the semiconductor side, or enters the semiconductor from the metal side and moves away from the interface, the electron will feel an electric field created by the charge redistribution in the metal to meet the requirement that the electric field at the interface must be perpendicular to the interface. This electric field can be calculated as if there is a positive charge (the image charge) with the same magnitude as an electron located at the mirror-image position of the electron in the metal, with respect to the interface. Due to the additional potential energy from the image charge, the apparent SBH that the electron “sees” is lowered by

$$\Delta \phi_{Bi} = \frac{qE_{max}}{4\pi\varepsilon_0 \varepsilon'_s}$$

(2.1)

where \( q \) is the unit charge, \( E_{max} \) is the maximum electric field in the semiconductor side near the interface, \( \varepsilon_0 \) is the vacuum permittivity, and \( \varepsilon'_s \) is the relative high frequency dielectric constant of the semiconductor [77,79]. The reason why the high-frequency dielectric constant of the semiconductor is used is because the electron is assumed to move at the thermal velocity (~10^5 m/s) and hence there may not be enough time for ions in the semiconductor to fully respond to the image field.

This image-force lowering has to be included when the SBH at the M/S interface is measured with macroscopic \( I-V \), Internal Photo Emission (IPE), and BEEM, since these techniques are based on monitoring carrier transport through the interface. It should not be included when the SBH is measured by macroscopic \( C-V \), since this technique
measures charge redistribution in the semiconductor, and not actual transport of carriers over the SBH.

2.3.3 I-V and C-V Characteristics of Schottky Contact

According to the thermionic-emission theory, the current density of a M/S contact that has a spatially homogeneous Schottky barrier can be described as

\[ J = A^\text{**} T^2 \exp(-q\phi_b/k_B T)[\exp(qV/k_B T) - 1] \]  \hspace{1cm} (2.2)

where \( A^\text{**} \) is the effective Richardson constant, and \( V \) is the sample bias, provided the forward bias is not too large.

However, in reality, the experimentally measured current-voltage curves show non-ideal behavior that differs from Eq. 2.1, and can be better described by

\[ J = A^\text{**} T^2 \exp(-q\phi_b/k_B T)[\exp(qV/nk_B T) - 1] \]  \hspace{1cm} (2.3)

with an empirical parameter \( n \) called the ideality factor that is greater than unity. There are many possible reasons why \( n \) should exceed unity (non-ideal Schottky contacts), the most common being a bias dependence of \( \phi_b \) mainly due to image-force lowering difference for different biases. However, \( n>1 \) also has been argued to be due to spatial non-uniformity of Schottky barriers related to the interface states [77,79].

In practice, Eq. 2.3 is used to deduce the SBH of a M/S contact that includes image-force lowering together with \( n>1 \) by fitting the measured \( J-V \) (or \( I-V \) with the area of contact encountered) curves to it.

Because of the depletion region on the semiconductor side near the M/S interface where no free carriers are present, a uniform Schottky contact behaves as a parallel capacitor. Also the width of depletion region changes as the sample bias changes. Hence
the bias-dependence of the capacitance of the Schottky contact is another interesting and useful characteristic to investigate. If the semiconductor has a uniform dopant density, the “depletion approximation” which assumes the abrupt change of the free-carrier density from a value equal to the dopant density to a negligible value (almost zero) across the boundary of depletion region predicts that the differential capacitance per unit area \( C = \frac{dQ}{dV} \) under reverse bias \( V_r \) should be given by

\[
C = \sqrt{\frac{qN_d \varepsilon_s \varepsilon_0}{2}} \left( \phi_B - \xi + V_r - \frac{k_B T}{q} \right)^{-1/2}
\]

(2.4)

where \( N_d \) is the donor (n-type case) density, \( \varepsilon_s \) is the static dielectric constant of the semiconductor, and \( \xi \) is the difference in energy between the Fermi level and the bottom of the conduction band in the semiconductor bulk. Then it can be easily shown that the inverse of squared capacitance is linearly proportional to the applied reverse bias as

\[
C^{-2} = 2/qN_d \varepsilon_s \varepsilon_0 \left( \phi_B - \xi + V_r - \frac{k_B T}{q} \right).
\]

(2.5)

As in \( I-V \) curves, this relation (Eq. 2.5) is often used as another method to estimate the SBH that will be obtained from the extrapolated voltage intercept \( (V_i) \) of the straight line as \( \phi_B = -V_i + \xi + k_B T/q \). Additionally, the dopant density in the semiconductor can also be obtained from the slope of the straight line as shown in Eq. 2.5 [77,79].
CHAPTER 3

EXPERIMENTAL METHODOLOGY AND SETUP

3.1 Ballistic Electron Emission Microscopy (BEEM)

BEEM is a variant of Scanning Tunneling Microscopy (STM) [82] that can be used to investigate local energy barrier and electron transport property at buried interfaces. It was initially developed to study metal/semiconductor interfaces [19] and later its use has been further extended to study metal/insulator/semiconductor systems [83,84]. Since BEEM is based on STM, it essentially has high spatial resolution which would be several nm even after the hot electron scattering in the top metal layer is included. The energy resolution of BEEM is also known to be high, typically about 10-20 meV, and it can be higher depending on signal-to-noise ratio (in some cases as good as ~5 meV). Hence, BEEM has special merits in searching for spatial non-uniformity of the interface energy barrier and carrier transport with high spatial and energy resolutions. This advantage with BEEM has been used as the key element in studying our SiC inclusions.
3.1.1 Basic Principle of BEEM

STM is a two-terminal measurement based on the tunneling phenomena of electrons through the vacuum gap between the STM tip and the sample, which occurs when the tip is brought close enough to the sample surface. If one monitors the change of tip height vs. tip position while maintaining the same tip-sample separation (and hence the tunnel current) by using a feedback loop, the topographic information on a conducting sample surface can be obtained. Also we can measure the energy distribution of local density of states of the sample surface by taking the spectrum of the tunnel current as a function of the bias voltage between the tip and the sample while the gap between them is held fixed with the feedback loop disconnected. Figures 3.1(a) and 3.1(b) show the schematic diagram of a typical STM setup and the corresponding energy level diagram.

BEEM is a three-terminal measurement requiring one more terminal than STM, usually supplied by the metal overlayer deposited on the semiconductor or insulator/semiconductor sample surface. Figure 3.2(a) shows the schematic configuration of the BEEM setup in the case of making a metal contact on a semiconductor. In BEEM, the metal overlayer is electrically grounded during the measurements and the STM tip is biased negatively \((-V_T)\) referenced to the grounded metal film (“base”). As in normal STM, the STM tip is first brought to the sample surface (this time, the surface of the metal film). When the tip approaches close enough to the sample surface, vacuum tunneling of electrons from the tip (“emitter”) into the metal film will occur. These electrons injected into the metal film by tunneling have been argued to be sharply forward-focused in their momentum distribution and are so called “hot” electrons.
Figure 3.1 (a) Schematic configuration of STM setup and (b) corresponding energy level diagram (Here $\phi$ and $E_F$ represent the work function and Fermi energy of tip ($T$) or sample ($M$), respectively)
Figure 3.2 (a) Schematic configuration of BEEM setup and (b) corresponding energy level diagram. \( q\phi_B \) represents the Schottky barrier at the M/S interface.
because their energy distribution is higher than the metal Fermi level. Provided the metal film is sufficiently thin compared with the electron mean free path, a non-negligible fraction of the injected hot electrons can travel through the metal film \textit{ballistically} (which means without scattering), and can reach the buried interface. Among them, some of electrons with energy higher than local energy barrier at the interface can get over the barrier, propagate into the substrate, and finally be collected as the BEEM “collector” current \((I_c)\). This working principle of BEEM can be well visualized by Figure 3.2(b) which shows its energy level diagram together with the energy-dependent electron flux injected into the metal film. We note that a number of studies [85,86] have suggested that hot electrons might in fact undergo several elastic or “quasi-elastic” collisions (with energy loss of only a few meV) before they surmount the energy barrier. The very recent studies demonstrate conclusively that hot electrons can spread laterally by >10 nm in thin Au film [87].

\subsection{3.1.2 Measurement Modes}

BEEM can be operated basically in two different modes, one of which is the BEEM \textit{imaging} mode and the other is the BEEM \textit{spectrum} mode.

In the BEEM \textit{imaging} mode, the substrate BEEM current \((I_c)\) is measured and recorded as a function of the tip lateral position while the tip scans over the top metal film with \(V_T\) fixed at a constant value. If \(eV_T\) is higher than the local energy barrier at the buried interface, then a BEEM image can be used to study spatial variations of hot electron transmittance across the metal film and interface. Normally, the surface morphology of the metal film is also taken simultaneously with the BEEM image and in
Figure 3.3: Typical (a) STM morphological image over a Pt/4H-SiC contact and (b) simultaneous BEEM image, taken at $V_T = 2.0$ V and $I_T = 5$ nA. Grey scale is 5 nm in (a) and 6 pA in (b).
Figure 3.4: Typical BEEM spectrum averaged over ~100 individual spectra taken on a Pt/4H-SiC Schottky contact. An additional threshold higher than the first one was detected, revealing the existence of the second CBM at an energy higher than the lowest CBM.
some cases it is compared to the BEEM image to find any correlation between the
topographical features of the metal film revealing the surface structure of the underlying
sample and hot electron transmittance. Figures 3.3(a) and 3.3(b) show a typical STM
morphological image of the top surface of the metal film and simultaneously-taken
BEEM image on a Pt/4H-SiC Schottky contact. The small (~5 nm) grain structure
observed in the STM image represents the Pt polycrystallites which are typical in the
metal film deposited at room temperature.

In the BEEM spectrum mode, the tip is positioned at one location on the sample
surface and $I_c$ is measured while ramping up $V_T$, from which $I_c-V_T$ curves are obtained.
The local energy barrier at the interface can then be estimated by determining the
“threshold” tip voltage ($V_{th}$) of the $I_c-V_T$ curve at which electrons start to enter the
conduction band of the sample substrate. For the determination of threshold voltage, a
relation $I_c = C(V_T - V_{th})^2$ or $I_c = C(V_T - V_{th})^{5/2}$ where $C$ is proportional constant can be
used to fit the measured data at low temperatures. However, at room temperatures, due to
the thermal smearing of the Fermi distribution of electrons in the tip, a few hot electrons
can have energy higher than $eV_{th}$ even when $V_T$ is just below $V_{th}$, and thus the BEEM
current appears to turn on a bit earlier (at lower voltage) than the actual $V_{th}$. In order to
take this aspect into account, we usually fit measured BEEM spectrum to the Bell-Kaiser
model which includes the temperature-dependent electron Fermi distribution. The fitted
$V_{th}$ is then interpreted as the local energy barrier at the interface.

In addition to measuring the local energy barrier, BEEM $I_c-V_T$ curves can be
further used to investigate the conduction band structure of a semiconductor or an
insulator by looking for additional turn-ons (thresholds) in a spectrum. For example, 4H-SiC is known to have a second CBM at an energy ~0.12-0.14 eV higher than the lowest CBM from its band structure calculation, and this second CBM has in fact been probed in the BEEM spectrum taken on the Pt/4H-SiC contact shown in Figure 3.4.

In practice, the two measurement modes can be combined by having the tip stop at predetermined grid locations during the scanning of an image, and measuring a BEEM $I_c-V_T$ curve at each location. In our measurements, we use a slightly rotated rectangular grid with respect to the two scan directions (x and y directions in Figures 3.1 and 3.2) to minimize disruptions in the STM and BEEM images caused by sample drift and piezocrystal creep in the scanner. Details can be found in Ref. 22.

### 3.1.3 Bell-Kaiser Theory

When the BEEM technique was originally invented by Kaiser and Bell in 1988 and applied to study subsurface Schottky barrier interfaces (Au/Si and Au/GaAs), they also proposed a simple one-dimensional theoretical model to describe BEEM spectra which considers hot electron motion only along the direction perpendicular to the buried M/S interface [19]. This simple one-dimensional theory assumes the hot electron transmittance at the interface to be a step function, which means that any electron with energy higher than the energy barrier at the interface will have unity transmittance while any electron with lower energy than the energy barrier will have zero transmittance.

A bit later in the same year, 1988, Bell and Kaiser proposed a more refined theory (two-dimensional) which invokes conservation laws of both energy and transverse momentum of electron at the M/S interface [19]. The transverse momentum conservation
relies on the assumed transverse symmetry of the interface which leads to the requirement that no transverse (lateral) force acts on electrons crossing the interface. In the case of \( m_t < m_0 \) (where \( m_t \) is the electron effective mass parallel to the interface in the semiconductor or insulator, and \( m_0 \) is the free electron mass), this transverse momentum conservation causes a refraction of the electrons as they cross the interface and eventually results in the existence of a “critical angle” of electron incidence with respect to the interface normal outside of which electrons may not cross the interface. Accordingly, the transverse energy of electron is restricted to be

\[
E_t \leq \frac{m_t}{m_0 - m_t} \left[ E_x - E_F + e(V_T - V_{th}) \right]
\]

where \( E_t \) and \( E_x \) are the electron energies associated with the components of the electron wave vector parallel and perpendicular to the interface and \( V_{th} \) is the threshold voltage.

Then, the BEEM collector current \( (I_c) \) in the refined theory is described as

\[
I_c = R I_t \frac{\int_{E_{\text{min}}}^{E_{\text{max}}} D(E_x) \int_{E_{\text{min}}}^{E_{\text{max}}} f(E) dE_x dE_t}{\int_{0}^{\infty} D(E_x) \int_{0}^{\infty} [f(E) - f(E + eV_T)] dE_x dE_t}
\]

where \( R \) is a measure of hot electron attenuation due to scattering in the metal base layer, \( I_t \) is the tunnel current, \( D(E_x) \) is the electron tunneling probability through the vacuum barrier, and \( f(E) \) is the Fermi function. \( E_{\text{max}} \) is the largest allowed transverse energy of electron as indicated in Eq. 3.1 and \( E_{\text{min}} = E_F - e(V_T - V_{th}) \) is the minimum required energy normal to the interface to surmount the energy barrier at the interface.

Since the refined theory assumes a parabolic conduction band minimum in the semiconductor (more generally, in the insulator also), the theory itself is valid only in the
region near threshold. Therefore, in practice, Eq. 3.2 is fitted to the measured BEEM spectra in the range within ~0.2-0.25 eV above threshold by adjusting $V_{th}$ and $R$, and the best-fit $V_{th}$ is taken as the estimation of the energy barrier at the interface.

### 3.1.4 Ballistic Hole Emission Microscopy (BHEM)

Ballistic hole emission microscopy (BHEM), which was initially proposed by Hecht et al., is another version of BEEM which can be used to study hole transport properties at the buried interface [20]. In contrast to BEEM, in BHEM holes are created in the metal base layer by vacuum tunneling of electrons from the metal layer into the tip with a positive tip bias, and these holes may propagate ballistically through the metal base to reach the interface since hole attenuation lengths are known to be as large as several hundred angstroms in clean metal films. Then the hole current which has the sign opposite to the BEEM current is measured from the substrate side.

Figure 3.5 shows energy level diagram of BHEM in the case of M/S Schottky contact with energy-dependent hole flux in the metal layer shown. From this figure and Figure 3.2(b), we can note that there is a difference between BHEM and BEEM. For BEEM, the collected electrons originate from the upper part in energy of the tunnel distribution (above the CBM of the semiconductor at the interface) where the flux of tunneling electrons near the Fermi level in the tip remains nearly constant as the tip bias increases. On the other hand, in BHEM, the collected holes originate from the lower part of the tunnel distribution (below the VBM of the semiconductor at the interface) where the hole flux near the tip Fermi level decreases as the tip bias increases. Hecht et al. pointed out that this distinction between BHEM and BEEM would make the increase of
the BHEM current appear to slow down more quickly as the tip bias increases, as compared with BEEM current. This aspect of BHEM has been indeed observed experimentally in the BEEM and BHEM spectra on Au/Si(001) Schottky contact measured by them [20].

Figure 3.5: Energy level diagram of BHEM in the case of M/S contact with energy-dependent hole flux in the metal layer shown.

The basic ideas of the Bell-Kaiser (BK) theory for BEEM are also applicable to BHEM. As for electron transport, conservations of energy and transverse momentum of holes at the interface should be valid, which lead to only the holes with an incidence angle less than a critical angle being allowed to transmit through the interface. Hence, in
the same manner as BEEM, the p-type local energy barrier and additional VBM information can be obtained from fitting BHEM spectra ($I_c$ vs. $V_T$) to the BK theory for holes.

Several authors [88,89] have argued that transverse momentum is NOT conserved at the interface even for electron transport. Therefore it should be noted that transverse momentum conservation is not universally accepted yet. However, the BK theory is still a good phenomenological model to fit BEEM and BHEM spectra, which includes the Fermi-level smearing and well describes the shape of measured spectra near thresholds.

### 3.2 Ultra High Vacuum (UHV) System

All the measurements presented in this dissertation including BEEM/BHEM and macroscopic $I-V/C-V$ have been performed in a UHV system (named “UHV3”) that was initially designed and assembled by Darrell Jones and further upgraded to have BEEM capability by Benjamin Kaczer later. UHV environment is required particularly for sample cleanliness, which is crucial for stable and reproducible measurements during an extended period of time.

Figure 3.6 is the photograph showing our UHV system with the STM/BEEM control unit and the electronics for sustaining and monitoring vacuum on both sides (not shown in the figure). The UHV system is composed of three main parts which are the STM/BEEM chamber, the preparation chamber, and the airlock for introducing samples and tips into the system. The STM/BEEM chamber and the preparation chamber are normally kept at UHV pressure of $\sim 10^{-10}$ Torr by the ion pumps with titanium sublimators and the pressure is monitored with an ion gauge mounted in each chamber.
Figure 3.6: Photograph of our UHV system composed of the STM chamber (left) with BEEM capability added and the preparation chamber (right) with e-beam evaporator installed inside. Samples and tips are introduced into the system and taken out from it via the airlock.
The preparation chamber has a residual gas analyzer (RGA) attached also, which is used to analyze the gas components in the chamber. There is no dedicated pumping system for the airlock. Instead, a carrying turbo-pump station is used to pump the airlock when samples or tips are introduced or taken out. The STM/BEEM control unit consists of the computer containing all necessary programs, digital-to-analog (D/A) and analog-to-digital (A/D) converters, feedback loop electronics, and high voltage electronics for controlling the STM scanner, the tip, and sample coarse positioners. The electronics for the vacuum system includes power supplies for the ion pumps and controllers for the vacuum gauges and the RGA.

3.2.1 STM/BEEM Chamber

The STM/BEEM chamber contains a home-built STM setup assembled on an 8” ConFlat-type support flange, which is inserted into the chamber from the bottom opening. The STM scan stage (a circular disk made from “invar” steel with a small coefficient of thermal expansion) to which the tip/scanner stage and the sample stage are mounted, is hung by three #027 viton O-rings from the support rods for vibration isolation. This O-ring suspension provides sufficient vibration isolation so that atomic resolution images can be obtained even with the external turbo pump station connected to the airlock and running. In addition to the STM, a custom-designed “grabber” mounted on an x-y-z rotatable manipulator and used for both sample and tip exchange is introduced from the top of the chamber. For the details of the STM setup and other parts of the chamber, the reader is encouraged to refer to the dissertation of Darell Jones [21].
For BEEM measurements, a thin 0.1-mm (diameter) Au wire has been added to the chamber by Benjamin Kaczer, which is attached to the grabber assembly so that its position can be adjusted precisely while electrically connected to the body of the whole UHV system.

3.2.2 Electron-Beam Evaporator

The preparation chamber is equipped with an evaporation system custom-designed by Benjamin Kaczer, enabling in-situ metal evaporation on a sample surface in clean environment. The evaporation system consists of three Thermionics 3 kW mini e-beam evaporators mounted on a 2-3/4” ConFlat flange. Each water-cooled e-beam evaporator can accept a crucible liner with an internal volume of ~2.2 cm³ in which evaporation source material is loaded. A tungsten filament installed in each evaporator emits thermal electrons when alternating current flows through it, and the emitted electrons are accelerated by the electric field due to the filament potential lowered by several kV with respect to the grounded crucible. The electron beam is guided by a perpendicular static magnetic field onto the evaporated material. Vitreous carbon or glassy coated graphite crucibles are used for several commonly evaporated metals such as Pt, Au, and Ni while alumina crucibles are needed for Al evaporation because Al wets the surface of a carbon-based crucible.

In order to make circular metal patterns on a sample surface, an evaporation mask with 19 circular holes of ~0.5 mm diameter is used, against which the sample surface faces during evaporation. Three standard quartz-crystal-based microbalances, each dedicated to one e-beam evaporator, are used to measure the thickness of the deposited
film. Calibration of the film thickness has been done for each metal by evaporating thick (several hundred Å) films through the mask onto a “dummy” sample and measuring the averaged thickness of them with a surface profiler.

3.2.3 UHV Optical Fiber Subsystem

To extend the measurement capability of our UHV system, a UHV optical fiber setup has been added to the existing STM/BEEM chamber by Corey Campbell and the author. A UHV compatible optical fiber that can transmit light up to the ultraviolet range was introduced into the chamber through a 2-3/4” port where a 45° reducing T-fitting was attached. One end of the optical fiber was connected via a coupler to an optical feedthrough mounted on the reducer flange of the 45° T-fitting, through which we can deliver light into the chamber from the outside or vice versa. On the main flange of the 45° T, a manipulator assembly composed of a linear motion feedthrough (with an Al extension tube) and a gimble allowing tilt motion in two independent directions was mounted. This manipulator assembly is used for positioning the other end of the optical fiber close to a sample surface. In order to guide the optical fiber properly in the chamber without any conflict between the fiber and the existing elements, the optical fiber was tied with copper wires and glued with “Torr-Seal” brand UHV epoxy onto a stainless steel wire, which was optimally shaped to give large range of motion to the fiber. A shallow trench along the guiding wire was machined close to the sample side end of the wire to make the optical fiber sit on the wire securely. The other end of the guiding wire was connected to the Al extension tube.
Figure 3.7: Photographs showing (a) the configuration of the optical fiber inside the STM chamber and (b) the fiber manipulator and optical feedthrough attached on the chamber.
Figure 3.7 shows (a) the spatial configuration of the optical fiber inside the chamber set by the guiding wire together with the central parts of the STM setup and (b) the manipulator assembly and the optical feedthrough.

Using this UHV optical fiber setup, in-situ Internal Photo Emission (IPE) measurement, which is another commonly-used experimental technique to measure the energy barrier at buried interfaces, can be performed, as well as other experiments that collects light from samples.

3.3 Experimental Procedures

3.3.1 Sample Preparation

The SiC samples used in this work are small pieces of bare semiconductor cut from the original processed or as-grown wafers and they are obtained from our several collaborators. The single SF 3C inclusion and the 8H inclusion samples were supplied by Marek Skowronski’s group in Carnegie Melon University in Pittsburgh (the 8H inclusion sample was in fact grown by Jim Capano’s group in Purdue University in West Lafayette, IN), the double SF 3C inclusion sample was from Brian Skromme’s group in Arizona State University, and the p-type 3C-SiC epilayer on 4H-SiC mesa sample was from Phil Neudeck’s group in the NASA Glenn Research Center in Cleveland.

All samples are first chemically cleaned (detailed cleaning procedure for each sample will be given in the section describing its experimental results). Then a sample is immediately mounted on a sample block and introduced into the UHV preparation chamber via the airlock to minimize unwanted surface oxidation. Substrate ohmic contacts are achieved by making mechanical contacts of the sample backside to the posts.
on a sample block. The sample is pressed from the sample front side against the posts by tantalum clips.

After introduced into the preparation chamber, the sample block is mildly outgassed at a temperature less than 230 °C for several hours by flowing electric current through a tungsten filament mounted on the backside of sample block. This sample outgassing also helps to remove volatile species from the sample surface. If necessary, the sample could be heated directly by passing an electric current through it for an additional, high-temperature cleaning.

Metal contacts are made by depositing Pt (in most cases) through the shadow mask with the e-beam evaporator. Other metals have been also used, such as Pd, Au, Ni, and Al but they are mainly for test purposes. The electron acceleration voltage of the e-beam evaporator ranging 3.8 to 4.1 kV is used to keep the e-beam spot hitting the central area of the source material that is put into a crucible liner. The required e-beam current varies by a large amount (50-250 mA) depending on the melting point of the material to be evaporated (the current is highest in the case of Pt). The typical evaporation rate is 0.04-0.10 nm/sec and the thickness of evaporated metal film ranges 4-8 nm.

The sample with evaporated metal dots is then transferred in UHV to the adjacent STM/BEEM chamber where the BEEM and macroscopic $I$-$V$/$C$-$V$ measurements are performed.

### 3.3.2 $I$-$V$ and $C$-$V$ Measurements

After the samples are transferred into the STM/BEEM chamber, macroscopic $I$-$V$ curves are first measured by touching the top metal dots with the Au wire, which is used
also for BEEM measurement grounding. For $I$-$V$ measurements, a Keithley 428 current amplifier is used, which converts the current input from the sample substrate to a voltage output with a gain up to $10^{10}$. This current amplifier can also apply a bias voltage to the substrate, as referenced to the grounded metal film. The voltage output from the current amplifier is read by a HP 3478A multimeter. The measurement procedure is fully automated by controlling the current amplifier and the multimeter with a computer program written with HP Instrument BASIC, which was initially developed by Hseung Jai Im and later modified by the author. The $I$-$V$ curves of all accessible metal dots on a sample are obtained by measuring the substrate current as the sample bias is changed. The typical voltage range used in the measurements is from $-(1.0-1.5)$ V to 1.0-1.5 V. From the measured $I$-$V$ curves, the diode resistances near zero-bias voltage are estimated. Non-leaky (> 100 MΩ) metal dots are then chosen for the following BEEM measurements.

In $C$-$V$ measurements, the Au grounding wire is connected to a Tenma function generator (model 72-380) that can apply a small AC dither voltage to the metal dots. The $C$-$V$ curves are obtained by measuring the small AC substrate currents as a function of the DC substrate bias voltage. This AC current then can be used to determine the sample capacitance at a given DC bias. The same current amplifier and multimeter as in the $I$-$V$ measurements are used to measure the AC substrate currents while applying the DC biases. Sometimes, a Stanford Research Systems lock-in amplifier (model SR530) is used between the current amplifier and the multimeter to get cleaner signals, by minimizing noise current with frequencies different from the AC dither voltage. The frequency and
rms amplitude of the dither voltage used in most of the measurements are \( \sim 1 \text{kHz} \) and \( \sim 25 \text{mV} \), respectively.

### 3.3.3 STM/BEEM Measurements

Once a non-leaky diode is chosen, the metal is grounded with the Au wire and the STM tip/scanner assembly is approached to the metal surface using the tip coarse positioner, which is based on a Burleigh piezoelectric micro inchworm. The coarse approach is automatically performed by a control program written in HP Instrument BASIC. During the auto approach, the STM scanner is extended by a distance larger than one step of the inchworm motion and tunnel current is checked. If tunnel current is not sensed, the control program retracts the tip and moves the tip/scanner assembly forward by one inchworm step. This process is continued until tunnel current is detected.

When the coarse approach is done, the tip is put into tunneling range by increasing the z-voltage on the scanner (see Figure 3.1) manually and we then start scanning. In all our measurements, the STM is operated under a constant-current mode that allows us to measure the surface morphology of the metal film by recording the scanner z-voltage as a function of tip position. I note that most of the tunnel current does not enter the semiconductor substrate, but rather thermalizes in the metal film and is removed through the Au grounding wire. During tip scanning over the metal film, a BEEM image is taken simultaneously by measuring the substrate current (a fraction of tunnel current) using the same current amplifier that is used for \( I-V \) and \( C-V \) measurements. The output of the current amplifier is usually further amplified using an additional voltage amplifier (Stanford Research Systems, SR560). BEEM \( I_c-V_T \) curves
can be measured either by positioning the tip at an arbitrary location without scanning or by suspending scanning momentarily at pre-defined locations (normally a grid pattern) during scanning.

### 3.3.4 STM Tip Preparation, Cleaning, and Modification

Tungsten (W) tips made by electrochemically etching 10 mil W wire in NaOH have been mainly used in the measurements. The detailed etching procedure and setup can be found in Ref. 21. Commercial controlled-geometry platinum/iridium (Pt/Ir) tips purchased from Materials Analytical Services and Pt/Ir tips made by scissor-cutting a 10 mil Pt/Ir wire have also been used, particularly when the etched W tips don’t work continuously despite of trying several different ones.

In the case of W tips, a tip is first mounted on a tip holder and is cleaned by dipping it in HF (49%) for ~1 min followed by a methanol rinse. This procedure is thought to remove the oxide (WO$_2$) on the tip surface. The cleaned tip is then introduced into the preparation chamber via the airlock as when introducing samples. In the preparation chamber, the tip can be further cleaned by electron bombardment, which is also thought to be an efficient method to remove contaminants, including oxide on the tip. Pt/Ir tips in principle don’t require the cleaning steps described above since the material is known to be inert in the atmosphere. However, the electron bombardment has been usually used also for Pt/Ir tips when they are introduced into the system for the first time.

In many cases, the initial cleaning itself does not guarantee an atomically sharp tip that can produce stable and good STM/BEEM images with large enough BEEM current.
amplitude. Hence additional tip modification is necessary to have a sharp apex at a well-defined location at the end of tip. One common and quite efficient way is to apply a pulse to the z-piezo when the tip is in tunneling, which drives the tip onto the sample (metal) surface. After the pulse is over, the feedback loop pulls the tip back to the normal tunneling conditions. The gentle crash of the tip onto the metal surface can modify the tip to sharpen it atomically by picking-up some metal atoms from the metal film. After each modification, the tip condition is checked by taking STM/BEEM images and inspecting the image qualities. The typical indication of having a good tip is the following: Both STM and BEEM images are continuous with no line or point glitches, the metal polycrystalline grains are shown clearly with sharp boundaries in the STM image, and the BEEM current amplitude in the BEEM image is large enough.

However, if the tip cannot be improved by such a mild crashing since for instance the tip is very blunt, the tip apex is loosely attached, or it has multiple protrusions in shape at the end, then several more violent ways are used to modify it in sequence. The first one is to crash the tip into some depth of metal film with a manual control of z voltage. Even further, the tip is sometimes moved sideway by adjusting the x- and y-voltage while the tip end is still buried in the metal. The hope of doing this is that the tip may drop some loose atoms on the surface and/or pick up a set of metal atoms at one time and these picked-up atoms can serve as an end of the tip with atomically sharp apex. The second way is to pull the tip out of tunneling, retreat it far enough away from the sample, and brush the tip end with the Au grounding wire by using the manipulator assembly where the Au wire is attached. As in the first method, brushing the tip is expected to
remove some “floppy” atoms at the tip end and/or put some Au atoms on it, possibly
supplying a sharp apex. In fact it is likely that a large cluster of Au atoms may be put on
the tip using this method. If these two methods don’t work, the tip is picked up by the
grabber from the scanner and scratched against a tungsten wire with the shape of pigtail
that is mounted on a sample/tip transport arm in the STM/BEEM chamber. Scratching is
a lot more violent than crashing or brushing, and it can change the shape of the tip
drastically (sometimes breaking the tip) to give some chances of making a tip with sharp
end. When all three methods mentioned fail to improve the tip, the tip can be cleaned by
electron bombardment after being transferred to the preparation chamber, and be tried
again. However, if the tip is still in poor condition, we normally switch to another tip.

3.3.5 STM Tip Bias Induced Au Nanodeposition

In this section, we describe an interesting phenomenon we have discovered when
a tip that was brushed with the Au wire was biased to a high negative voltage. When $V_T >$
~3.0 V, a topographical growth localized right underneath the tip has been observed as
shown in Figure 3.8. This phenomenon has never been observed at positive tip biases,
even at $V_T = -10$ V and it has been observed only for the tips brushed with the Au wire. As
noted in the previous section, it is expected that a large number of Au atoms is transferred
from the Au wire to the tip during tip-brushing since Au is a soft material. Hence, it is
very likely that the species deposited under the tip might be these Au atoms transferred
from the Au wire to the tip end. In fact, Au deposition under a STM tip at a negative tip
bias has been previously observed on Au(111) surface in the air by Mamin et al., [90] and
also on Si(111) surface in the air or nitrogen ambient by Hsiao et al. [91].
Figure 3.8: (a) The STM morphology of the top Pt layer before (left) and after (right) taking local BEEM $I_c-V_T$ curves at 49 grid points. The red-dotted circle represents the area where BEEM $I_c-V_T$ curves are taken up to $V_T=5.0$ V and the growth of protrusions is clearly visible. (b) The STM morphology (left) and simultaneously-taken BEEM image (right) at $V_T=5.0$ V after leaving the tip at the center for ~1 min with $V_T=5.0$ V.
The Au atom transfer from tip to sample surface is proposed to occur in the form of the anion \( \text{Au}^{2-} \) [91].

Although this phenomenon is very interesting in terms of the deposition of Au nanostructure, it is undesirable for BEEM measurements (particularly for BEEM \( I_c-V_T \) measurements) because the growth of Au protrusion under the tip reduces BEEM current amplitude significantly as shown in Figure 3.8(b). When the growth is slow enough, we can actually measure several local BEEM \( I_c-V_T \) curves successively at one location. However, when the growth is fast, it is almost impossible to measure even single BEEM \( I_c-V_T \) curve and further the scanning itself becomes unstable to take affordable STM/BEEM images.

Hence, the tip-brushing with the Au wire should be avoided as a tip-modification method when the samples requiring high tip voltages (\( > \sim 3.0 \) V) are studied.

### 3.4 Data Collection and Processing

While a tip scans over a sample, the z-piezo voltage which is directly related to the surface topography of the sample and BEEM current are collected through the A/D converter installed in the system control computer and are displayed line by line in real time on a separate monitor by using a custom developed program. BEEM \( I_c-V_T \) measurements are also managed by the same program. We usually create bitmap files of the measured STM/BEEM images and two-column spreadsheet data file (MS Excel format) of measured BEEM \( I_c-V_T \) curve for data fitting using the built-in functions of the program. However, to perform additional data processing that cannot be done in the
program, we developed small programs to convert the raw data into formats which can be read by commercial softwares.

3.4.1 STM/BEEM Control Program

The program controlling STM/BEEM measurements was initially written only with STM capability, based on the STM control software developed in the IBM Thomas Watson Research Center. It was later updated for BEEM measurements. It is written in BASIC and runs in MS-DOS environment. The details of control mechanism of the program and the file formats created by it are described well in Ref. 22.

Here one specific functionality of the program, “tip-locking”, which has been used very frequently and efficiently in this work is briefly discussed. It is well known that the STM tip can slowly drift with respect to the sample, which could be due to subtle temperature fluctuations in the STM setup (thermal drifting) and/or due to the tip piezocrystal scanner creep: when the tip moves laterally from one location to another by the change of the voltage applied to the electrodes sandwiching the piezocrystal, it has a tendency of moving continuously in the moving direction after it reaches the new location, due to the slow relaxation of the piezocrystal lattice. The speed of tip drifting with respect to the sample is estimated to be typically several nm per hour in the thermal drift case, and several nm per minute in the case of piezocrystal creep. In taking STM/BEEM images, tip drifting caused by piezocrystal creep is of major concern, since this causes distortions of the measured images. Piezocrystal creep is larger as the tip moves by a larger distance and it decreases slowly over time. Hence, tip drifting is usually largest at the beginning of a scan since the tip has just been moved from an
arbitrary location to the starting point of a scan (the lower left corner of the image area) and diminishes gradually as the scanning continues. In the case that we want to study a particular region of the sample over a long period of time or take a large number of consecutive local BEEM spectra at the same location, thermal tip drifting is also a concern as well as drifting due to piezocrystal creep.

In order to handle this issue, a technique known as “tip-locking” allowing us to lock the tip onto one location has been implemented into the control program. This technique was first used by Swartzentruber et al. [92]. Tip-locking can be achieved by choosing a local extreme (either a local maximum or minimum) in the sample topography or in the BEEM current amplitude. Tip-locking using topographical features in our control program was originally implemented by Benjamin Kaczer and later a tip-locking functionality dedicated for BEEM $I_c-V_T$ measurements using either topographical features or spatial contrast of the BEEM current was added by Yi Ding and the author. Particularly, the idea of using BEEM current contrast for tip-locking was motivated by the need to take a large number of BEEM spectra at one location on a quantum well, which bears a long and narrow (several nm wide) stripe of enhanced BEEM current, but with no BEEM signal on the surrounding and does not have particularly distinguishable features in topography. These quantum-well structures will be discussed in detail in Chapter 4.

The basic principle of the tip-locking algorithm is the following: once the tip-locking functionality is turned on, the program first evaluates the tip z-position or the BEEM amplitude at the current tip location and the tip is then moved slightly sideway in
one (x or y) direction, followed by measuring the z-position or the BEEM amplitude again. Depending on the sign of the z-position/BEEM amplitude change, the tip proceeds in the same or the reverse direction (determined by which of local maximum and minimum is chosen as a locking position) in the next step. The same procedure is alternately performed along the other direction. In this way, the tip can seek the nearest maximum or minimum in the sample morphology or BEEM current amplitude and can be locked on the extreme, although the tip drifting relative to the sample is present.

Again, this tip-locking functionality has been very effective especially in taking many (around 100) local BEEM spectra over a particular location on a quantum well. This improves signal-to-noise ratio of the BEEM $I_c-V_T$ curve at that location by taking the average of the measured individual spectra.

**3.4.2 Converting Raw Data to WSxM Format**

For each scan, the STM/BEEM control program creates one text file (*.inf) carrying the parameter information for the scan and two binary-format files (*.dat and *.i) containing the measured raw data (STM/BEEM scan data and BEEM spectra, respectively). As stated previously, the control program can export STM/BEEM images in bitmap format and measured BEEM spectra in MS Excel spreadsheet format. Thus the basic data processing for presenting the measurement results can be done conveniently with the control program. However, sometimes additional data processing beyond the scope of the control program, especially for STM/BEEM images (for example, taking height or BEEM current profile along a line), is necessary to extract more information from the measured data. Several programs written in C language were previously
developed by Yi Ding to convert the binary-format raw data files into the space-limited text files which can be read in MS Excel so that the additional data processing can be done in it.

Since the MS Excel is not designed for image processing, there were still limitations in handling measured STM/BEEM images. Hence the author has updated the existing program to create two files (each for STM and BEEM images) in the format that can be read in a freeware image processing program WSxM (Nanotech Electronica [93]) from the raw data file of STM/BEEM scan (*.dat). The converted files are also space-limited text files with a short header and three columns of data (tip x, y positions, and height or BEEM current amplitude). By reading the converted files in WSxM and using its functionalities, various image processing jobs can be performed very conveniently such as filtering, taking profiles, and creating three-dimensional images, etc. The program source is shown in Appendix A.

3.4.3 Savitzky-Golay Digital Filter

The existence of additional thresholds higher than the lowest one in BEEM/BHEM spectra can be observed more clearly as slope changes in the first derivative of the spectra \( \frac{dI_c}{dV_T} \). Two methods are typically used to get \( \frac{dI_c}{dV_T} \) curves. One is to measure them directly by adding a small dither AC voltage to the tip bias and detecting the corresponding AC component in the BEEM current. The other is to numerically calculate them directly from the measured spectra. We here introduce one common algorithm, the Savitzky-Golay digital filter [94] to calculate \( \frac{dI_c}{dV_T} \) curves as an
example of the second method. We have sometimes used this to verify the existence of the second thresholds in the BEEM/BHEM spectra on 4H-SiC.

The Savitzky-Golay digital filter is a general method applied to smoothing measured data or to calculating their derivatives (first and higher order) for a series of equally spaced data \( f_i = f(x_i) \), where \( x_i = x_0 + i\Delta \) (\( \Delta \) is the spacing between adjacent data points in \( x \) and \( i \) is an integer). The idea of the algorithm is to locally fit the measured data points within a moving window which includes the filtered data point and \( n_L \) and \( n_R \) adjacent points on its left and right sides to a polynomial of order \( M \leq N-2 \). If a least-squares procedure is used for the fitting, the coefficients of the fitted polynomial \( (g_i = a_0 + a_1i + \cdots + a_M i^M) \) satisfy the following relation with the measured data in the moving window,

\[
\bar{a} = (A^T A)^{-1} A^T \cdot \bar{f} \tag{3.3}
\]

where \( A \) is a matrix the components of which are defined as \( A_{ij} = i^j, i = -n_L, \ldots, n_R \) and \( j = 0, \ldots, M \), \( \bar{a} \) is a column vector of the polynomial coefficients, and \( \bar{f} \) is a column vector of the measured data \((f_{-n_L}, \ldots, f_{n_R})\). The essence of this Savitzky-Golay method is that Eq. 3.3 is linear and hence there exists a universal matrix defined as \( C = (A^T A)^{-1} A^T \) that transforms any column vector of the measured data into the column vector of the polynomial coefficients of the best fit. This means that we don’t have to repeat the least-squares fit for every set of data points, rather we can “pre-calculate” the matrix \( C \) and continuously use it to find the best-fit polynomial coefficients for all sets of data points in the whole filtering process done by moving the window from one side to the other of the
measured data range. A sample Maple program for calculating the matrix $C$ is listed in Appendix A.

Once the best-fit coefficients are calculated for a particular set of data points from Eq. 3.3, the smoothed value at the central point ($i=0$) in the window is given as $a_0$ (zeroth-order coefficient) and the derivatives up to $M$th order at that point can be obtained by the relation,

$$
\left[ \frac{d^n g_i}{di^n} \right]_{i=0} = \frac{n! a_n}{\Delta^n}, \quad n = 1, \cdots, M .
$$

(3.4)
CHAPTER 4

RESULTS ON SiC SAMPLES

4.1 Single SF 3C Inclusions in 4H-SiC p-i-n Diode

As described in subchapter 2.2, the formation and propagation of SF 3C inclusions were first discovered during high-current device operation of \( p-i-n \) diodes fabricated with 4H-SiC [11,12]. The SFs formed this way are all found to be “single-layer” Schockley type (“single” SF) produced by the motion of a basal plane partial dislocation. High resolution TEM studies showed clearly thin planar inclusions with local cubic (3C) stacking sequence embedded in the 4H host [62,63]. Due to the conduction band offset between 3C and 4H (~0.925 eV), these SF inclusions were proposed to behave as electron QWs. This QW behavior has been supported experimentally by temperature dependent luminescence quenching measurements by Sridhara \textit{et al.}, which suggested a QW energy depth of ~0.282 eV [75]. In our BEEM measurements, these single SF inclusions were observed as the parallel stripe regions with greatly reduced local SBHs compared with the surrounding 4H host. The measurement of lower SBHs on the stripe regions with BEEM indicates that on those regions injected hot electrons can locally enter propagating conduction band states (at energies lower than CBM of the
surrounding 4H), propagate through the wide depletion region, and be collected from the SiC substrate. This confirms directly that the inclusions are QWs supporting propagating two-dimensional (2D) QW electron states. The measured QW subband energy depth is ~0.25 eV below the surrounding 4H CBM, which agrees quite well with the luminescence measurement and theoretical calculations [72,95].

4.1.1 SF formation and propagation during Diode Operation

The p-i-n diode used in this study was fabricated at Cree Inc., on a heavily doped (8×10^{18} cm^{-3}) n-type 4H-SiC substrate oriented to the [11ar{2}0] direction. The lightly doped (~10^{14} cm^{-3}) n-type blocking layer with a thickness of about 30 µm and the p-type anode were grown epitaxially by CVD. The diode metal contacts on both the p anode and the substrate were formed by following the standard procedures for making ohmic contacts [96]. The top metal contact was patterned in a grid with windows in order to observe the SF inclusions by electroluminescence. Then the diode was electrically stressed by flowing the forward current in the range of 1-100 A/cm^2 for 1 to several tens of minutes. During the diode stressing, the optical emission microscopy (OEM) images mapping the top plane-view of electroluminescence of the diode were taken using a UV sensitive camera. The diode stressing together with taking OEM images were performed by our collaborators (Skowronski’s group) in Carnegie Melon University. Figure 4.1 shows the OEM images taken (a) right before stressing, after (b) 20 min biasing at 1.0 A/cm^2 and (c) 10 min of further biasing at much higher current density of 100 A/cm^2. The black grid lines in the images are the top metal contacts, and the preexistent dislocations and the SF inclusions (which mostly develop from the dislocations) appear as bright dots and lines,
respectively [63]. In this [11\overline{2}0] sample orientation, the SF inclusions residing in the basal planes are perpendicular to the sample surface and hence the projection of SF inclusions on their edges is seen in the OEM images. The SF inclusions were found to form and propagate mainly in the intrinsic blocking layer, which is the preferential region for electron-hole recombination. This fact explains how the evolution of the SF inclusions can be observed clearly by electroluminescence and suggests strongly that the electron-hole recombination in the blocking layer aids the glide of partial dislocations bounding the SF inclusions, resulting in the extension of the inclusions.

Figure 4.1: Optical Emission Microscopy images of SF development in a 4H-SiC p-i-n diode (a) before stressing (preexistent dislocations are seen) (b) after 20 min stressing at 1.0 A/cm² (c) after 10 min further stressing at 100 A/cm², showing the extension [(a) → (c)] of basal plane dislocations (from Ref. 63).

### 4.1.2 Sample Processing for Measurements

As pointed out just in the previous section (Section 4.1.1), the SF inclusions in the 4H-SiC p-i-n diodes form and start propagating in the blocking layer. It was further found that most of these SF inclusions thread through the blocking layer down to some depth of the substrate, but they stop at a depth of about 100 nm from the sample surface
in the p anode. Hence, in order to study the SF inclusions with BEEM and other electrical measurements such as macroscopic $I-V$ and $C-V$, it is necessary to expose the inclusions to the sample surface in a cross-sectional geometry, enabling fabrication of the metal contacts directly on the inclusions. Further, the SF inclusions are expected to be conduction band electron QWs [while the valence band offset of 3C- and 4H-SiC is quite small (see Section 2.1.2)], and so it is required to make the metal Schottky contacts on the n-type region of the sample to study the QW behavior of the inclusions directly. Accordingly, the top metal contact, the p+ layer, and a part of the intrinsic blocking layer were removed using mechanical polishing. The final surface was finished by chemomechanical polishing, leaving a very flat surface with the $rms$ roughness of several angstrom. The polishing step was also performed by our collaborators in Carnegie Melon University following the diode stressing.

After polishing, the sample surface was rubbed with a methanol-soaked cotton tip, degreased with Trichloroethylene, acetone, and methanol for 10 min each in ultrasonic, and cleaned with two cycles of 30 min ultraviolet ozone oxidation followed by HF (49 %) dipping for 30 sec and methanol (anhydrous) rinse. This is the standard cleaning procedure that our group uses to prepare SiC surfaces prior making Schottky diodes [22,31,32]. Then, the sample was introduced into the UHV main chamber (with base pressure: $\sim 1\times10^{-10}$) through the airlock and outgassed overnight at a temperature less than 230 °C by heating the W filament mounted on the other side from the sample in the sample block. A set of Schottky diodes (19) each $\sim$5 nm thick and $\sim$0.5 mm in diameter was formed in-situ by evaporating Pt through a shadow mask at room temperature. After
Pt evaporation, the sample was transferred in UHV to an adjacent STM chamber and then the BEEM measurements and macroscopic $I-V$ and $C-V$ measurements were performed.

### 4.1.3 $I-V$ and $C-V$ Measurements

Once the sample was transferred to the STM chamber, macroscopic $I-V$ curves were first measured on twelve diodes among the total nineteen Pt Schottky diodes to investigate their qualities in terms of leakage. As discussed later, it was found that the polishing step left a number of narrow and linear scratches that were randomly oriented on the sample surface. However, those twelve diodes were measured to be highly rectifying and non-leaky. The resistance of most of the twelve diodes near zero bias was more than 1000 G$\Omega$ and the smallest resistance was measured to be $\sim$1.4 G$\Omega$ on one diode. Macroscopic $C-V$ curves were also measured on ten diodes among the twelve diodes used for $I-V$ measurements.

Figure 4.2(a) is an image of the sample before the polishing, while Figure 4.2(b) shows a map of the sample after the formation of the Pt Schottky diodes. In Figure 4.2(b) indicating the locations of the evaporated Pt diodes, the SBHs from $C-V$ curves were recorded for the ten diodes where the $C-V$ measurements were done. As seen in the figure, the SBHs on four of the ten diodes (indicated in red font) are smaller than the others the SBHs of which are quite uniform with an average of $\sim$1.64 eV. The four diodes with the lower SBH also had a larger range of measured SBH ($\sim$0.1 eV) than the others. If comparing Figure 4.2(a) and 4.2(b), we can notice that the four diodes with lower $C-V$ measured SBHs are located on the region where the top metal grid patterns were initially made to define the areas of $p-i-n$ diodes. Since the SF inclusions are expected to develop
Figure 4.2: (a) Sample image before the polishing step and (b) sample map after polishing and depositing Pt dots. In (a), the top metal grid patterns are shown and the black lines representing intentional mechanical scratches to create more initial dislocations in the intrinsic layer are visible on some of the $p$-$i$-$n$ diodes (diode 1, 2, 3, 4, and 5). The number on each Pt dot in (b) represents the SBH measured from $C$-$V$ curve.
Figure 4.3: Macroscopic (a) $I$-$V$ and (b) $C$-$V$ curves of four Pt Schottky diodes among the twelve diodes tested for leakage. The vertical axis in (a) is in logarithmic scale and the horizontal axis in (b) is the reverse bias applied to the SiC substrate ($V_r = -V_b$).
mostly in the regions that received direct electrical stressing, the lower SBHs of the four diodes are thought to be caused by SF inclusions residing underneath the Pt contacts. The actual mechanism by which the SF inclusions affect macroscopic $C-V$ curves will be addressed in Sections 4.2.2 and 4.2.3.

Figure 4.3(a) and 4.3(b) show the measured $I-V$ and $C-V$ curves on four characteristic diodes of the ten diodes. Among these diodes, the diode D1 positioned on the region directly stressed with the initial metal grid patterns shows consistent behaviors in $I-V$ and $C-V$ curves, implying the influence of SF inclusions. More concretely, their $I-V$ curves indicate additional electrical current paths with barriers lower than the normal Pt/4H-SiC contact, compared with the $I-V$ curves of the diode B3 located on the region which was not stressed directly. The additional current paths with lower barriers are very likely to be supplied by the SF inclusions exposed on the surface although other types of extended defects are also possible sources. As mentioned just previously, the SBH of diode D1 extracted from its $C-V$ curve is lower than the $C-V$ determined SBH on the diode B3. The lowering of $C-V$ extracted SBH turns out to be unique effect of the inclusion QWs and a detailed discussion regarding this will be presented in Section 4.2.3. However, the $I-V$ and $C-V$ curves of diodes C1 and C2 show somewhat inconsistent behaviors. In the case of C2, the $I-V$ curve indicates the existence of lower barrier paths whereas its $C-V$ determined SBH is the same as for normal Pt/4H-SiC. When considering the location of C2 (just outside the stressed region), its $C-V$ behavior is quite understandable since very few (if any) SF inclusions are expected on it. In this case, the lower barrier paths shown in the $I-V$ curve could be supplied by other extended defects.
rather than the SF inclusions. Things are most puzzling for diode C1 which is located almost at the center of the stressed region. Since the C-V determined SBH on this diode is the smallest of the measured diodes, it is likely to contain the largest number of SF inclusions among the ten diodes. However, there is no sign of additional lower barrier paths in the I-V curve. One way to explain this is to assume that all the SF inclusions on C1 terminate below the surface so that none of them makes direct contact with the Pt film and hence they don’t affect I-V curves. As will be discussed in Section 4.2.3, such sub-surface inclusions still could affect the C-V curves. However, we do not have independent evidence that this proposed explanation is correct.

4.1.4 Identifying the Inclusions with BEEM Imaging

After the I-V and C-V measurements, the diode D1 that was expected to possess SF inclusions exposed on the surface was chosen for BEEM measurements. Figure 4.4(a) and 4.4(b) show a STM topographic image of the Pt film top surface and a simultaneously taken BEEM image respectively with a tip voltage of $V_T=1.55$ V. The STM image shows the characteristic metal grains of the polycrystalline Pt film with the diameter of ~5 nm, but shows no sign of the buried SF inclusions. In the BEEM image, most of the area exhibits no BEEM current. This is expected since the SBH of the Pt contact on this 4H-SiC substrate was measured to be ~1.59 eV on average and hence hot electrons injected into the metal layer from the tip with $V_T=1.55$ V don’t have enough energy to get over the energy barrier at the M/S interface. However, we can clearly see a long line of nonzero BEEM current in the BEEM image, indicating that the hot electrons injected on the line can locally enter propagating conduction band states at energies
Figure 4.4: (a) STM image of a 5-nm-thick Pt overlayer on chemi-mechanically polished (11\textoverline{2}0) plane of 4H-SiC containing single SF 3C inclusions (grey scale: 4 nm) and (b) simultaneously taken BEEM image (grey scale: 1 pA) taken at $V_T = 1.55$ V and $I_T = 5$ nA, (c) STM image and (d) simultaneous BEEM image (grey scale: 9.5 pA) taken on the same area at $V_T = 2.00$ V and $I_T = 5$ nA. The straight narrow stripe of enhanced BEEM current in (b) reveals where the 3C inclusion intersects the M/S interface.
lower than 1.55 eV, propagate through the wide depletion region, and be collected from the 4H-SiC substrate. A large number of such linear features were observed while performing a survey by taking spatially successive BEEM images, and they are all found to be parallel to each other with an average spacing expected from the TEM measurements of the SF inclusions. We therefore conclude that these lines represent the locations where the cross-sectioned SF inclusions intersect the M/S interface. We also can conclude that these SF inclusions behave as electron QWs since they supply propagating 2D conduction band states at an energy below the conduction band of the surrounding 4H-SiC host material.

Figure 4.4(c) and 4.4(d) show the simultaneously taken STM and BEEM images taken on the same area as Figure 4.4(a) and 4.4(b), but this time with $V_T = 2.00$ V, which is larger than the SBH on the surrounding Pt/4H-SiC interface. As expected, we see BEEM currents essentially everywhere on the sample surface. However, we do observe randomly oriented long lines of greatly reduced BEEM current. These lines turn out to represent the surface scratches produced during the polishing step, and their effect on BEEM current and the morphological feature in the STM image will be discussed in more detail in Section 4.1.7.

4.1.5 Determining QW Energy Level from BEEM Spectra

Once we identified an inclusion on the sample surface, we next measured the energy of 2D CBM in the inclusion QW by positioning the tip over the inclusion and taking local BEEM spectra. The circular data points in Figure 4.5 show a typical averaged BEEM spectrum of 96 individual spectra taken at one location on the inclusion
and the solid line going through the measured data is a single-threshold fit to the BK model with a best-fit threshold voltage of 1.34±0.01 V. This indicates that the QW CBM at the M/S interface is 1.34±0.01 eV above the metal Fermi level since this is the energy at which injected hot electrons are first able to enter propagating states in the inclusion. The triangular data points in the figure show a typical averaged BEEM spectrum of 100 individual ones measured at one location >20 nm away from the inclusion, over the normal 4H-SiC host material. The dashed line is a “two-threshold” BK fit, giving a lowest CBM of 1.59±0.01 eV. Two thresholds are required here because 4H-SiC is known to have a second CBM at ~0.12-0.14 eV above the lowest CBM and this has been already confirmed experimentally with BEEM [41-43].

Based on these BEEM measurements, the QW energy depth referenced from the CBM of the surrounding 4H-SiC is estimated to be $E_{QW}=0.25±0.01$ eV at the M/S interface. It was previously shown that the differences in CBM between 4H, 6H, and 15R-SiC measured at M/S interface with BEEM are equal to the corresponding differences in CBM in the bulk within about ±0.03 eV [41-43]. Also the BHEM measurements on p-type 3C- and 4H-SiC shows that the p-type SBH is ~0.060 eV larger on 3C- than 4H-SiC, which is consistent with the calculated ~0.050 eV lower VBM energy of 3C-SiC compared with 4H-SiC [7] (Section 4.5.4). These measurements show that in the case of SiC, SBHs measured from BEEM at M/S interfaces (either on n- or p-type material) can reveal the conduction or valence band offset between different polytypes with fairly good precision (within 30 meV). Furthermore, the interface pinning effect of 4H-SiC with double SF 3C inclusions has been found to be nearly the same as
Figure 4.5: Typical BEEM spectra ($I_c - V_T$ curves) averaged over ~100 individual curves on a single SF 3C inclusion (open circle) and on the surrounding 4H-SiC ([1120] oriented) away from the inclusion (open triangle). The solid and dashed lines going through the measured data points are fitted curves using the BK model. The arrows indicate the BEEM thresholds determined by fitting. On the surrounding 4H-SiC, two thresholds (the local SBH and second CBM) are observed at the same energies as previously measured on [0001]-oriented samples (Refs. 41-43). ~0.25 eV lower SBH is measured over the inclusion with respect to the surrounding 4H-SiC, which represents the QW energy depth in the inclusion.
4H-SiC without the inclusions [15]. This indicates that any conduction band shift due to the interface pinning, directly affecting the SBH at the interface, would be almost the same for the 3C inclusions (both single and double SFs) as for the 4H-SiC host.

Hence, by considering all these facts, we can take $E_{QW}=0.25\pm0.03$ eV as the estimation of the QW energy depth in the inclusions relative to the CBM of the surrounding 4H-SiC far from the metal interface. Our estimation is consistent with the previous report of 0.282 eV from luminescence measurement [75] and the theoretical calculations ranging 0.2-0.3 eV [72,95].

4.1.6 Schottky Barrier on a-face 4H-SiC

Another important thing to note on the 1SF inclusion sample is that the interface of Pt contacts on the host 4H-SiC is oriented perpendicular to [1\overline{1}20] direction. All the previous BEEM studies of Pt/4H-SiC Schottky contacts deposited in the same way had a (0001) on-axis interface orientation [41-43], or a (0001) interface miscut by 8° toward the [1\overline{1}20] direction [47,97]. We can therefore investigate the influence of interface orientation on SBH by comparing the SBH on the current sample with those on the previous two samples. The SBH on the current (1\overline{1}20) sample with $\sim1\times10^{15}$ cm$^{-3}$ n-type doping is measured to be $\sim1.59$ eV as described before, while it was measured to be $\sim1.58$ eV for the (0001) on-axis sample with the n-type doping of $\sim3\times10^{16}$ cm$^{-3}$ and $\sim1.54$ eV for the 8° miscut (0001) sample with $\sim1.5\times10^{17}$ cm$^{-3}$ n-type doping. In order to compare the measured SBHs directly, we must consider the relatively small image force lowering depending on the sample doping. This lowering is estimated to be $\sim0.022$ eV,
\(~0.052\) eV, and \(~0.077\) eV for the three samples respectively by using the conventional formula assuming the abrupt depletion zone with the known static dielectric constant of 9.72 and high frequency one of 6.70 for 4H-SiC. Then the corrected SBHs are \(~1.61\) eV for \((11\bar{2}0)\) oriented, \(~1.63\) eV for \((0001)\) on-axis, and \(~1.62\) eV for \(8^\circ\) miscut \((0001)\) sample. The values are nearly the same, indicating that the effect of any interface pinning on the SBH is almost identical for the \((11\bar{2}0)\) and \((0001)\) interface orientations that are perpendicular to each other.

We also note that the Pt/4H-SiC BEEM spectra is nearly the same for both \((11\bar{2}0)\) and \((0001)\) orientations in shape (they are both best described by two thresholds separated by \(~0.12-0.14\) eV) and magnitude. This is not expected from the original BK theory, which assumes the transverse momentum conservation of a hot electron crossing the M/S interface. One clear difference between the two orientations is that the CBMs of 4H-SiC occurring at the M point in the first BZ are completely off by \(90^\circ\) from the interface normal in the \((0001)\) orientation (see Section 2.1.2), whereas the CBMs are either aligned with the interface normal or off by \(60^\circ\) from it in the \((11\bar{2}0)\) orientation. The transverse momentum conservation of an electron at the M/S interface requires that injected hot electrons should have appropriate transverse momentum upon arriving at the interface in order to enter the available states of the conduction band of 4H-SiC substrate for both orientations. The planar tunneling theory (which is adopted in the BK theory) predicts that the hot electrons injected into the metal film from the tip should be sharply forward (perpendicular to the M/S interface) focused. Therefore, the probability that an electron crosses the M/S interface into the CBM pockets of 4H-SiC with the required
momentum is expected to be much smaller in the (0001) orientation than in the (11\bar{2}0) orientation. Our case is quite analogous to the well-known observations in comparison of the BEEM spectra on Au/Si(001) and Au/Si(111) [85] and for the BEEM currents onto X- and L-valley in Au/GaAs(001) [19,98], showing that there is almost no distinction between on- and off-axis CBMs in BEEM. One possible explanation for this observation is that there could be sufficient redistribution of electron momentum caused by elastic scattering in the metal film and at the M/S interface, enabling the conduction of highly forward directed electrons into off-axis CBMs in semiconductor [85,86].

4.1.7 Effect of Polishing Scratches on BEEM

As pointed out in Section 4.1.4, a significant number of long lines of strongly reduced BEEM current are observed in the BEEM image taken at \( V_T = 2.00 \) V that is larger than the SBH on the 4H-SiC host (~1.59 eV). In Figure 4.4(d), it can be seen that the long dark lines have various orientation, width, and intensity. We believe that these long lines represent the effect of surface scratches on BEEM current, which were produced during the mechanical polishing step prior to the final chemi-mechanical polishing step. Careful inspections of the simultaneously-taken STM image of the top Pt layer surface [Figure 4.4(c)] show the faint linear topographic features (valleys or ridges) corresponding to most (but not all) of the dark lines in the BEEM image, probably indicating the polishing scratches on the SiC surface that were present before Pt evaporation.

Figure 4.6 shows a BEEM spectrum taken over one of the dark lines in the BEEM image [Figure 4.4(d)] together with the BEEM \( I_C - V_T \) measured on a region between the
Figure 4.6: Averaged BEEM $I_c-V_T$ curves taken (1) over one of the dark lines and (2) on a region between the lines in Figure 4.4(d). The solid lines going through the measured data are fitted curves to the BK model and the best-fit thresholds are indicated as arrows. Data have been offset vertically and scaled for clarity.
lines. The SBH on the line was measured to be ~1.55 eV, fairly close to the value on the 4H area without scratches, implying that the effect of the polishing scratches on local SBH is small. It is known that scratches on SiC produce subsurface defects [99]. Hence we propose that the greatly reduced BEEM current over the scratches is due to scattering of injected electrons off subsurface defects, which causes a fraction of these electrons to be scattered back into the Pt layer. However, it requires further systematic study to verify this proposal.

4.2 Double SF 3C Inclusions in 4H-SiC

Another type of SF 3C inclusion was discovered to form and develop in heavily n-type doped epilayers or substrates of 4H-SiC that had gone through high-temperature processing, either thermal oxidation in dry oxygen or annealing in an argon ambient [13-16]. High resolution cross-sectional TEM measurement showed that the 3C inclusions formed in this way were all of the “double” SF (2SF) type (Shockley type), resulting in 3C slabs thicker than the single SF case [15,16]. These 2SF 3C inclusions were actually studied with BEEM prior to the 1SF 3C inclusions and the results were well described in Refs. 32 and 97. Here, a brief review of the BEEM measurements on the 2SF 3C inclusion sample will be first given with the sample preparation procedures. Then the macroscopic $C-V$ measurements affected drastically by the existence of the 2SF inclusions in 4H-SiC, which is somewhat unexpected, will be shown. The $C-V$ curves are strongly shifted with respect to normal 4H-SiC without SF inclusions. Finally, the finite-element electrostatic modeling to calculate the energy band profile and theoretical $C-V$ curves when inclined QWs (SF inclusions) are present in the substrate will be described.
in detail. Besides explaining the origin of the strong shift in the $C-V$ curves, the measured shifts along with the modeling enable an estimation of the QW sub-band energy of the inclusions in the bulk, which is found to be in good agreement with BEEM-measured QW energy near the M/S interface.

### 4.2.1 Sample Preparation and Previous BEEM Measurements

Two pieces of 4H-SiC samples were studied, which were cleaved from the original 35 mm diameter wafer purchased from Cree, Inc. The original wafer had a 2 µm lightly n-type nitrogen-doped (1-1.5×10^{17} cm^{-3}) epilayer on a heavily n-type nitrogen-doped (~3×10^{19} cm^{-3}) Si-face substrate with an 8° surface miscut from the basal plane. The whole wafer was thermally oxidized at 1150 °C for 90 min in dry oxygen, and after the oxidation it was found that the central part of the wafer with a higher substrate doping level than the periphery appeared dimpled. After the oxidation procedure, the wafer was characterized structurally, optically, and electrically by our collaborators in Arizona State University [15]. High resolution cross-sectional TEM images taken by them showed that the central transformed region contained 3C inclusions (all of the 2SF type) embedded in the 4H-SiC host. In contrast, SF inclusions did not form on the periphery of the wafer, probably because the heavily doped 4H-SiC substrate had lower doping near the wafer periphery [15]. One of the two pieces studied was cleaved from the central region, hence containing plenty of 2SF 3C inclusions. The other piece was from the periphery without any inclusion and was used mainly as a reference sample for $C-V$ measurements.

The two cleaved and oxide-stripped pieces were degreased, cleaned with two cycles of 30 min UVO oxidation followed by 2 min etching in 1:10 diluted HF and
methanol rinse. Then the samples were studied with BEEM measurements and also with macroscopic $I$-$V$ and $C$-$V$ measurements in UHV after going through the same sample cleaning and metal (Pt) evaporation procedures as the 1SF 3C inclusion case.

In the BEEM measurements on the sample with 2SF 3C inclusions, the inclusions were identified on the sample surface by taking BEEM images and looking for the long stripes with enhanced BEEM current at $V_T = 1.5$ V below the SBH on the 4H-SiC host (measured to be $\sim 1.54$ eV), as done for the 1SF 3C inclusion sample. The average local SBH over the inclusions measured by taking BEEM spectra on them was found to be $\sim 0.53$ eV lower than that on the surrounding 4H-SiC, indicating that the 2D conduction band energy in the inclusion QWs is lower than the CBM of the 4H-SiC host by the same amount, $\sim 0.53$ eV. As with the 1SF sample, this indicates that the 2SF inclusions support propagating states at $\sim 0.53$ eV below the CBM of the surrounding 4H-SiC host, giving strong and direct evidence that these 2SF inclusions also behave as electron QWs. Again, the detailed description on the BEEM measurements on this 2SF 3C inclusion sample can be found in Refs. 32 and 97.

4.2.2 Schottky Barriers from $I$-$V$ and $C$-$V$ Measurements

The initial macroscopic $I$-$V$ and $C$-$V$ measurements using several different metals on the processed (high temperature oxidation) wafer were performed by our collaborators in Arizona State University, and the results were reported [15]. The SBH from the $I$-$V$ measurements on the central transformed region with 3C inclusions was found to be $\sim 0.42$-$0.47$ eV lower than the untransformed periphery without 3C inclusions for all the metals used. As discussed in Section 4.1.3, this is expected because the 3C inclusions
exposed on the surface can supply electrical paths into the substrate with lower barrier height than the surrounding 4H area, and because the macroscopic $I-V$ will be dominated by these lower barrier paths.

However, very interestingly, the SBH from macroscopic $C-V$ curves on the transformed region was also measured to be ~0.47 eV lower than the untransformed region. Later we have performed similar $C-V$ measurements on our two samples, and the $C-V$ extracted SBH on the sample cleaved from the transformed central region was measured to be ~0.45 eV lower than the other sample from the untransformed periphery, in good agreement with the initial report by Skromme et al. [15]. This is a somewhat unexpected behavior since SBHs determined from macroscopic $C-V$ curves are thought to represent the average SBH of the M/S interface, and TEM [15] and BEEM [97] measurements show that ~98% of the M/S interface on the transformed sample is still normal Pt/4H-SiC despite of a large number of thin (~1.25 nm thick) 3C inclusions with the average bulk spacing of ~90 nm. The detailed discussion for the physical origin of this phenomenon will be given in the next section, by calculating how the energy band profile is affected by the existence of the 3C inclusions, and in turn how this affects $C-V$ curves on the sample with the 3C inclusions.

### 4.2.3 Finite-Element Electrostatic Modeling and Bulk QW Level

In order to investigate the effect of 3C inclusions on macroscopic $C-V$ curves of the sample from the transformed region, finite-element electrostatic modeling [100] was performed using the commercial software package FlexPDE [101]. The example script for the modeling is given in Appendix B and the sample geometry for the modeling is
Figure 4.7: (a) Schematic cross-sectional view of sample showing the 2SF 3C inclusions (gray+black lines) which start to fill with free carriers (electrons) at the depth $L_{eff}$ below the M/S interface, while the surrounding 4H area remains depleted even in the bulk (b) BEEM image (taken with $V_T = 1.5$ V) of a Pt contact on 4H-SiC containing the 2SF 3C inclusions. The bright straight lines show that the SBH is locally reduced where the 3C inclusions intersect the M/S interface.
Figure 4.8: The calculation domain for the finite-element electrostatic modeling of the double SF 3C inclusion sample. The thick red lines represent 9 inclusions used in the calculation and $N_c$ is the effective density of states of 4H-SiC. The relative apparent lengths of the relevant dimensions of the domain are adjusted in the figure, differently from their actual ones, for clarity.
shown in Figure 4.7(a).

In the semiclassical model for describing the electron dynamics in a periodic lattice potential, the energy of the bottom of conduction band (here denoted as $\phi_{\text{tot}}$) can be described simply as the sum of its original energy when charge is neutralized in a material and the additional electrostatic potential energy ($\phi$) caused by the charge redistribution for achieving thermal equilibrium [102].

Following this idea, for our sample with the 3C inclusions, we define the energy of the conduction band bottom in the host 4H-SiC as

$$\phi_{\text{tot}}^{\text{host}}(x, y, z) = \phi(x, y, z) + E_{SB}^{\text{host}}$$

(4.1)

where $E_{SB}^{\text{host}}$ is a constant equal to the host (4H) SBH at the metal interface. Then the energy of the conduction band bottom in the inclusion QWs is

$$\phi_{\text{tot}}^{\text{QW}}(x, y, z) = \phi(x, y, z) + (E_{SB}^{\text{host}} - \Delta E_{\text{QW}})$$

(4.2)

where $\Delta E_{\text{QW}}$ is the QW energy depth in the inclusions relative to the 4H CBM. The electrostatic potential energy $\phi(x, y, z)$ for electrons is calculated by solving the Poisson equation

$$\nabla^2 \left( \frac{\phi}{-q} \right) = -\frac{\rho(x, y, z)}{\varepsilon_s \varepsilon_0}$$

(4.3)

where $\rho(x, y, z)$ is the net charge density, $q$ is the elementary charge, $\varepsilon_0$ is the vacuum permittivity, and $\varepsilon_s$ is the relative dielectric constant of the semiconductor. Here the metal Fermi level is the reference energy. The net charge density is
\[ \rho(x, y, z) = q[N_d - n_e(x, y, z)] \] where \( N_d \) is the donor density and \( n_e \) is the free electron density. In the host 4H-SiC, \( n_e \) is given by [77]

\[
n_e \equiv \left( \frac{M_e}{4} \left( \frac{2m^*k_BT}{\pi\hbar^2} \right) \right)^{3/2} \exp\left(-\frac{\phi_{\text{host}}^\ast - E_F^\ast}{k_B T} \right)
\]  

where \( E_F^\ast = -qV_r \) is the Fermi level in the semiconductor with an applied reverse bias \( V_r \), \( M_e \) is the number of equivalent conduction band minima of 4H-SiC, \( m^* \) is the effective electron density-of-states mass in 4H, \( k_B \) is Boltzmann’s constant, and \( \hbar \) is the reduced Planck’s constant. In the inclusion QWs, \( n_e \) is given by

\[
n_e \equiv \sigma_{QW}/d, \quad \sigma_{QW} = \left( \frac{M_e m^*_i k_B T}{\pi\hbar^2} \right) \ln \left[ 1 + \exp\left(-\frac{\phi_{\text{tot}}^\ast - E_F^\ast}{k_B T} \right) \right]
\]  

where \( \sigma_{QW} \) is the sheet electron density in a QW, \( m^*_i \) is the QW in-plane effective electron density-of-states mass, and \( d \) is the QW width. The structure of the calculation domain and boundary conditions for solving the Poisson equation are shown in Figure 4.8. In most of our modeling, 9 inclusions have been included in the calculation domain. We have further performed some additional calculations with 11 inclusions included and also using periodic boundary conditions at the two side boundaries, and the results were found to be almost identical for these three cases. As can be noted, the electrostatic potential energy (\( \phi \)) is solved self-consistently until it satisfies the boundary conditions, since the energy band profile (\( \phi_{\text{tot}} \)) directly affected by \( \phi \) determines the net charge density (\( \rho \)) and \( \rho \) is the source term in the Poisson equation from which \( \phi \) is calculated.
In addition to the energy band profile, we can also calculate the local surface charge density on the metal side as

\[ \sigma_M(x, y, 0) = \varepsilon_s \varepsilon_0 \frac{\partial}{\partial z} \left( \frac{\phi}{-q} \right) \]

which enables calculating the spatially-averaged surface charge density, \( Q(V_r) \) as a function of applied bias. Then theoretical \( C-V \) curves are obtained by taking the first derivative of the average surface charge density with respect to the bias, \( dQ/dV_r \). In this modeling, the effects of spontaneous polarization in the 4H host producing a strong electric field across the 3C inclusions are included.

Figure 4.9 shows the calculated \( C-V \) curves (1/\( C^2 \) vs. \( V_r \)) from the modeling for the samples both with (transformed central region) and without (untransformed periphery) 3C inclusions, together with the experimentally measured data on the two samples. The top two curves (dashed and solid) are the calculated \( C-V \) curves for the sample without 3C inclusions, using identical parameters except for somewhat different donor density. As expected, the calculated \( C-V \) curves are straight lines with a slope depending on the doping, but with an intercept voltage almost independent of doping [77,79]. In order to check the correctness of our finite-element modeling, we analyzed these calculated \( C-V \) curves in the conventional way as introduced in Section 2.3.3, and extracted values for \( N_d \) and \( E_{SB}^{host} \) that are (as expected) identical to the respective parameter values used to calculate the \( C-V \) curves.

The bottom two curves (dot-dashed and dotted) in Figure 4.9 were calculated with the same parameters, but now with 3C inclusion QWs with an average spacing \( s_\perp = 95 \)
Figure 4.9: Top two lines: calculated $C-V$ curves without double SF 3C QWs, with $N_d = 1.4 \times 10^{17} \text{ cm}^{-3}$ (dashed line) and $N_d = 1.7 \times 10^{17} \text{ cm}^{-3}$ (solid line). Bottom two lines: calculated $C-V$ curves with inclined QWs present, with $\Delta E_{QW} = 0.50 \text{ eV}$, $s_\perp = 95 \text{ nm}$, and with $N_d = 1.4 \times 10^{17} \text{ cm}^{-3}$ (dot-dashed line) and $N_d = 1.7 \times 10^{17} \text{ cm}^{-3}$ (dotted line). Other parameter values for the calculations are listed in Table 4.1. Introducing QWs strongly reduced the intercept voltage, but not the shape or slope of the calculated $C-V$ curves. (○) Measured $C-V$ data from a diode on the wafer periphery without inclusions. (□) Measured $C-V$ data from Diode A from central part of the SiC wafer with inclusions.
nm in the bulk and each with the same QW energy depth $\Delta E_{QW}$. Even in this case the two calculated $C-V$ curves are still straight lines with the same respective slopes as the $C-V$ curves without the inclusion QWs, but with the intercept voltages shifted by essentially the same amount for both curves. This shift, resulting in a lower $C-V$ extracted SBH compared with the sample without QWs, depends strongly (almost linearly) on $\Delta E_{QW}$, but depends rather weakly on $s_\perp$. At the first glance, it is surprising that the shape and slope of the $C-V$ curves do not change, because the QWs are expected to greatly alter the free carrier distribution. However, since the inclusion QWs are inclined with respect to the sample surface due to the $8^\circ$ miscut, the free carriers in the QWs can quickly respond to an applied AC or DC voltage, producing a $C-V$ response that mimics a uniform material of the same doping but with a much lower SBH. To verify the plausibility of this idea, we note that in a uniform semiconducting material the measured capacitance under reverse bias is determined by the depletion width $L$, which terminates at the physical depth where the semiconductor conduction band minimum approaches $E_F$ and accumulates sufficient free carriers to screen the fixed donor charge. In contrast, with inclined QWs the measured capacitance is determined by an “effective” depletion width $L_{\text{eff}}$ [see Figure 4.7(a)], which is approximately equal to the physical depth where the conduction band of the QWs approach $E_F$ and accumulates sufficient carriers to effectively screen the fixed donor charge in the surrounding host material. The electrostatic modeling shows that this in actual occurs in our sample with the inclusion QWs (generally, any material system with inclined QWs) as illustrated in Figure 4.10. Since the QW conduction band has lower energy than that of the 4H host, it reaches $E_F$ at a shallower depth $L_{\text{eff}}$ than in the
Figure 4.10: Calculated electron potential energy profiles for Diode A along the particular path perpendicular to the metal/SiC interface shown as a dotted line in Figure 4.7(a). The solid line represent the three-dimensional CBM for bulk 4H- and 3C-SiC, while the horizontal dotted lines represent the two-dimensional CBM of the QW states, including quantum confinement energy. The overall band bending is decreased with respect to pure 4H-SiC (dashed line) by charging of the QWs deep in the bulk, with a corresponding reduction in $C-V$ measured SBH. Inset: close-up view of QW profile around an inclusion.
uniform material case, producing a larger capacitance, and hence a smaller intercept voltage in C-V curve. However, the shape of the C-V curve remains the same since it is still the host donor density $N_d$ that determines how much $L_{\text{eff}}$ must change when the applied bias ($V_r$) is changed. One thing to be emphasized is that the shifted intercept voltage is not due to any change in the M/S interface. In fact, the calculated C-V curves would be the same even if the QWs happened to terminate just below the metal interface, because no free carriers exist in the QWs (or in the host) close to the metal interface (depletion region).

We next compare the modeling results with the measured C-V data on the two samples (with and without the 3C inclusion QWs). The open circles in Figure 4.9 are the measured C-V data from the periphery sample without inclusions. These data were fit to a straight line (not shown) from which were extracted the SBH of $\sim 1.60$ eV and the local epilayer doping $N_d \approx 1.7 \times 10^{17}$ cm$^{-3}$. The solid line through the open circles is the calculated C-V curve based on the measured SBH and $N_d$, which as expected matches the measurements exactly. Literature values were used for $m^*$, $m_i^*$, $\varepsilon_s$, $M_c$, $d$, and SP in the calculation and they are listed in Table 4.1.

<table>
<thead>
<tr>
<th>$m^*$</th>
<th>$m_i^*$</th>
<th>$\varepsilon_s$</th>
<th>$M_c$</th>
<th>$d$</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>[8]</td>
<td>[64]</td>
<td>(4H and 3C, [103])</td>
<td>[8]</td>
<td>[64]</td>
<td>[56]</td>
</tr>
<tr>
<td>0.39 $m_0$</td>
<td>0.36 $m_0$</td>
<td>9.7</td>
<td>3</td>
<td>1.25 nm</td>
<td>$1.1 \times 10^{-2}$ C/m$^2$</td>
</tr>
</tbody>
</table>

Table 4.1: The parameter values from literature used in finite element electrostatic modeling. ($m_0$: free electron mass, SP: Spontaneous Polarization)
The open squares in Figure 4.9 are the C-V data measured from a Schottky diode on the sample with inclusions (denoted as “Diode A”) from the wafer central region. These data were also fit to a straight line (not shown) which was analyzed in the conventional way to estimate the local doping $N_d \cong 1.4 \times 10^{17}$ cm$^{-3}$ on this part of the wafer. Since the inclined QWs do not change the slope of the C-V curves (as discussed previously), they can still be used to determine the local epilayer doping. Using this value of $N_d$ and $E_{SB}^{host} \cong 1.60$ eV, we then calculated C-V curves with various values for $\Delta E_{QW}$ and the perpendicular QW spacing $s_{\perp}$ to investigate their effects on the calculated C-V curves. These calculated C-V curves all had the same slope as the measured C-V curve, but with shifted intercept voltages depending strongly on $\Delta E_{QW}$ and weakly on $s_{\perp}$. It is noted that the measured doping on the sample with inclusions (from the wafer center) is somewhat less than that measured on the sample taken from the SiC wafer periphery. We do not think this difference is significant since variations in doping across an epilayer are common, and since the calculations indicate that the change in intercept voltage of C-V curve due to inclined QWs is nearly independent of doping.

From our modeling, it is quite suggestive that we could use the measured C-V data to determine the QW energy $\Delta E_{QW}$ in the bulk, provided we have an independent measurement of the average perpendicular separation $s_{\perp}$ between the QWs. Accordingly, we measured $s_{\perp} \cong 95$ nm on Diode A by using BEEM to directly image and count individual inclusions [see Figure 4.7(b)], sampling 10% of the diode diameter along a line perpendicular to the inclusions. Because all parameter values except $\Delta E_{QW}$ are known from the literature or from direct measurements (Table 4.1), we varied $\Delta E_{QW}$ until the
calculated $C-V$ curve best fits the measured data, as shown by the calculated dot-dashed line through the open-square data points in Figure 4.9. This $C-V$ curve was calculated with the best fit value $\Delta E_{QW} \approx 0.50$ eV. Similar measurements were also made (not shown) on another diode (Diode $B$), which had $\sim 50$ mV smaller intercept voltage in measurement, and had a slightly smaller measured average inclusion spacing of $s_\perp \approx 79$ nm. In this case the best fit QW energy depth was $\Delta E_{QW} \approx 0.52$ eV, close to the best fit value for Diode $A$. We note that spontaneous polarization in 4H-SiC was included in these calculations as noted earlier. For comparison, we made similar calculations assuming zero spontaneous polarization, and found essentially identical best-fit $C-V$ curves but with a best fit values $\Delta E_{QW} \approx 0.58$ eV and 0.60 eV for Diode $A$ and Diode $B$, respectively.

Hence, based on the modeling and measurements on the two diodes ($A$ and $B$), the QW energy depth in the 2SF 3C inclusions is estimated to be $\sim 0.51$ eV below the 4H CBM in the bulk far from the M/S interface, and this estimation agrees quite well with an estimate of $\sim 0.53$ eV measured with BEEM at the interface.

Although our finite-element electrostatic modeling has been dedicated for the sample with 3C inclusions, its key result that the presence of inclined QWs under a Schottky contact with sufficient density to deplete the host semiconductor bears a $C-V$ curve with the same shape and slope as without the QWs, but with a significantly reduced intercept voltage will be applicable to any material system possessing QWs in the similar geometry.
4.3 SF 8H Inclusions in 4H-SiC

It has been reported very recently by Izumi et al. and Fujiwara et al. [17,18] that SFs could also form during the growth of an epilayer grown on a 4H-SiC substrate using CVD (Section 2.2.2). In this case, the SF inclusions were found to have one complete unit of 8H stacking sandwiched by the 4H-SiC host, as determined from the high-resolution TEM measurements [17,18]. We have characterized the electronic properties of these in-grown 8H inclusions also using BEEM together with I-V and C-V measurements. The sample is a 4H-SiC epilayer grown on n-type 4H-SiC substrate 8° miscut from (0001) towards (11̅20) orientations using CVD, which was received from Skowronski’s group at Carnegie Melon University after grown by Capano’s group at Purdue University. According to our C-V measurements, the epilayer doping is \( \sim 2.1 \times 10^{14} \) cm\(^{-3}\) (n-type). The 8H stacking of the SF inclusions on this sample was confirmed by the high-resolution TEM image taken by our collaborators, Skowronski’s group. Their scanning electron microscope measurements show that the average spacing between the inclusions on surface is \( \sim 30 \) µm. This is quite a large spacing compared to the typical scanning range of our STM.

4.3.1 Sample Preparation and BEEM-Measured QW Level

After received, the sample was first cleaned using the same procedures as for other SiC samples, which included the standard degreasing and the UVO oxidation followed by the final HF (49%) dipping and methanol rinse. The sample was then mounted on a sample block and introduced into the UHV preparation chamber through the airlock. A Pt film with \( \sim 5 \) nm thickness was evaporated onto the sample surface.
through the shadow mask after outgassing the sample block mildly overnight and the sample was then transferred into the STM/BEEM chamber.

Because of the wide separation (~30 µm) of the inclusions on surface and the limitation in the scan size of our STM setup (maximum scan size of ~1.6 µm in normal operation, a special procedure was developed to search for the inclusions in a reasonable amount of time. In order to maximize searching efficiency, the sample was mounted on the sample block in the orientation where the inclusions on surface would be perpendicular to the fast scan direction (normally the horizontal direction in our STM configuration) in the beginning. Then the STM/BEEM images with a size of ~(1.6 µm)×(50 nm) (vertically narrow and horizontally elongated) are taken successively at a tip bias $V_T$ that is below the SBH on the surrounding 4H-SiC while marching the sample horizontally along the fast scan direction between successive images. The sample marching step is chosen to be smaller (~1 µm) than the horizontal size of an image to make sure there is some overlap between successive images to avoid missing an inclusion. The STM tip is pulled out of tunneling while the sample is moved in order to prevent possible tip-crashing on the sample surface. The searching is continued until an inclusion is observed, showing up as a narrow stripe in the BEEM image with enhanced BEEM current. This 8H inclusion sample is found to have a characteristic V-shaped deep groove structure near the opening of an inclusion on surface (i.e., where the plane of the inclusion intersects the sample surface), which will be discussed in the following sections. Thus the STM morphologies of the top Pt overlayer could also be used to search for inclusions in this case. This is in contrast to the 3C inclusion samples discussed earlier,
Figure 4.11: Typical BEEM spectra ($I_c$–$V_T$ curves) averaged over ~100 individual curves on an in-grown 8H inclusion (open circle) and on the surrounding 4H-SiC away from it (open triangle). The solid and dashed lines going through the measured data points are fitted curves with the BK model. The arrows indicate the thresholds of the BEEM spectra, determined by fitting. ~0.39 eV lower SBH on the inclusion is measured, representing the QW energy depth in the inclusion.
which had little or no topographic features near the openings of those inclusions on the sample surface.

Once an inclusion was located on the sample surface, we measured the local BEEM spectra on and away from the inclusion as done for the 3C inclusion samples. Figure 4.11 shows typical BEEM $I_c$-$V_T$ curves, each averaged over ~100 individual curves measured at a particular location on the 8H inclusion and on the surrounding 4H-SiC (>150 nm away from the inclusion). The SBH on the 8H inclusions was measured to be $0.39 \pm 0.01$ eV lower than on the surrounding 4H-SiC host, indicating that these inclusions are also QWs with the QW energy level lower than the 4H-SiC CBM by the same amount.

4.3.2 Asymmetry of BEEM Threshold near Inclusion Opening

In addition to confirming the QW behavior of the 8H inclusions, we have made two interesting observations on this sample. Figure 4.12 shows the STM morphological image of the Pt overlayer and simultaneously measured BEEM image near an 8H inclusion on the sample surface with $V_T = 2.00$ V, which is higher than the SBH on the surrounding 4H-SiC area. Below each image, the averaged profile taken across the inclusion along the direction indicated by the red-dotted line in the corresponding figure is also shown. As mentioned previously, this sample has an asymmetric V-shaped deep (~15 nm) groove structure around the 8H inclusion on the surface, and we believe that the “edge” or “opening” of the inclusion lies along the lowest portion in the groove [Figure 4.12(a)]. In the STM profile, both sides of the groove near the inclusion appear to be quite linear. In particular, the linear portion on the left side from the inclusion in the
Figure 4.12: (a) STM morphology of the 5nm-thick Pt overlayer and (b) simultaneously taken BEEM image near an 8H inclusion opening found in the 4H-SiC epilayer grown using CVD with $V_T = 2.0$ V and $I_T = 5$ nA. The averaged profiles shown below each image were taken along the direction of the red-dotted lines indicated in the images.
figure extends almost up to ~135 nm away from the inclusion. If considering the tilt angle of this linear portion with respect to the flat surface area far away from the groove (beyond the scope of the figure), the left side from the inclusion seems to be parallel to basal plane. Since the sample cleaning procedure does not significantly alter the sample morphology, it is believed that this deep groove structure with one side parallel to basal plane formed during epilayer growth. One interesting (but as yet unresolved) question is what mechanism can lead to the formation of the groove structure during epilayer growth.

One possible explanation for the formation of this groove structure is the following: The growth of the epilayer during CVD is driven by step-flow growth, and for some reason the growth of steps that bound SiC bilayers in the 8H inclusion is slower than the growth of steps that bound the underlying 4H-SiC host material in the early stage of epilayer growth. Then, the advance of the edges of 4H layers residing over the inclusion may be retarded compared with the edges of the 4H layers underlying the partly-grown inclusion layers [as illustrated in Figure 4.13(d)]. This results from the notion that one complete unit of 8H layer should be first grown to enable the growth of 4H layers on top of it, by making the stacking sequence in phase with the existing 4H layer over the buried 8H inclusion. Hence, as the Si-C bilayers within the 8H inclusion grow on the surface, the 8H inclusion at the surface would not be completely formed [Figure 4.13(d)], and so would be thinner than a complete 8H layer. We will call this partially-formed inclusion on the sample surface a “remnant” of the 8H inclusion. In this case, an asymmetric V-shaped groove structure would be expected, and the exposed inclusion layers on the left side of the groove would be almost parallel to the host basal
Figure 4.13: (a) Profiles of BEEM-measured SBHs across the 8H inclusion before (as-grown: dark blue data points) and after (pink data points) polishing the top groove structure. Schematic cross-sectional view of the proposed structure of (b) a groove for the as-grown sample with the remnant of 8H inclusion on the left side in the groove and (c) the polished sample. For the as-grown sample, the corresponding energy band diagrams on the normal 4H-SiC area and the area with the remnant of 8H inclusion are shown. (d) Schematic illustration of the proposed mechanism of the groove structure formation near the inclusion opening. The length of the arrows in (d) represents the relative growth speed of steps bounding Si-C bilayers in the 8H inclusion and the surrounding 4H host in the early stage of epilayer growth.
plane. This is consistent with the groove structure we observe on this 8H inclusion sample.

One interesting observation we made on this groove structure in terms of its electronic property is that the local SBH immediately to the left side in the groove structure was measured to be higher than the SBH on the other (right) side of the groove, and was also higher than the SBH measured over 4H-SiC area far away from the groove [Figure 4.13(a)]. The dark blue data points in Figure 4.13(a) represent the profile of BEEM-measured SBHs across the inclusion. As shown in the figure, the SBH is highest just to the left side of the bottom of groove (near the opening of the 8H inclusion QW) and it decreases somewhat gradually (but not quite) as one moves away from the groove bottom towards the left. Related to the proposed mechanism of the groove formation, a possible/likely explanation for the observed asymmetry in the SBH around the groove bottom is the following. If, as discussed above, the surface of the left side of the groove is covered with a partially-formed 8H inclusion layer, the difference in the spontaneous polarization (SP) in 4H-SiC and the (partial) 8H inclusion would naturally produce the asymmetric SBH. In more detail, since the SP in the remnant of 8H inclusion is smaller than in the 4H-SiC host, then a net negative bound “polarization’ charge, corresponding to the SP difference of the inclusion remnant and the underlying 4H-SiC, would be induced at their interface. When covered by a metal film, this negative interface charge would create a strong electric field across the inclusion remnant and produce an increase in the local SBH, as shown in the energy band diagram in Figure 4.13(b). This proposal is analogous to the control of the effective SBH of a GaN/Al\textsubscript{x}Ga\textsubscript{1-x}N/GaN heterostructure.
field-effect transistor using the piezo-electrically induced polarization charge at the buried GaN/Al$_x$Ga$_{1-x}$N interface demonstrated by Yu et al. [104].

In order to test this proposal, we have performed the same type of measurements (local SBH profiling across the 8H inclusion) on another piece of sample cut from the same wafer as the initial 8H inclusion sample, but this time the sample surface was chemi-mechanically polished to remove the groove structure near inclusions on the sample surface. The expected sample structure after polishing is such as the one shown in Figure 4.13(c). Since this polishing removes the partially-grown inclusion at the sample surface, there should be no enhancement of measured SBH on the left side of the groove. The pink data points in Figure 4.13(a) represent the measured profile and obviously the asymmetry in the local SBH around the inclusion opening is no longer present, strongly supporting our proposal for the origin of the asymmetry on the initial as-grown 8H inclusion sample [dark blue data in Figure 4.13(a)].

As pointed out previously, the SBHs on the left side of the inclusion opening decreases gradually to the value on the surrounding 4H-SiC area as the tip is moved away from the inclusion. If the inclusion remnant on that side had a uniform thickness, the increase of SBH would be expected to increase somewhat abruptly just to the left side of the inclusion opening, and remain uniform until the edge of the inclusion remnant, where it would somewhat abruptly return to the “normal” value measured on the rest of the sample. Hence the observed gradual decrease of SBH seems to indicate that the inclusion remnant is not uniform in thickness, but rather gets thinner as the position is moved away from the groove bottom. In this case, the increase of SBH caused by the negative
Figure 4.14: AFM images near 8H inclusion on surface and height profiles across the inclusion. The location where each profile is taken is indicated as a line in the image.
interface bound charge would be smaller as the spacer layer (the inclusion remnant) between the metal and the host 4H-SiC is thinner.

Further support for the proposal that the thickness of the inclusion remnant is not uniform comes from the AFM measurements we made on regions of a bare surface (not covered by Pt) around the inclusion opening. These AFM measurements indeed show that the inclusion remnant appears to have step structures of height where its thickness decreases by a certain multiple of Si-C bilayer (stacking unit) across each step (Figure 4.14). For the particular inclusion shown in Figure 4.14, the steps along the several profile lines indicated, if any, are measured to have a height of either ~2.5 Å (one bilayer) or ~5.0 Å (two bilayer).

Based on the AFM height profile measurements, the step structure of the inclusion remnant is very likely to be random across the remnant area. Thus it is quite difficult to know the actual local layer structure at the positions where the local SBHs were measured to take their profile across the inclusion [Figure 4.13(a)] on the initial (as-grown) 8H inclusion sample. Because of this difficulty, it is almost impossible to study the increase of SBH over the inclusion remnant in a quantitative manner by directly relating the SBH increase to the local layer structure. Accordingly we here just point out that our measured BEEM-threshold profile and AFM height profiles strongly support the proposal that the partly-grown inclusion remnant with step structures exists on the left side of the observed groove structure near the 8H inclusion opening on surface.
4.3.3 Hot Electron Reflection from Subsurface Inclusion

Another interesting observation we made on this 8H inclusion sample is that BEEM current is strongly suppressed on the right side of the inclusion opening where the 8H inclusion resides below the surface in an inclined geometry by the sample miscut (8°) from the surface (Figures 4.13 and 4.14). More concretely, the BEEM current amplitude close to the inclusion opening (~20 nm away) is only ~15 % of that (~1.4 pA) on the normal 4H area with no subsurface inclusion, and it gradually increases as one moves away from the opening. The increase looks quite linear in the range shown in the figure with the rate of ~0.025 pA (corresponding to ~1.8 % increase with respect to the value on normal 4H area) per each 10 nm. If considering the sample structure on the right side from the opening, this observed suppression of BEEM current amplitude indicates that the subsurface 8H inclusion strongly reflects the injected hot electrons back into the metal overlayer.

Regarding this observation, it should be first addressed what physical mechanism can cause such strong hot electron reflection off the subsurface 8H inclusion. As can be seen in the energy band profile perpendicular to the M/S interface [Figure 4.15(a)], electrons injected to the right side of the inclusion opening have to go through both a 4H-SiC region (between the top metal layer and the inclusion) and the 8H inclusion in order to reach the 4H substrate and to be collected as BEEM current. Due to the energy band offset and the difference in effective electron mass between adjacent regions, the quantum-mechanical reflection occurring at each interface and resulting interference effect in electron transport is expected, which might reduce the electron transmittance. In
addition to that, the energy band increase across the 8H inclusion due to the SP difference of 8H- and 4H-SiC makes the energy band at the far side [indicated as an arrow in Figure 4.15(a)] of the inclusion from the M/S interface exceed the barrier height at the M/S interface. This increase of the energy band at the far side of the inclusion can also reduce the BEEM current by blocking more electrons with energies lower than the tip voltage than the normal 4H area. To see whether or not these two effects in combination can cause the observed strong suppression of BEEM current, we have used the transfer matrix method [105] to calculate the electron transmittance through the stacked regions, using the expected energy band profile in the semiconductor depletion region. The energy band profile used in the calculation was obtained by considering the measured SBH at the Pt/4H-SiC interface, the depletion field due to the sample doping (n-type, $\sim 2.1 \times 10^{14}$ cm$^{-3}$), the conduction band offset of 8H and 4H (0.495 eV from the calculation of our collaborator, Lambrecht’s group in Case Western University), and the electric field caused by the SP difference of 8H and 4H. (the SP in the 8H inclusion is assumed to be the half of the SP of 4H-SiC). The thickness of the 8H inclusion was assumed to be 2 nm (one complete 8H stacking) and the experimentally measured value ($1.1 \times 10^{-2}$ C/m$^2$) by Bai et al. [56] was used for the SP of 4H-SiC.

Figure 4.15(b) shows the resulting calculated BEEM current (blue data points) together with the measured profile (red line) relative to the averaged value on normal 4H area, as a function of distance toward the right from the inclusion opening. As is obvious in the figure, the BEEM current suppression expected from the quantum interference effect and the energy band increase at the far inclusion side is way too small to explain
the observed strong suppression. The BEEM current suppression from the two effects is only ~16% and is quite uniform over a large range of distance. The 4H region between the metal and 8H inclusion becomes thicker as the distance from the inclusion opening increases (8° sample miscut) and the energy band increase at the far side of the inclusion reduces correspondingly because of the depletion field. However, the reduction in the distance range shown in the figure is quite small (~30 meV between the closest and farthest point from the opening) because of the low sample doping ($N_d = 2.1 \times 10^{14} \text{ cm}^{-3}$). Thus the calculated uniform suppression in BEEM current is somewhat understandable. At this moment, it is not clear what mechanism can cause the significant reflection of hot electrons from the subsurface 8H inclusion. Hence, in order to figure out the exact mechanism, further systematic investigation, which considers other possible mechanisms, is required.

Regarding the gradual recovery of BEEM current to the value on the normal 4H area as the tip moves away from the inclusion opening, we propose that it is due to electron scattering processes occurring in the 4H region between the metal layer and the 8H inclusion. As illustrated in Figure 4.15(c) and 4.15(d), the total “round-trip” travel distance of injected hot electrons in the 4H region as they move toward and then are reflected back from the inclusion increases almost linearly as the injection point (the location of STM tip) moves away from the inclusion opening. When the travel distance increases, more of the injected hot electrons would be scattered in random directions (before and after the reflection off the inclusion) and some of those electrons are very likely to travel sideways (probably scattered continuously and thermalized), propagate
Figure 4.15: (a) Energy band profile perpendicular to the sample surface on the right side of the inclusion opening, under which the 8H inclusion resides, (b) the measured (red) and calculated (blue) profile of BEEM current amplitude as a function of distance from the inclusion opening on the surface for $V_T = 2.0$ V, and schematic illustrations of hot electron reflection off the subsurface inclusion and scattering in the 4H area between the top metal and the 8H inclusion when the tip is (c) close to and (d) away from the inclusion opening.
down to the 4H substrate, and contribute to the BEEM current eventually rather than going back into the metal layer. According to this gradual BEEM current recovery mechanism, we should in fact be able to roughly estimate the hot electron attenuation length in 4H-SiC. If we assume the electron travel path indicated as a black arrow line in Figure 4.15(c) and the perfect (100 %) reflection from the inclusion, the total electron travel distance from the moment when an electron is injected into the 4H-SiC area across the M/S interface to the moment when the electron reaches the interface back after being reflected off the 8H inclusion will be \(d(1+1/\cos2\theta)\). Here \(d\) is the depth of the 8H inclusion from the M/S interface at a lateral position where hot electrons are injected and \(\theta\) is the sample miscut. In this case, the injected electrons will scatter while traveling through the 4H-SiC region between the metal overlayer and the 8H inclusion with a probability \(\{1-\exp[-d(1+1/\cos2\theta)/\lambda]\}\) \[106\] where \(\lambda\) is the electron attenuation length in 4H-SiC. Then the BEEM collector current \((I_c)\) which is contributed by the electrons that scatter in the 4H-SiC region will be described by the relation,

\[
I_c = I_{c^{4H}} \left\{1-\exp\left[-\frac{d(1+1/\cos2\theta)}{\lambda}\right]\right\} \quad (4.7)
\]

where \(I_{c^{4H}}\) represents the amount of electrons injected across the M/S interface and it is equivalent to the BEEM current on the normal 4H area. By fitting the measured BEEM profile to the Eq. 4.7, \(\lambda\) is estimated to be \(~115\) nm. This estimation would supply the lower bound of the electron attenuation length in 4H-SiC since the actual electron travel distance could be longer than the assumed one and hot electron reflectance from the inclusion might be less than 100 %.

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4.4 Numerical Calculation of QW Energy Level in Inclusion

Aside from comparing the QW energy levels in SF inclusions estimated from our BEEM and C-V measurements with the first principle calculations, we have separately estimated the QW energy levels by numerically solving the 1D time-independent Schrödinger equation for a square well with a triangular bottom that results from the electric field in inclusions due to the SP difference between inclusions and the surrounding 4H-SiC host. These estimated values were then compared with our measurements and the first principles calculations.

It is especially investigated how the difference of SP between SF 3C inclusions and the surrounding host 4H-SiC, creating strong electric fields across inclusions, affect the calculated QW energy levels. It will be shown that we may in fact estimate the magnitude of SP of the 4H host by comparing the BEEM-measured QW energy levels and the calculated values for 1SF and 2SF 3C inclusions which have the same potential well depth but different widths.

4.4.1 Calculation Method

The numerical method used to solve the 1D Schrödinger equation to find QW bound states in the SF inclusions is the so called “shooting method” [94]. In this method, the wavefunction ($\psi$) of an electron and its first derivative ($\psi'$) are given fixed values at the boundary of the spatial range for calculation (here $x$) on one side from a square well (let’s take the leftmost point), and then their values at the boundary on the other side (the rightmost point) are calculated by numerically integrating the Schrödinger equation.
where \( m \) is the effective electron mass that may be different inside and outside the potential well, \( V(x) \) is the electron potential energy, and \( E \) is the electron energy, from the leftmost to rightmost points through the whole spatial range. The two boundaries are far enough from the potential well to enable the assumption that both \( \psi \) and \( \psi' \) for a correct solution should approach zero at the boundaries for bound states in the well.

The conditions for a bound-state is satisfied automatically at the leftmost point by assuming very small values for \( \psi \) and \( \psi' \), and then we vary the electron energy \( E \) (the shooting parameter) in an iterative way until the both \( \psi \) and \( \psi' \) at the rightmost point calculated from the integration of Schrödinger equation become very close to zero (the bound-state conditions). All allowed bound states in the well can be found in this way by sweeping \( E \) from the bottom to the top value of potential energy in the well.

### 4.4.2 Calculation Results and Comparison with BEEM Measurements

For the 3C inclusions (1SF and 2SF), the depth of the potential energy well is assumed to be 0.925 eV which is the conduction band offset between 3C- and 4H-SiC [56]. The effective electron mass (along the direction perpendicular to the hexagonal basal plane) is assumed to be \( 0.313 m_0 \) (\( m_0 \) : free electron mass) in the 3C inclusions and \( 0.330 m_0 \) in the surrounding 4H-SiC, respectively [56]. For the well width, we have used 0.5 nm (two Si-C bilayers) for the 1SF and 1.25 nm (five bilayers) for the 2SF by following the proposal of Qteish et al. [54] which defines the boundary between 3C- and 4H-SiC based on the difference in the bulk SP between 3C- and 4H-SiC. This choice for
the thickness of a SF 3C inclusion is discussed in more detail in Section 2.2.1. The electric field produced inside the inclusions by the SP in 4H-SiC is included in the calculation.

Figure 4.16 illustrates the potential energy (conduction band) profile for the 1SF 3C inclusions by assuming the SP in 4H to be $1.1 \times 10^{-2}$ C/m$^2$ which is the value reported by Bai et al. [56]. The parameter values used for the calculations and the calculated QW energy depths are indicated. The lowest QW energy level in the 1SF 3C inclusions was calculated to be $\sim 0.245$ eV below the surrounding 4H-SiC CBM, whereas a deeper level, $\sim 0.554$ eV was calculated for the 2SF 3C inclusions (not shown). These calculated QW energy depths are very close to our BEEM-measured values, i.e., $\sim 0.25$ eV for 1SF and $\sim 0.53$ eV for 2SF.

We have performed additional calculations to see how the calculated QW energy depths for different 3C inclusion widths (different number of Si-C bilayers) depends on the SP in 4H-SiC. The open circles in Figure 4.17 represent the calculated QW energy depths vs. number of Si-C bilayers in 3C inclusions for three different assumed SP values in 4H-SiC. These assumed SP values are zero (no SP), $1.1 \times 10^{-2}$ C/m$^2$ (measured value by Bai et al. [56]), $1.7 \times 10^{-2}$ C/m$^2$ (extrapolation from the calculated values for other hexagonal polytypes [32]). The solid squares in the figure are the BEEM-measured QW energy depths of the 1SF and 2SF 3C inclusions. As can be seen in the figure, the BEEM-measured QW depths match fairly well the calculation for the assumed 4H SP value of $1.1 \times 10^{-2}$ C/m$^2$. This seems to indicate that the assumed value of $1.1 \times 10^{-2}$ C/m$^2$ is a reasonable value for the SP in 4H-SiC. In fact, if we could have the samples containing
3C inclusions with other widths (besides just the 1SF and 2SF inclusions), a systematic comparison of our measured QW energy depths and the calculation could be a good way to estimate the SP in 4H-SiC. However, currently, only the two types of SF 3C inclusions have been available experimentally, and only the two data points are not sufficient to confirm that the measured QW depths really track the calculation assuming $1.1 \times 10^{-2}$ C/m$^2$ as the SP in 4H-SiC.

Figure 4.16: Schematic view of the conduction band profile of a single SF 3C inclusion QW (~0.5 nm wide) embedded in 4H-SiC. The assumed QW width and the calculated QW energy depth ($E_{QW}$) are indicated. The spontaneous polarization (SP) of 4H-SiC causes a strong electric field in the inclusion resulting in a potential drop across the inclusion. Literature values were used for the SP and the conduction band offset of 3C and 4H-SiC.
Figure 4.17: Calculated QW sub-band energy levels referenced from the CBM of 4H-SiC vs. the number of Si-C bilayers in the 3C inclusions, for three different assumed values of SP in 4H-SiC. The unit of SP is C/m².
For the 8H inclusions, the potential well depth is assumed to be 0.495 eV and the effective electron mass in the 8H inclusions is assumed to be 0.570\(m_0\) (noticeably larger than 3C), both of which have been obtained from the first-principle calculation done by our collaborator, Dr. Lambrecht’s group in Case Western Reserve University. The SP in the 8H inclusions is assumed to be the half of that (1.1\(\times10^{-2}\) C/m\(^2\)) of 4H-SiC by adopting the general notion that SP in hexagonal SiC varies linearly depending on hexagonality. Regarding the width of an 8H inclusion, we use 2.00 nm (eight bilayers) which is the width of one complete unit of 8H stacking. This is based on the same criteria as in the case of 3C inclusions, which uses the bulk SP of a polytype as a guideline in determining the boundary between two different polytypes. By assuming the parameter values described above, the QW energy depth for the 8H inclusions embedded in 4H-SiC is calculated to be ~0.36 eV lower than the surrounding 4H-SiC CBM. This calculated value is close to the BEEM-measured value of ~0.39 eV although not as close to the measured value as compared with the 3C inclusion case (1SF and 2SF).

4.5 p-type 3C-SiC on 4H-SiC Mesa Structure

This subchapter describes measurements and analysis that are quite different from those discussed in the earlier parts of this chapter, as it does not concern inclusions in SiC.

As discussed in Section 3.1.4, we can measure the SBHs on p-type semiconductor and investigate additional valence band structure using BHEM with high energy resolution. In this subchapter, we present the BHEM measurements on a p-type 3C-SiC epilayer grown on 4H-SiC mesa structure with greatly reduced defect density. The measured lowest threshold (p-type SBH) and the shape of BHEM spectra will be
compared with our previous BHEM measurements on p-type 4H-SiC. From this comparison, the valence band offset (VBO) of 3C- and 4H-SiC can be obtained, and further the difference in crystal-field splitting between the two polytypes which are predicted theoretically can be also investigated.

4.5.1 3C Epilayer Growth on Step-Free 4H Mesa

For many years, there has been a large amount of research effort to grow 3C-SiC heteroepitaxial films on Si and 4H- and 6H-SiC substrates [107,108]. However, all of these efforts resulted in 3C epifilm with a significant number of extended crystal defects such as double-positioning boundaries (DPBs) and SFs, causing the poor electrical properties of devices fabricated on these films. Recently, our collaborators, Neudeck et al. in NASA Glenn Research Center developed a new growth process named “step-free surface heteroepitaxy” where 3C epi-growth is performed on step-free 4H- and 6H-SiC substrate mesas, and succeeded in achieving 3C epifilms completely free of DPB and SF defects [109].

In the new growth process, an array of isolated growth mesas are first formed on commercially available on-axis (usually within 0.3° miscut) 4H- or 6H-SiC wafers by fabricating trench patterns into the wafer surface, using dry etching procedures. Then pure stepflow homoepitaxial growth is performed at 1620 °C in which 2D terrace nucleation is suppressed to grow all initial surface steps on top of a mesa over to the edge of the mesa, leaving the top mesa surface with no atomic steps. After producing the step-free basal plane 4H mesas, the in-situ growth temperature is lowered by 120-190 °C over a certain time period to facilitate initial nucleation of single 3C-SiC island (with a low
island nucleation rate) on the large basal plane surface, and the growth at the lowered temperature is kept so that the 3C-SiC island expands laterally via stepflow to cover the entire mesa before nucleation of a second 3C-SiC island. The growth at the lowered temperature is continued for an additional 60 and 70 min by keeping the process of single 3C-SiC island being nucleated and extended laterally to cover the entire mesa.

Our p-type 3C-SiC sample consists of such epilayers grown on 4H-SiC mesas which have the shape of ~0.2 mm either square or hexagon, using this new growth process. The sample was unintentionally boron-doped during growth with an estimated dopant density of $1-5 \times 10^{17}$ cm$^{-3}$. After growth, the sample was thermally dry-oxidized for 5 hours at 1150 °C to form a thick SiO$_2$ protective top layer [110]. SiO$_2$ grows on different polytypes with different growth rate, and its growth rate is also different on defects from pure crystalline structures. Hence the final SiO$_2$ protective layer was used also for mapping polytypes and revealing defects on a mesa [110].

### 4.5.2 Sample Preparation for BHEM Measurement

Once we received the p-type 3C on 4H mesa sample, we fabricated 27 circular openings through the SiO$_2$ protective top layer (0.17 mm diameter) each isolated completely on top of a 3C mesa. The fabrication of circular openings was done by first patterning the circular holes in a photoresist layer spin-coated on the sample surface (using the standard photolithography steps) and finally completed by etching through the top oxide layer with HF (1:5 diluted). The detailed photolithography and etch procedures are described in Appendix C. The exposed 3C surfaces were then cleaned with one cycle of 30 min ultraviolet ozone (UVO) room-temperature oxidation followed by 10 sec HF
Figure 4.18: Schematic sample cross-section and electrical connections for BHEM measurements. The Pt dot (~0.5 mm diameter) completely cover the ~0.17 mm circular opening through the oxide on top of the mesa. One side-wall of the mesas may not be covered by Pt due to shadowing during evaporation.
(1:10 diluted) dip and methanol rinse. This HF etch was long enough to remove the thin UVO oxide over the holes, but not the surrounding thick protective oxide. The sample was then introduced into an UHV sample preparation chamber (base pressure: $\sim 1 \times 10^{-10}$ torr) and outgassed mildly overnight at temperature lower than 230 °C. A set of Pt Schottky diodes with $\sim 5$ nm thickness and $\sim 0.5$ mm diameter (larger than the circular openings) was formed in-situ using e-beam evaporation through a shadow mask at room temperature. After evaporation, the sample was transferred in UHV to an adjacent STM/BEEM chamber for BHEM measurements.

Although Pt evaporation was done somewhat blindly without aligning the Pt dots onto the circular openings, several dots covered the openings completely and BHEM measurements were done on some of these dots that were found to be not leaky. Figure 4.18 shows a schematic cross-sectional view of the final sample structure and electrical connections used for BHEM measurements.

4.5.3 Schottky Barrier and Valence Band Structure from BHEM

Figure 4.19(a) shows a typical BHEM spectrum averaged over $\sim 100$ individual spectra taken at one location of the Pt contact on one of the p-type 3C-SiC mesas covered by the Pt dots at the tunnel current of 20 nA. The solid line in the figure represents the best fit of the data to the standard BK model with one threshold. The reason why the standard BK model for BEEM is used to extract the threshold of BHEM spectra of 3C-SiC is because the overall shape of its BHEM spectrum is better described by the theoretical spectra of the BK model for electron transport rather than the model for hole transport proposed by Hecht et al. differently from Au/Si(001) case [20]. Also, it is
Figure 4.19: Typical BHEM spectra averaged over ~100 individual $I_c - V_T$ curves taken on (a) Pt/3C-SiC and (b) Pt/4H-SiC contacts. Solid lines are fits to Bell-Kaiser Model with fitted thresholds indicated by arrows. Insets show close-ups of the near-threshold data points, and show that the 3C spectrum is well-fit with one threshold, while the 4H spectrum requires two thresholds. The dashed line in the inset of (b) shows that a single-threshold fit on 4H-SiC noticeably misses the measured data.
known that the fitted threshold in the critical near-threshold region is almost independent of which one of the two models is used.

The best-fit threshold for this 3C-SiC sample was found to be 1.58±0.01 V on average. However, to get the true “intrinsc” SBH, we must correct for the effects of image force lowering [77,79]. After accounting for the image force lowering for the estimated doping range (1-5×10^{17} \text{cm}^{-3}) of the 3C-SiC sample, the intrinsic p-type SBH of the Pt/3C-SiC contact is estimated to be 1.67±0.02 eV.

For the shape of the BHEM spectrum, as pointed out just above, the measured data for the 3C-SiC sample are well described by assuming one threshold. This indicates that there is no additional valence band maximum (VBM) in the energy range of ~0.14 eV (the range of the BK fit) below the highest VBM in the valence band structure of 3C-SiC. As discussed in Section 3.1.4, an additional VBM would provide another channel for hole transport into the 3C-SiC, and so should produce an additional threshold in the BHEM spectrum.

4.5.4 Comparison with Previous BHEM on 4H-SiC

We also have previously measured p-type SBH of Pt/4H-SiC contact which were prepared with the nominally identical sample cleaning and Pt deposition conditions to those for the 3C-SiC sample using BHEM, and the results are reported in Ref. 47. Figure 4.19(b) shows a typical averaged BHEM spectrum on such a Pt/p-type 4H-SiC contact. The solid line in Figure 4.19(b) again represents the best fit of the measured data to the standard BK model as in Figure 4.19(a). This time, two thresholds are required to reasonably fit the data to the BK model while (as discussed above) a single threshold is
sufficient for p-type 3C-SiC. The dashed line in the inset of Figure 4.19(b) shows a close-up of the single-threshold best fit on 4H-SiC, and we see that it misses the measured data points quite obviously just above threshold, compared with the inset of Figure 4.19(a) showing that a single threshold makes quite good fit for 3C-SiC.

The p-type SBH on this Pt/4H-SiC contact was measured to be 1.45±0.01 eV. Including the image force effect for the sample doping of ~5×10^{18} cm^{-3}, the estimated intrinsic SBH of the Pt/4H-SiC is 1.61±0.01 eV, which is ~0.06 ±0.02 eV lower than the intrinsic SBH on the Pt/3C-SiC sample (1.67±0.02 eV). We here note that the 3C sample has on-axis surface orientation while the 4H sample was 8° miscut from the basal plane. Thus any effect of sample miscut on the measured SBH could be a concern in directly comparing the SBHs on the two samples. However, our group has previously measured n-type SBHs on the 4H-SiC samples with different sample miscut (one on-axis [41-43], two 8° miscut [47,97], and one a-face [111]) using BEEM, and the measured SBHs after correcting for image force lowering have been found to be close within 0.03 eV at most with no systematic trend on sample miscut. Therefore we believe that the sample miscut difference does not matter for the comparison of our 3C and 4H samples.

According to the previous BEEM measurements on n-type 4H-, 6H-, and 15R-SiC, the measured n-type SBHs closely follow the respective bandgaps of these polytypes [41-43]. This seems to indicate that differences in the BEEM-measured n-type SBHs at M/S interface between SiC polytypes track the corresponding bulk conduction band offsets since the bandgap differences of SiC polytypes mainly come from the differences in their conduction bands. This conclusion is supported by the macroscopic I-V
measurements of the n-type 4H-SiC sample containing 2SF 3C inclusions discussed in subchapter 4.2 where the interface-state pinning strength was found not to be affected by the existence of the 3C inclusions, compared with the reference 4H-SiC sample without any 3C inclusions [15]. This means that the interface pinning strength is almost the same for both 3C- and 4H-SiC. If the interface pinning strength is the same (for a given metal) on different SiC polytypes, then the measured n-type SBH should track the conduction band energy.

From these measurements on n-type SiC, one would expect that differences in the measured SBHs between different p-type SiC polytypes should also track the corresponding bulk valance band offsets. Hence the observation of p-type SBH on 3C-SiC being 0.06±0.02 eV higher than on 4H-SiC would indicate that the bulk VBM of 3C-SiC is lower than 4H-SiC by the same amount, which is consistent with the calculated ~0.05 eV lower bulk VBM for 3C-SiC [7]. Figure 4.20 is a schematic representation of the estimated bulk energy band alignments between 3C- and 4H-SiC, based on our measured valence band offset and the known band gaps of 3C- and 4H-SiC. These measured alignments show a type-II band alignment between 3C- and 4H-SiC, with band offset values that are in good agreement with calculations. We note that the effects of the different spontaneous polarization expected between 3C- and 4H-SiC, producing electric fields in the vicinity of an actual 3C/4H interface are not included in Figure 4.20.

We next consider the difference in shape of the measured BHEM spectra on 3C- and 4H-SiC. As noted, the 3C spectra can be fitted reasonably well to the BK model by assuming one threshold while the 4H spectra require two thresholds to be fitted
Figure 4.20: The schematic representation of the energy band line-up of a 3C/4H heterostructure. Our BHEM measurements suggest a type-II heterostructure with valence and conduction band offsets that are consistent with theoretical calculations.
adequately. For all spectra measured at six different randomly selected locations on the 4H sample, the second threshold is observed to be on average ~0.11±0.01 eV above the first one, strongly suggesting that on 4H-SiC an additional VBM exists below the highest VBM by the same amount. It has been calculated that the highest valence bands in hexagonal SiC are split due to the crystal field. Several groups [4,7,8] have calculated this crystal-field splitting for 4H-SiC and have predicted values of 56 – 130 meV depending on the calculation method. We strongly believe that the second threshold observed in the BHEM spectra on the 4H sample represents this crystal-field split band because (1) the measured splitting is consistent with theoretically calculated values, and (2) we do not observe a second threshold on p-type 3C-SiC. Crystal-field splitting is not expected in 3C-SiC because of its cubic symmetry. Another type of valence band splitting due to the spin-orbit interaction has been calculated to exist for both 3C- and 4H-SiC, but is expected to be very small (<10 meV) [8,45,46]. This would be very difficult to observe in room-temperature BHEM measurements because it is less than the ~25 meV thermal smearing of the metal Fermi energy.

To our knowledge, our BHEM measurements are the first experimental confirmation of the difference of calculated crystal-field splitting between 3C (cubic crystal symmetry) and 4H (hexagonal symmetry). The linear dependence of this crystal-field splitting on hexagonality of SiC polytypes, predicted theoretically (Section 2.1.3), is also an interesting topic that can be studied by performing BHEM measurements on other experimentally-available hexagonal polytypes, such as 6H-SiC.
CHAPTER 5

DENUDED-ZONES IN SILICON HOMOEPITAXY

5.1 Adparticle Diffusion Anisotropy on Si(001) : Motivation

This chapter describes a joint work done between the author and Prof. Charles Ebner at the Ohio State University, and former graduate student Jon-Frederik Nielsen.

Surface diffusion is a central kinetic factor in the evolution of surface morphology during growth and material processing. On many semiconductor surfaces such as the technologically important Si(001) surface, diffusion is known to be significantly anisotropic. Hence it is an interesting and important topic to understand both the degree and implications of this surface diffusion anisotropy in technological viewpoints as well as fundamental physical ones. To address this issue, we particularly consider the case of Si homoepitaxy on Si(001) surface as a model system. In the case of Si(001) surface, the diffusing adparticles could be a single Si atom or a Si dimer.

Earlier, Mo et al. dealt with the low-temperature limit with a critical cluster size equal to two, meaning that a stable island can nucleate by the meeting of just two diffusing adparticles [112,113]. In their work, it was suggested that the diffusion anisotropy $D_f/D_s$ (where $D_f$ and $D_s$ are the diffusion constants along the fast and
slow directions, respectively) could be quantified by measuring the relative width of the fast and slow “denuded zones” $W_f$ and $W_s$, these being regions close to a step at a terrace boundary where relatively few islands nucleate when the step is oriented perpendicular to the fast and slow diffusion directions, respectively. A more direct method to estimate the diffusion anisotropy would be to directly observe the diffusion of individual adparticles, and in recent years, STM has in fact been used to directly monitor diffusion anisotropy by following the motions of individual diffusing adparticles at low growth temperatures [92,114]. However, this technique is so far not applicable at higher temperatures relevant for most semiconductor growth and processing since diffusion is too rapid for STM to follow in that temperature range. Therefore, the investigation of denuded zones is very useful and probably the only way to study diffusion anisotropy at high temperatures at present.

Using dimensional arguments and Monte Carlo (MC) simulations, Mo et al., argued that the denuded-zone width $W$ should be proportional to a power of the diffusion constant $D$, $W \propto D^\alpha$ where $\alpha=1/6$ for isotropic diffusion in two dimensions, $\alpha=1/4$ for one-dimensional or highly anisotropic two-dimensional diffusion, and $\alpha$ being between the two extreme values for intermediate anisotropic cases [112,113]. Based on this, they further suggested that $W_f/W_s \approx \left(D_f/D_s\right)^\beta$ where $\beta$ is the same as $\alpha$, i.e., it should vary between 1/6 in the isotropic limit and 1/4 in the extremely anisotropic limit, by assuming that the relation $W \propto D^\alpha$ is satisfied along each (fast or slow) direction and the relation between $r_w = W_f/W_s$ and $r_D = D_f/D_s$ would be obtained simply as the direct ratio of
\( W \propto D^\alpha \) for the fast and slow directions. We note here that Mo et al. have simulated only for the fast-diffusion direction (periodic boundary conditions in the slow-diffusion direction) to investigate the relation \( W \propto D^\alpha \) and their argument for the exponent \( \beta \) assumes no correlation in adparticle motion between the fast and slow directions and treats them separately. However, this is somehow unrealistic when we consider island nucleation during epitaxy and related adparticle lifetime which is the time before an diffusing adparticle is incorporated into a step or an existing island. For instance, the adparticle lifetime along one direction can be shorter than expected just by considering the motion along that direction if an adparticle diffuses along the other direction and meets an existing island before it meeting an island by diffusing along the original direction.

Hence, in order to study the relation between \( r_w \) and \( r_D \) in a more proper way, we have performed MC simulations of diffusion in two dimensions mainly for two critical-cluster limit with a rectangular terrace geometry where the four edges (two perpendicular to fast diffusion direction and the other two perpendicular to slow diffusion direction) act as sinks for adparticles. We have also investigated the high-temperature case where the critical cluster size is much larger than two and MC technique is not applicable because of the necessary size of the simulation cell and length of the simulations, by developing and numerically solving an analytical continuum model of cluster nucleation. In both the MC simulation and the continuum model, we found that the exponent \( \beta \) is close to 1/2 independent of a wide variety of conditions including the degree of anisotropy, which is significantly inconsistent with the prediction of Mo et al.. This inconsistency makes a
large difference in particular for any attempt to determine the degree of anisotropy of the diffusion from measurements of the denuded zone widths.

5.2 Modeling of Denuded-Zone Formation

As noted above, a rectangular terrace geometry where the edges are perpendicular to either fast or slow diffusion direction is used for both the MC simulation (low-temperature cases) and the continuum model (high-temperature cases) to investigate how $W_f$ and $W_s$ vary for different diffusion anisotropies at the same time. The MC simulation which was completely done by our collaborator, Prof. Charles A. Ebner will be first introduced. Then the analytical continuum model (our main work) for high-temperature cases will be presented in detail. The modeling results have been published in Ref. 115.

5.2.1 Monte Carlo Simulation (Low Temperature Case)

The simulation model treats adparticles on a two-dimensional $N \times N$ square lattice, typically with $N=1000$. The adparticles are placed randomly on lattice sites at a steady rate $R$ particles per site, starting at time $t=0$ and continuing until time $t_0$ at which the adparticle deposition is stopped. Thus the number of monolayers (MLs) deposited is $f = Rt_0$ and is typically on the order of 0.01 ML. Once deposited, an adparticle engages in a random walk to nearest-neighbor lattice sites and the walks can be anisotropic in that the probability of a step in the fast direction may be greater than the probability of a step in the slow direction.

To simulate the situation of critical cluster size being two (low-temperature cases), walkers join to form an immobile island when they encounter each other. When a walker
encounters an edge of the system, it is removed (The edges are perfect sinks of adparticles), and when a walker encounters an island, it is incorporated into that island. The random walks are continued until no mobile adparticles are left. In many of the simulations, an island was treated as a point object, occupying a single lattice site. However, some simulations have been performed with the consideration of finite island size and anisotropy in island shape to investigate their consequences on the simulation results compared with the point islands. We have also investigated the consequences of different sticking coefficients for $S_A$ and $S_B$ steps on Si(001) (the sticking probability at $S_A$ steps appears to be smaller than the sticking probability at $S_B$ steps assumed to be unity in our simulations [113,116]), meaning that when a adparticle moving in the fast direction encounters an edge, island, or another diffusing adparticle, it adheres to that object with probability $p$ less than 1.

For a given set of conditions, simulations were repeated 3000-10000 times and the results averaged. The density of islands was computed and the denuded-zone width was determined from the criterion that the island density be, at the edge of the denuded-zone, 60% of its value at the center of the terrace. Other possible criteria were examined (such as 50% or 70% of the central island density) and were found to essentially equivalent as regards the relative size of the denuded zones.

Among the simulation results, we first consider the dependence of $W_f$ on $D_f$ for fixed $r_D$. Figure 5.1 shows results for $W_f/N$ as a function of $D_f$ for $r_D=1, 4, 9, 99, 999,$ and $9999$. Here $D_f$ is expressed in arbitrary units such that $D_f=1$ is the smallest diffusion constant simulated. The solid lines, included for reference purposes, have slopes (on a
Figure 5.1: The width of the denuded zone in the fast direction, in units of the total system width, as a function of $D_f$ for diffusion anisotropies of 1 (■), 4 (□), 9 (●), 99 (○), 999 (▲), and 9999 (△). Lines of slope (on a log-log plot) $1/6$ and $1/4$ are included for comparison.
log-log plot) of 1/6 and 1/4, describing the behavior predicted by Mo *et al.* for isotropic ($r_D = 1$) and strictly 1D ($r_D \to \infty$) diffusion. The simulation results for the isotropic diffusion (■) fit quite well a line of slope 0.19, almost 14% larger than 1/6. The deviation of the simulation results from the prediction by Mo *et al.* is believed to come about because Mo *et al.* assumes $N_v \sim N_s$ for isotropic 2D random walk in their dimensional argument where $N_v$ is the number of sites visited by a random walker and $N_s$ is the number of steps in the walk. The more correct relation is $N_v \sim N_s / \ln(N_s)$ and this can be reasonably approximated as $N_v \sim N_s$ only if $N_s$ is very large. Even for $N_s = 10^8$, the best approximated relation is $N_v \sim N_s^{0.95}$. The typical number of steps an adparticle makes in the diffusion process before hitting another object (island, adparticle, or terrace edge) is $\sim 10^3$ in our simulations. Thus $N_v$ is significantly less than proportional to $N_s$ in typical diffusion processes which is reflected in the value of extracted from the simulations. In the case of highly anisotropic diffusion, $r_D = 9999$, the system does not yet show strict 1D behavior in that the slope of log($W_f$) against log($D_f$) is still smaller than 1/4. We have done separate simulations of a strictly 1D diffusion and found that the results are best fit by a line of slope 0.256 which is very close to the prediction of Mo *et al.*

We next discuss the simulation results of the behavior of $r_w$ as a function of $r_D$. Figure 5.2 shows a plot of log($r_w$)/log($r_D$) against $r_D$ using ten different values of $D_f$ (the same as the ones shown in Figure 5.1) at each of four values of $r_D$ (4, 9, 99, and 999). The plot strongly supports the notion that $r_w$ is equal to $r_D^\beta$ where $\beta$ is close to 1/2; the simulations actually give on average a value slightly larger than 1/2. Most of the data points in the figure have an uncertainty on the order of 0.01 which comes mainly from
Figure 5.2: The logarithm of \( r_w \) divided by the logarithm of \( r_D \) as a function of \( r_D \) for \( D_f = 1 \) (■), 2 (□), 4 (●), 8 (○), 16 (▲), 32 (△), 64 (▼), 128 (▽), 256 (◆), and 512 (◇) in arbitrary units.
determining the average width of denuded zone from many individual simulations. The uncertainty becomes larger for large $r_D$ and small $D_f$ since then $W_s$ is very small and hence becomes difficult to determine precisely from our simulations. We have done further simulations to test how much the finite island size with anisotropy in shape included and the difference in adparticle sticking at $S_A$ and $S_B$ steps affect the results just described, i.e., $r_w \approx r_D^{V_2}$. For the finite island size, there is almost no effect compared with the point island cases, to the extreme that each island’s size in the fast direction is just one lattice site in extent while its length in the slow direction is equal to the number of adparticles in the island. The smaller sticking probability ($p<1$) at $S_A$ step also turns out to make relatively little differences from what is found for $p=1$ unless $p$ is less than 0.1.

More details of the simulations and other results that are not covered here are well presented in Ref. 115.

### 5.2.2 Continuum Model (High Temperature Case)

At high temperatures where a critical island consists of several hundreds of adparticles, the nucleation and growth of islands are much harder to simulate with direct MC techniques, both because the simulations must be much longer to grow the necessarily large islands and because a larger simulation cell should be used to accommodate numerous islands, each of which occupies several thousand sites. Hence we developed a continuum model of island nucleation and denuded-zone formation which considered the spatial and temporal evolution of adparticle concentration and nucleation rather than tracking the motion of each adparticle.
Figure 5.3: LEEM images of island formation on a rectangular terrace (~6 µm × 5 µm) at (a) 2 sec and (b) 16 sec, after starting Si deposition at 560 °C with a deposition rate of 0.2 ML/min.
The model is designed to closely match the experimental conditions of island nucleation and growth in the temperature range of 530-700 °C studied by Nielsen et al. [117], who used low-energy electron microscopy (LEEM) to observe Si island nucleation on large (>5 µm) step-free Si(001)-(2×1) terraces prepared by the method proposed by Tanaka et al. [118]. Figure 5.3 shows a typical nucleation sequence on a ~6 µm × 5 µm rectangular terrace measured at 560 °C and using a Si deposition flux of 0.2 ML/min. We note two main features from this sequence. First, at the time that islands start to be visible somewhat clearly to LEEM, Figure 5.3(a), around 2 sec after the start of depositing Si, they appear almost simultaneously and uniformly across the central part of the terrace, leaving well-defined denuded zones around terrace edges. (In fact, the actual island nucleation would occur before we could see the islands in LEEM because the islands the sizes of which are close to critical islands are still too small to be visible due to the limitations on the spatial resolution of LEEM.) During subsequent growth, the existing islands generally increase in size, but there is very little nucleation of new islands [Figure 5.3(b)]. Clearly, the denuded zones in the fast-diffusion direction are larger than those in the slow direction [arrows in Figure 5.3(b)]. These basic features were present for the same flux and at deposition temperatures ranging from 530 to 700 °C.

These observations suggest the following picture of island nucleation: After the Si flux is turned on at t=0, the adparticle concentration \(c(x, y, t)\) increases uniformly over the terrace except close to the edges where it is suppressed by step-edge sticking. After \(c(x, y, t)\) has reached a certain critical value (several percent above the equilibrium concentration) nucleation starts to occur [119]. Since nucleation depends strongly on
$c(x,y,t)$ according to the homogeneous nucleation theory [120] and $c(x,y,t)$ is almost constant over the central part of the terrace, initial island nucleation occurs almost simultaneously throughout the central region. Very soon after these islands appear and start to grow, they deplete surrounding areas of adparticles. Shortly thereafter the island-near areas depleted of adparticles start to overlap and quickly suppress new nucleation. The islands continue to grow as they absorb deposited Si, but few new islands form. With the continuum model, we model and test this scenario.

The basic scheme of the continuum model is the following. We solve the time-dependent diffusion equation to find how adparticle concentration $c(x,y,t)$ increases with time by assuming a set of step and adparticle parameters, including $D_f$, which are appropriate for a given experimental growth condition; these parameters are obtained from the literature [92,114,119,121,122]. Then we estimate the time-integrated island density $\omega(x,y,t)$ across the terrace using an expression for the island nucleation rate proposed by Theis and Tromp [119], based on the homogeneous nucleation theory. The calculation is continued up to the time $\tau_n$ when the area-integrated total number of islands $\Omega(t)$ is equal to the measured number of islands for that growth condition. The size of the fast ($W_f$) and slow ($W_s$) denuded zones is determined by finding the contour along which island density $\omega(x,y,t)$ is equal to a fixed fraction (70 or 90 %) of the value at the terrace center. Finally, the denuded-zone ratio $r_w$ is compared to the diffusion constant ratio $r_D$. 
The time-dependent diffusion equation describing the adparticle concentration on
the terrace prior to island nucleation is written as [123,124]

\[
D_f \frac{\partial^2 c(x,y,t)}{\partial x^2} + D_s \frac{\partial^2 c(x,y,t)}{\partial y^2} + R = \frac{\partial c(x,y,t)}{\partial t},
\]

(5.1)

where \( R \) is the Si deposition rate. The equation 5.1 is subject to the following boundary
conditions at the terrace boundary [123,125] balancing the net diffusion current toward
the step edge with the net rate at which adparticles attach to the step edge:

\[
D_f \frac{\partial c(x,y,t)}{\partial x} = \mp \kappa A \left[ c(\pm L_f/2,y,t) - c_{eq} \right],
\]

(5.2)

\[
D_s \frac{\partial c(x,y,t)}{\partial y} = \mp \kappa A \left[ c(x,\pm L_s/2,t) - c_{eq} \right],
\]

(5.3)

where \( \kappa_{A,B} \) is the adparticle attachment rate at \( S_{A,B} \) step edges, and \( c_{eq} \) is the equilibrium
adparticle concentration. The terrace size in the fast direction \( (L_f) \) is 6 µm and that in the
slow direction \( (L_s) \) is 5 µm.

The nucleation rate of stable islands based on the homogeneous nucleation theory
[119,120] has been given as

\[
\omega(x,y,t) = 2\sqrt{\pi N} \frac{\Gamma}{a^2 k_B T} c e^{-\beta a \sqrt{\pi N}},
\]

(5.4)

which is rewritten as

\[
\omega(x,y,t) = \frac{2\Gamma}{a^2 k_B T} \left( \frac{c}{\ln(c/c_{eq})} \right) \exp \left[-\frac{A}{\ln(c/c_{eq})} \right],
\]

(5.5)

where \( A = \left( a^2 \sqrt{\pi/k_B T} \right)^2 \), \( a^2=0.29 \) nm \(^2\) is the squared lattice spacing for a diffusing
adparticle, assumed here to be a Si dimer [114,122,124,126], \( N \) is the number of dimers

\[152\]
in a critical island, $\Gamma$ is the step mobility, which is related to the step attachment rate by $\kappa = \Gamma / \left( a^4 c_{eq} \right) [123]$, and $\beta$ is the step-free energy. Here it is considered that the relation of $N$ and the adparticle chemical potential ($\mu_{\text{adparticle}}$) is given as $\sqrt{N} = a \beta \sqrt{\pi} / \mu_{\text{adparticle}}$, derived from the condition $d\Delta G / d\rho = 0$ where $\Delta G$ is the free energy cost of creating an island with radius $\rho [119]$. The $\mu_{\text{adparticle}}$ relates to the local adparticle density ($c$) as $\mu_{\text{adparticle}} = k_B T / \ln \left( c / c_{eq} \right) [119,120]$.

Table 5.1 lists the parameter values used in the modeling for $T = 560$ °C, except for $D_s$. In our modeling, $D_s$ is a variable giving rise to different $r_D$ (1, $10^{1/2}$, 10, $10^{3/2}$, $10^2$, $10^{5/2}$, and $10^3$) with $D_f$ fixed because its temperature-dependent values have not been well-established experimentally yet as well as the other parameters.

<table>
<thead>
<tr>
<th>$c_{eq}$ (nm$^{-2}$)</th>
<th>$D_f$ (nm$^2$/s)</th>
<th>$\beta$ (eV/nm)</th>
<th>$\Gamma$ (nm$^3$/s)</th>
<th>$\kappa_A \approx \kappa_B$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02587 [122]</td>
<td>$6.1 \times 10^5$ [92,114]</td>
<td>0.072 [121]</td>
<td>19.60 [119,121]</td>
<td>8.71 $\times 10^3$ [119]</td>
</tr>
</tbody>
</table>

Table 5.1: Model parameter values at 560 °C referred to the literature in the table: $R = 3.5 \times 10^{-3}$ ML/s

Figure 5.4 shows how the total island number $\Omega(t)$ varies with the deposition time for $r_D = 10^{3/2}$. We see that $\Omega(t)$ increases very abruptly after “first” island nucleates at $t \approx 0.11$ sec until $\Omega(t) \approx 177$ (the measured number of islands at $T = 560$ °C) at $t \approx 0.17$ sec. These times roughly correspond to the experiment, where the actual island nucleation was expected to occur well before it became visible to LEEM at $t \approx 2$ sec.
Figure 5.4: Number of stable islands depending on deposition time at 560 °C for $r_D=10^{3/2}$; it reaches one around 0.11 sec and ~177 (the number observed in the experiment) around 0.17 sec after starting Si deposition.
Figure 5.5: Adparticle concentrations with respect to equilibrium adparticle concentration (dotted lines) and stable island densities with respect to the terrace center density (solid lines) in the (a) fast and (b) slow directions at 560 °C for \( r_{D} = 10^{3/2} \) when the number of nucleated islands reaches \( \sim 177 \) observed in experiment; the arrows represent the denuded zones based on 70 % island density criterion for the denuded-zone boundary.
Figure 5.5 shows profiles of the adparticle concentration $c(x,y,t)$ and the island density $\omega(x,y,t)$ in the (a) fast and (b) slow directions for $r_D=10^{3/2}$, at $t=\tau_n$ when nucleation is assumed to stop. We see that both $c(x,y,t)$ and $\omega(x,y,t)$ are roughly constant around the terrace center, and are suppressed at the terrace edges with longer-range suppression in the fast direction. However, the suppression is significantly stronger for $\omega(x,y,t)$ than for $c(x,y,t)$, which is due to the strong dependence of the island nucleation rate on adparticle concentration as shown in Eq. 5.5. This modeling result is consistent with the experimental observation of relatively distinct denuded-zone boundaries. The arrows in Figures 5.5(a) and 5.5(b) indicate the fast and slow denuded-zone widths, respectively assuming a 70 % criterion for the denuded-zone boundary.

The relation between $r_w$ and $r_D$ from the modeling is illustrated in Figure 5.6, clearly showing that $r_w \approx r_D^{\beta}$ where $\beta$ is very nearly 1/2. We have used another criterion (90 % island density) to determine the width of denuded zones to see if the arbitrariness in defining denuded zones affects the exponent $\beta$. Although the denuded-zone width itself in each direction definitely depends on the choice, $r_w$ is found to be quite insensitive to it.

The relation $r_w \approx r_D^{1/2}$ from our modeling is in fact quite reasonable physically. As Mo et al. pointed out, denuded-zone formation is related to a characteristic maximum adparticle lifetime $\tau_n$ before it is incorporated into a step or an existing island. As discussed previously, this corresponds to the moment when nucleated islands on the terrace become sufficiently numerous and large as to soak up diffusing adparticles, effectively suppressing the adparticle concentration and hence also new island nucleation.
Figure 5.6: $r_w$ vs. $r_D$ at 560 °C: The slope (on a log-log plot) is 0.48±0.002.
During this time period, an adparticle can diffuse characteristic distances $\sqrt{D_f \tau_n}$ and $\sqrt{D_s \tau_n}$ in the fast and slow directions, respectively. If an adparticle encounters a step during this time, it may attach to the step and hence reduce the local adparticle concentration. Consequently, there will be generated “zones” of reduced adparticle concentration, eventually resulting in reduced nucleated island density (denuded zone), with approximate width $W_f \propto \sqrt{D_f \tau_n}$ and $W_s \propto \sqrt{D_s \tau_n}$ near steps along the fast and slow directions, respectively. Hence the relation $W_f / W_s \approx (D_f / D_s)^{1/2}$ is naturally expected. Consistently with the earlier discussion for the MC simulations, this approximate relation only breaks down if sticking at step edges is highly anisotropic, since this would affect the relative sizes of $W_f$ and $W_s$, quite independently of $D_f$ and $D_s$.

It is worthwhile to note that a similar relation was also used in the measurements of annealing-induced extension of denuded zones on Si(001) as a function of sample annealing time $t_{\text{anneal}}$ after depositing Si at room temperature, done by Doi et al. [127]. They also observed the annealing-induced denuded zones along the fast and slow directions to be anisotropic, and the denuded zone along each direction follows the approximate relation $W(t_{\text{anneal}}) \approx \sqrt{t_{\text{anneal}}}$. Based on this observation, they then assumed that $W_{f,s}(t_{\text{anneal}}) \approx \sqrt{D_{f,s} t_{\text{anneal}}}$ in each direction, from which the relation $W_f / W_s \approx (D_f / D_s)^{1/2}$ is deduced.
5.3 Summary

We have studied how the formation of denuded zones is related to adparticle diffusion during growth on surfaces with anisotropic diffusion by using MC simulations and a continuum model. In the limit of small critical clusters consisting of just two adparticles (low-temperature case), our MC simulations demonstrate that the relative size of denuded zones in the fast- and slow-diffusion directions is proportional to the ratio of diffusion constants with a power of 1/2, i.e., $W_f/W_s \approx (D_f/D_s)^{\beta}$, $\beta \approx 1/2$ [115]. The same relation was obtained in the large-critical-cluster limit (high temperature case) from a continuum model based on homogeneous nucleation theory [119,120]. These results are quite different from the earlier report of Mo et al. [112,113], which predicted the power between 1/6 and 1/4 depending on the degree of anisotropy in adparticle diffusion. The relation between the relative size of denuded zones and the ratio of diffusion constants obtained from our modeling can supply a relatively simple way to extract diffusion anisotropy from the denuded zones measurable in epitaxial growth experiments.

We have also investigated the effect of anisotropic sticking of adparticles to step edges on denuded-zone formation and anisotropy. It turned out that as long as the smaller probability of sticking is not less than about 0.1, the relation $W_f/W_s \approx (D_f/D_s)^{1/2}$ could be used to obtain the diffusion anisotropy with a relatively small error.
6.1 Major findings

We have used the noble technique of ballistic electron emission microscopy (BEEM) to characterize the electronic properties of stacking-fault (SF) planar inclusions with local either 3C (cubic) or 8H stacking sequence formed in hexagonal SiC in various circumstances. The conduction band quantum well (QW) behavior of the inclusions expected from the polytype-dependence of the electronic band structure of SiC was confirmed by directly measuring and comparing the local Schottky barrier heights (SBHs) of the identically-prepared metal (Pt) contact on and away from the inclusions. For the single Shockley type SF 3C inclusions (referred to as 1SF inclusions) formed during 4H-SiC p-i-n diode operation, the QW energy level was measured to be \(~0.25\) eV below the 4H-SiC conduction band minimum (CBM) [111]. This is shallower than the previously measured QW energy level (\(~0.53\) eV) of the double SF (2SF) 3C inclusions found in heavily n-type doped 4H-SiC processed at high temperature [97]. On the 2SF 3C inclusion sample, we have also found that the presence of inclined QWs under a Schottky contact could affect measured conventional capacitance-voltage (C-V) curves...
significantly by reducing the intercept voltage (but not the slope), resulting in the reduction of apparent $C-V$ determined SBH. Together with finite-element electrostatic modeling, the QW energy depth of the 2SF 3C inclusions in the bulk away from the M/S interface was estimated to be $\sim 0.51$ eV from measured C-V curves, close to the BEEM-measured QW energy depth ($\sim 0.53$ eV) near the interface [100].

The most recently-discovered SF 8H inclusions observed in 4H-SiC epilayer grown by chemical vapor deposition also have been studied with BEEM and their QW energy depth was measured to be $\sim 0.39$ eV (Section 4.3.1). Additionally, on the 8H inclusion sample, the local SBH on the remnant of 8H inclusion exposed on surface was measured to be larger than on the surrounding 4H-SiC area. This is very likely to be direct effect of the spontaneous polarization (SP) difference between the inclusion remnant and 4H-SiC host on measured SBH, which would induce a negative bound charge at the interface of the thin remnant layer and the underlying 4H-SiC (Section 4.3.2). The strong reflection of injected hot electrons from the subsurface 8H inclusion was observed as well, causing the asymmetry of BEEM current amplitude across the inclusion. Based on the observed suppression of BEEM current on one side from the inclusion opening on surface and its gradual increase as moving away from the opening, we could estimate the attenuation length of hot electrons in 4H-SiC (Section 4.3.3).

The valence band structures of 3C- and 4H-SiC and their valence band offset (VBO) have been investigated by measuring p-type SBHs on the identically prepared samples of the two polytypes using ballistic hole emission microscopy (BHEM) (Section 4.5.3). The p-type SBH on 3C-SiC was measured to be $\sim 0.06$ eV higher than that on 4H-
SiC measured previously [47]. This indicates that the bulk VBO between the two polytypes is the same amount with the valence band maximum of 3C-SiC lower than 4H-SiC. The difference in crystal-field splitting of 3C- and 4H-SiC, predicted theoretically, was also demonstrated experimentally for the first time, based on the existence of the second threshold in the BHEM spectra on 4H-SiC that was not observed in the BHEM spectra on 3C-SiC (Section 4.5.4). The crystal-field split band in 4H-SiC is estimated to be \(~110\) meV below the highest valence band [47].

In collaboration with Prof. Charles A. Ebner, we have studied the denuded-zone formation in Si epitaxy on Si(001) using Monte Carlo (MC) simulation and continuum model. Both MC simulation suitable for low-temperature cases (small critical cluster) and continuum model for high temperature cases (large critical cluster) show that the ratio of denuded zones along the fast and slow diffusion directions scales with the ratio of corresponding diffusion constants with a power of \(1/2\), which is quite different from the earlier prediction of the power between \(1/6\) and \(1/4\) [115].

6.2 Future directions

Although several important properties of SiC related to energy band structure have been studied in a quantitative way during the course of this work, there are still many issues with regard to its electronic properties that can be addressed using the unique capability of BEEM to measure local SBHs with nm-scale spatial resolution and high energy resolution. One of them is the SP difference between different polytypes. In the study of our 8H inclusion sample, we have observed the effect of SP difference on the local SBH but we could not quantify the difference and further the SP of 4H-SiC host
because of the difficulty in determining the detailed sample structure on surface. However, if we could have the sample structure suitable for this purpose such as well-isolated thin 3C layers epitaxially grown on 4H- or 6H-SiC, it would certainly be possible to measure the SP in the underlying hexagonal polytype quantitatively by measuring the increase of local SBH through the 3C layers with BEEM. The same type of measurement can also be performed to other material systems where the polarization effect on energy band profile is expected such as III-nitride heterostructures. Especially, by performing BEEM measurements on the cross-section of the heterostructure (its possibility has been already proven by the previous work in our group [87]), it would be possible to measure the energy band profile across the heterostructure interface with polarization effect expected. This measurement would be very meaningful in the sense of device application as well as fundamental physics sense.

Another valuable topic is to further confirm the hexagonality dependence of crystal-field splitting in SiC valence band structure. In our work, we have experimentally demonstrated the difference of the splitting between 3C- and 4H-SiC. However, if we can measure the crystal-field splitting on other available polytypes such as 6H- and 15R-SiC and investigate its dependence on hexagonality together with the measurements in this work, it could be a very systematic study to verify the validity of the theoretical prediction.

As shown in our study of single SF 3C inclusion sample, the chemi-mechanical polishing does not destroy the structural property of the material surface significantly, also not the electrical property of the metal contact made on the polished surface. Hence
we can adopt this polishing method to expose other types of extended defects on sample surface at least for SiC to investigate their electrical properties. This type of experiment would also be very valuable in both fundamental material property aspect and device application sense.
APPENDIX A

DATA PROCESSING PROGRAMS

Conversion of binary raw data file to WSxM format

convert_WSxM_stm_beem.cpp:

```c
#define version "convert_UHV3_WSxM v1"

#include <stdio.h>
#include <stdlib.h>
#include <string.h>
#include <stddef.h>
#include <ctype.h>
#include "WSxM_header.h"

int pixels, xsize, ysize, anggain, pagain, linecompt;
long ptnumber;
double factor_stm=32768, factor_beem=32768, xspace, yspace, x, y;
char infname[80], outfname_stm[80], outfname_beem[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_stm, infname);
strcpy(outfname_beem, infname);

strcat(infname, ".dat");
strcat(outfname_stm, ".stm");
strcat(outfname_beem, "_beem.stm");

if((fi=fopen(infname,"rb"))==NULL)
{
    printf("\nREAD: Can't open file %s\n\n",infname);
    return;
}
else
{
    pixels=getword(fi);
    fseek(fi,4L,SEEK_CUR);
    ysize=getword(fi);
    xsize=getword(fi);
    anggain=getword(fi);
    factor_stm/=(anggain/10);
    pagain=getword(fi);
    factor_beem/=pagain;
    linecompt=getword(fi);

    ptnumber=pixels*linecompt;
    xspace=((double)xsize)/((double)pixels)/10;
    yspace=((double)ysize)/((double)pixels)/10;

    fo=fopen(outfname_stm,"w");
    // WSxM requirements
    // Nanotec copyright
    fprintf (fo, NANOTEC_COPYRIGHT);
    // Is a three columns ASCII file
    fprintf (fo, WSXM_XYZ_ASCII_FILE);
    // Selecting units
    fprintf (fo, "X[nm]\tY[nm]\tZ[nm]\n");

    for(i=0; i<linecompt; i++)
    {
        for(j=0; j<pixels; j++){
            x=xspace*j;
            y=yspace*i;
            fprintf(fo, "%lf\%lf\%lf\n", x, y,
            getword(fi)/factor_stm);
        }
    }
    fclose(fo);

    fo=fopen(outfname_beem,"w");
    // WSxM requirements
    // Nanotec copyright
    fprintf (fo, NANOTEC_COPYRIGHT);
    // Is a three columns ASCII file
    fprintf (fo, WSXM_XYZ_ASCII_FILE);
// Selecting units
fprintf (fo, "X[nm]\t\tY[nm]\t\tZ[nm]\n");

for(i=0; i<linecompt; i++)
{
    for(j=0; j<pixels; j++){
        x=xspace*j;
        y=yspace*i;
        fprintf(fo, "%lf\t%lf\t%lf\n", x, y,
        getword(fi)/factor_beem);
    }
}
fclose(fo);

fclose(fi);
printf("\ndata converted successfully.\n");
}
Calculation of conversion matrix of Savitzky-Golay method in Maple V

```
> restart;
> with(linalg):

> nl:=10: nr:=10: k:=4: dn:=0.0000000001:
> f := (i,j) -> (i-(nl+dn+1))^(j-1):
> A := evalf(matrix(nl+nr+1,k+1,f));
> At := evalf(transpose(A));
> AtA := evalm(At &* A):
> inv_AtA := inverse(AtA):
> f2 := (a,b) -> if (a=b) then 1 else 0 fi:
> e_n := matrix(nl+nr+1,nl+nr+1,f2):
> C:=evalm(inv_AtA &* At &* e_n);

C :=

[[.0447204970 , -.0248447204 , -.0500163451 , -.0431513566 ,
  -.01515297192 , .02452935409 , .06789992889 , .1084168221 ,
  .1409918659 , .1619906544 , .1692325443 , .1619906544 ,
  .1409918659 , .1084168221 , .06789992889 , .02452935409 ,
  -.01515297192 , -.0431513566 , -.0500163451 , -.0248447204 , .0447204970],

[[.02313507751 , .00276052452 , -.01191054050 , -.02151183843 ,
  -.02667709017 , -.02804001660 , -.02623433859 ,
  -.02189377705 , -.01565205284 , -.008142886861 ,
  -.8248507009 10^-12 , .008142886861 , .01565205284 ,
  .02189377705 , .02623433859 , .02804001660 , .02667709017 ,
  .02151183843 , .01191054050 , -.0276052452 , -.02313507751],

[[-.00642292490 , .00197628458 , .00608487622 , .00703834686 ,
  .005838605469 , .003353973173 , .000319183218 ,
  -.002664618999 , -.005129875957 , -.006742617995 ,
  -.007302463319 , -.006742617995 , -.005129875957 ,
  -.002664618999 , .000319183218 , .003353973173 ,
  .005838605469 , .00703834686 , .00608487622 , .00197628458 , -.00642292490],

[[-.000548967940 , -.0002195871756 , .0000231144398 ,
  .0001887679235 , .0002870042917 , .0003274545610 ,
  .0003197497478 , .0002735208686 , .0001983989399 ,
  .00001040149782 , .1056201476 10^-13 , .00001040149782 ,
  -.0001983989399 , -.0002735208686 , -.0003197497478 ,
  -.0003274545610 , -.0002870042917 , -.0001887679235 ,
  -.0000231144398 , .0002195871756 , .000548967940]]
```

168
[.0000988142293, .1 \times 10^{-12}, -.0000520074891, 
-.0000693433187, -.00006271491320, -.00004140204031, 
-.00001325681093, .00001529632032, .00003926055548, 
.00005506675315, .00006057342846, .00005506675315, 
.00003926055548, .00001529632032, -.00001325681093, 
-.00004140204031, -.00006271491320, -.0000693433187, 
-.0000520074891, .1 \times 10^{-12}, .0000988142293]
APPENDIX B

FINITE-ELEMENT MODELING PROGRAM

Sample FlexPDE script of electrostatic modeling

{This program is for estimating the quantum well energy of 3C-inclusion in 4H SiC, based on C-V calculation, with considering Spontaneous Polarization.}
{Spacing between inclusions = 570 nm (Diode D3 on the dimpled sample), thickness of inclusion=1.25nm, Doping=1.25e23 m^-3, number of conduction band minima=3}

title '3C-inclusion in 4H-SiC'

select
errlim = 1.0e-5
gridlimit = 30
surfacegrid=12500

coordinates
cartesian('X','Z')

Variables
u(range= -5, 5)

definitions {length is in m, electronic potential is in V, and temperature is 300K.}
{fundamental constants}
eps0=8.854e-12 {vacuum permittivity, F/m}
ec=1.602e-19 {electron charge, coulomb}
h=1.05459e-34 {Planck's constant, Js}
m_0=9.11e-31 {electron rest mass, Kg}

{define geometry}
thick=1.25e-9 \{thickness of inclusion in the bulk\}
spacing = 570e-9 \{spacing between inclusions on the sample surface\}
Lxl= 6 * spacing + 1000e-9 \{lateral size to the left\}
Lxr=2 * spacing + 4500e-9 \{lateral size to the right\}
Lz= -650e-9 \{depth of sample = 650 nm\}
d_inc= -500e-9 \{depth of inclusion = 500 nm\}

theta=(3.141592/180)*(-8) \{sample miscut or tilt of inclusion from the surface\}
w3c=abs( thick / sin(theta) ) \{width of 3C-Inclusion opening\}

icenter6l= -6 * spacing \{the center of the 3C-inclusion6l opening\}
icenter5l= -5 * spacing \{the center of the 3C-inclusion5l opening\}
icenter4l= -4 * spacing \{the center of the 3C-inclusion4l opening\}
icenter3l= -3 * spacing \{the center of the 3C-inclusion3l opening\}
icenter2l= -2 * spacing \{the center of the 3C-inclusion2l opening\}
icenter1l= -1 * spacing \{the center of the 3C-inclusion1l opening\}
icenterc= 0e-9 \{the center of the 3C-inclusionc opening\}
icenter1r= 1 * spacing \{the center of the 3C-inclusion1r opening\}
icenter2r= 2 * spacing \{the center of the 3C-inclusion2r opening\}

\{material parameters\}
m_eff_3C=0.316*m_0 \{effective mass of electrons in 3C-SiC in [111] direction\}
eps=9.7 \{dielectric constant of SiC\}
P_4H=1.1e-2 \{spontaneous polarization of 4H-SiC, C/m^2\}
Nd=1.25e23 \{dopant density\}
Nc=1.83e25
N3c=(1.17e17)/thick

del_Ec = 0.925 \{difference of conduction band minimum of 3C and 4H\}
Ec_off_4H=1.60 \{4H SBH=1.60 eV w/o considering image force lowering\}
Ec_off_3C=E_{off, 4H} - del_Ec \{3C-Inclusion Schottky barrier\}

E_{0}=0.405

\{calculation parameters\}
Ec_{off}
n_c
dist

Vn=0.129
Vb= -0.0
dVb= -0.0

V = Ec_{off} - u
D_\_V = \text{if} \ ( (V_b+dV_b-V) > 8.5 ) \ \text{then} \ 8.5 \ \text{else if} \ ( (V_b+dV_b-V) < -8.5 ) \ \text{then} \ -8.5 \ \text{else} \ V_b+dV_b-V

Q = \text{line_integral}((DZ(u)) \cdot \varepsilon \cdot \varepsilon_0, 'chargeline')

\text{e_field} = DZ(u)

\text{equations}
\text{div}((-1) \cdot \varepsilon \cdot \varepsilon_0 \cdot \text{grad}(u)) = \text{elec} \cdot (N_d - n_c)

\text{boundaries}
\text{region 1 'entire'}
\text{dist}=0
\text{Ec_off}=\text{Ec_off}_4H
n_c=N_c \cdot \exp\left( \frac{D_\_V}{0.0259} \right)
\text{start}(-Lxl,0)
\text{natural}(u)=0 \text{ line to } (-Lxl,Lz)
\text{value}(u)=V_n + V_b+dV_b - Ec_off_4H \text{ line to } (Lxr,Lz)
\text{natural}(u)=0 \text{ line to } (Lxr,0)
\text{value}(u)=0 \text{ line to finish}

\text{region 2 '3C-inclusion6l'}
\text{dist}=\text{abs}( (X-icenter6l-w3c/2)*\sin(\theta) - Z*\cos(\theta) )
\text{Ec_off}=\text{Ec_off}_3C
n_c=N3c \cdot \text{LN}(1+\exp( \frac{D_\_V+P_4H/\varepsilon/\varepsilon_0*\text{dist}-E_0}{0.0259})
\text{start}(icenter6l - w3c/2,0)
\text{natural}(u)=(-1)*(-P_4H) \text{ line to } (d_{inc}/\tan(\theta)+(icenter6l-w3c/2),d_{inc})
\text{natural}(u)=0 \text{ line to } (d_{inc}/\tan(\theta)+(icenter6l+w3c/2),d_{inc})
\text{natural}(u)=(-1)*(P_4H) \text{ line to } (icenter6l+w3c/2,0)
\text{line to finish}

\text{region 3 '3C-inclusion5l'}
\text{dist}=\text{abs}( (X-icenter5l-w3c/2)*\sin(\theta) - Z*\cos(\theta) )
\text{Ec_off}=\text{Ec_off}_3C
n_c=N3c \cdot \text{LN}(1+\exp( \frac{D_\_V+P_4H/\varepsilon/\varepsilon_0*\text{dist}-E_0}{0.0259})
\text{start}(icenter5l - w3c/2,0)
\text{natural}(u)=(-1)*(-P_4H) \text{ line to } (d_{inc}/\tan(\theta)+(icenter5l-w3c/2),d_{inc})
\text{natural}(u)=0 \text{ line to } (d_{inc}/\tan(\theta)+(icenter5l+w3c/2),d_{inc})
\text{natural}(u)=(-1)*(P_4H) \text{ line to } (icenter5l+w3c/2,0)
\text{line to finish}
region 4 '3C-inclusion4l'
\[
\text{dist} = \text{abs}((X - \text{icenter4l} - 3c/2)\sin(\theta) - Z\cos(\theta))
\]
\[
\text{Ec\_off} = \text{Ec\_off\_3C}
\]
\[
\text{n\_c} = N3c \times \ln\left(1 + \exp\left(\frac{D_V + P4H/\varepsilon/\varepsilon0\times\text{dist}-E_0}{0.0259}\right)\right)
\]
\[
\text{start(icernter4l} - w3c/2,0)
\]
\[
\text{natural(u)}\被视为\line\to (d\_inc/tan(\theta)+(icernter4l-w3c/2),d\_inc)
\]
\[
\text{natural(u)}\被视为\line\to (d\_inc/tan(\theta)+(icernter4l+w3c/2),d\_inc)
\]
\[
\text{natural(u)}\被视为\line\to (icernter4l+w3c/2,0)
\]
\[
\text{line to finish}
\]

region 5 '3C-inclusion5l'
\[
\text{dist} = \text{abs}((X - \text{icenter5l} - 3c/2)\sin(\theta) - Z\cos(\theta))
\]
\[
\text{Ec\_off} = \text{Ec\_off\_3C}
\]
\[
\text{n\_c} = N3c \times \ln\left(1 + \exp\left(\frac{D_V + P4H/\varepsilon/\varepsilon0\times\text{dist}-E_0}{0.0259}\right)\right)
\]
\[
\text{start(icernter5l} - w3c/2,0)
\]
\[
\text{natural(u)}\被视为\line\to (d\_inc/tan(\theta)+(icernter5l-w3c/2),d\_inc)
\]
\[
\text{natural(u)}\被视为\line\to (d\_inc/tan(\theta)+(icernter5l+w3c/2),d\_inc)
\]
\[
\text{natural(u)}\被视为\line\to (icernter5l+w3c/2,0)
\]
\[
\text{line to finish}
\]

region 6 '3C-inclusion6l'
\[
\text{dist} = \text{abs}((X - \text{icenter6l} - 3c/2)\sin(\theta) - Z\cos(\theta))
\]
\[
\text{Ec\_off} = \text{Ec\_off\_3C}
\]
\[
\text{n\_c} = N3c \times \ln\left(1 + \exp\left(\frac{D_V + P4H/\varepsilon/\varepsilon0\times\text{dist}-E_0}{0.0259}\right)\right)
\]
\[
\text{start(icernter6l} - w3c/2,0)
\]
\[
\text{natural(u)}\被视为\line\to (d\_inc/tan(\theta)+(icernter6l-w3c/2),d\_inc)
\]
\[
\text{natural(u)}\被视为\line\to (d\_inc/tan(\theta)+(icernter6l+w3c/2),d\_inc)
\]
\[
\text{natural(u)}\被视为\line\to (icernter6l+w3c/2,0)
\]
\[
\text{line to finish}
\]

region 7 '3C-inclusion7l'
\[
\text{dist} = \text{abs}((X - \text{icenter7l} - 3c/2)\sin(\theta) - Z\cos(\theta))
\]
\[
\text{Ec\_off} = \text{Ec\_off\_3C}
\]
\[
\text{n\_c} = N3c \times \ln\left(1 + \exp\left(\frac{D_V + P4H/\varepsilon/\varepsilon0\times\text{dist}-E_0}{0.0259}\right)\right)
\]
\[
\text{start(icernter7l} - w3c/2,0)
\]
\[
\text{natural(u)}\被视为\line\to (d\_inc/tan(\theta)+(icernter7l-w3c/2),d\_inc)
\]
\[
\text{natural(u)}\被视为\line\to (d\_inc/tan(\theta)+(icernter7l+w3c/2),d\_inc)
\]
\[
\text{natural(u)}\被视为\line\to (icernter7l+w3c/2,0)
\]
\[
\text{line to finish}
\]

region 8 '3C-inclusion8l'
\[
\text{dist} = \text{abs}((X - \text{icenter8l} - 3c/2)\sin(\theta) - Z\cos(\theta))
\]
\[
\text{Ec\_off} = \text{Ec\_off\_3C}
\]
\[
\text{n\_c} = N3c \times \ln\left(1 + \exp\left(\frac{D_V + P4H/\varepsilon/\varepsilon0\times\text{dist}-E_0}{0.0259}\right)\right)
\]

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start(icenterc - w3c/2,0)
natural(u)=(-1)*(-P_4H) line to (d_inc/tan(theta)+(icenterc-w3c/2),d_inc)
natural(u)=0 line to (d_inc/tan(theta)+(icenterc+w3c/2),d_inc)
natural(u)=(-1)*(P_4H) line to (icenterc+w3c/2,0)
line to finish

region 9 '3C-inclusion1r'
  dist=abs( (X-icenter1r-w3c/2)*sin(theta) - Z*cos(theta) )
  Ec_off=Ec_off_3C
  n_c=N3c * LN( 1+exp( (D_V+P_4H/eps/eps0*dist-E_0) / 0.0259) )
start(icenter1r - w3c/2,0)
natural(u)=(-1)*(-P_4H) line to (d_inc/tan(theta)+(icenter1r-w3c/2),d_inc)
natural(u)=0 line to (d_inc/tan(theta)+(icenter1r+w3c/2),d_inc)
natural(u)=(-1)*(P_4H) line to (icenter1r+w3c/2,0)
line to finish

region 10 '3C-inclusion2r'
  dist=abs( (X-icenter2r-w3c/2)*sin(theta) - Z*cos(theta) )
  Ec_off=Ec_off_3C
  n_c=N3c * LN( 1+exp( (D_V+P_4H/eps/eps0*dist-E_0) / 0.0259) )
start(icenter2r - w3c/2,0)
natural(u)=(-1)*(-P_4H) line to (d_inc/tan(theta)+(icenter2r-w3c/2),d_inc)
natural(u)=0 line to (d_inc/tan(theta)+(icenter2r+w3c/2),d_inc)
natural(u)=(-1)*(P_4H) line to (icenter2r+w3c/2,0)
line to finish

feature 1 'focus'
start(-20e-9,0e-9) line to (-20e-9,-100e-9) to (80e-9,-100e-9) to (80e-9,0e-9) to finish

feature 2 'chargeline'
start(-spacing/2,0e-9) line to (spacing/2,0e-9)

monitors
elevation(e_field) from ( (-spacing/2)+(0e-9)/tan(-theta), 0e-9) to ( (spacing/2)+(0e-9)/tan(-theta), 0e-9)

elevation(V) from ( (-spacing/2)+(0e-9)/tan(-theta), 0e-9) to ( (spacing/2)+(0e-9)/tan(-theta), 0e-9)
elevation(V) from ( (-spacing/2)+(0.1e-9)/tan(-theta), -0.1e-9) to ( (spacing/2)+(0.1e-9)/tan(-theta), -0.1e-9)
elevation(V) from ( (-spacing/2)+(0.5e-9)/tan(-theta), -0.5e-9) to ( (spacing/2)+(0.5e-9)/tan(-theta), -0.5e-9)
elevation(V) from ( (-spacing/2)+(1e-9)/tan(-theta), -1e-9) to ( (spacing/2)+(1e-9)/tan(-theta), -1e-9)
elevation(V) from \((-\text{spacing}/2)+(10\text{e-9})/\tan(-\theta), -10\text{e-9})\) to \((\text{spacing}/2)+(10\text{e-9})/\tan(-\theta), -10\text{e-9})\)

elevation(V) from \((-\text{spacing}/2)+(50\text{e-9})/\tan(-\theta), -50\text{e-9})\) to \((\text{spacing}/2)+(50\text{e-9})/\tan(-\theta), -50\text{e-9})\)

elevation(V) from \((-\text{spacing}/2)+(150\text{e-9})/\tan(-\theta), -150\text{e-9})\) to \((\text{spacing}/2)+(150\text{e-9})/\tan(-\theta), -150\text{e-9})\)

elevation(V) from \((\text{thick}/2)*(-1), 0\text{e-9})\) to \((\text{thick}/2)*(-1), -50\text{e-9})\)

elevation(V) from \((\text{thick}/2)*(0), 0\text{e-9})\) to \((\text{thick}/2)*(0), -50\text{e-9})\)

elevation(V) from \((\text{thick}/2)*(1), 0\text{e-9})\) to \((\text{thick}/2)*(1), -50\text{e-9})\)

elevation(V) from \((\text{thick}/2)*(2), 0\text{e-9})\) to \((\text{thick}/2)*(2), -50\text{e-9})\)

elevation(V) from \((\text{thick}/2)*(5), 0\text{e-9})\) to \((\text{thick}/2)*(5), -50\text{e-9})\)

elevation(V) from \((\text{thick}/2)*(10), 0\text{e-9})\) to \((\text{thick}/2)*(10), -50\text{e-9})\)

elevation(V) from \((\text{spacing}/2)+(10\text{e-9})/\tan(-\theta), -10\text{e-9})\) to \((\text{spacing}/2)+(10\text{e-9})/\tan(-\theta), -10\text{e-9})\)

elevation(V) from \((-0\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))/\tan(-\theta) - 2.5\times\text{spacing}, -0\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))\) to \((-0\text{e-9}/\tan(-\theta)-1.5\times\text{spacing}, -0\text{e-9})\)

elevation(V) from \((-50\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))/\tan(-\theta) - 2.5\times\text{spacing}, -50\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))\) to \((-50\text{e-9}/\tan(-\theta)-1.5\times\text{spacing}, -50\text{e-9})\)

elevation(V) from \((-150\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))/\tan(-\theta) - 2.5\times\text{spacing}, -150\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))\) to \((-150\text{e-9}/\tan(-\theta)-1.5\times\text{spacing}, -150\text{e-9})\)

elevation(V) from \((-350\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))/\tan(-\theta) - 2.5\times\text{spacing}, -350\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))\) to \((-350\text{e-9}/\tan(-\theta)-1.5\times\text{spacing}, -350\text{e-9})\)

elevation(V) from \((-500\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))/\tan(-\theta) - 2.5\times\text{spacing}, -500\text{e-9}+\text{spacing}\times\sin(-\theta)\times\cos(-\theta))\) to \((-500\text{e-9}/\tan(-\theta)-1.5\times\text{spacing}, -500\text{e-9})\)

elevation(V) from \((-2.0\times\text{spacing}, 0\text{e-9})\) to \((-500\text{e-9}/\tan(-\theta)-2.0\times\text{spacing}, -500\text{e-9})\)

plots
elevation(V) from ((-spacing/2)+(0e-9)/tan(-theta), 0e-9) to ((spacing/2)+(0e-9)/tan(-theta), 0e-9) export(2500) file "dp_Nd125_t125_S570QW052B00d0_SP110_0h.txt" format "#x #b #1"
elevation(V) from ((-spacing/2)+(0.1e-9)/tan(-theta), -0.1e-9) to ((spacing/2)+(0.1e-9)/tan(-theta), -0.1e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_01h.txt" format "#x #b #1"
elevation(V) from ((-spacing/2)+(0.5e-9)/tan(-theta), -0.5e-9) to ((spacing/2)+(0.5e-9)/tan(-theta), -0.5e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_05h.txt" format "#x #b #1"
elevation(V) from ((-spacing/2)+(1e-9)/tan(-theta), -1e-9) to ((spacing/2)+(1e-9)/tan(-theta), -1e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_1h.txt" format "#x #b #1"
elevation(V) from ((-spacing/2)+(10e-9)/tan(-theta), -10e-9) to ((spacing/2)+(10e-9)/tan(-theta), -10e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_10h.txt" format "#x #b #1"
elevation(V) from ((-spacing/2)+(50e-9)/tan(-theta), -50e-9) to ((spacing/2)+(50e-9)/tan(-theta), -50e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_50h.txt" format "#x #b #1"
elevation(V) from ((-spacing/2)+(150e-9)/tan(-theta), -150e-9) to ((spacing/2)+(150e-9)/tan(-theta), -150e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_150h.txt" format "#x #b #1"

elevation(V) from ((thick/2)*(-1), 0e-9) to ((thick/2)*(-1), -50e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_n1halfthicksv.txt" format "#x #b #1"
elevation(V) from ((thick/2)*(0), 0e-9) to ((thick/2)*(0), -50e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_0halfhalfthickv.txt" format "#x #b #1"
elevation(V) from ((thick/2)*(1), 0e-9) to ((thick/2)*(1), -50e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_1halfthickv.txt" format "#x #b #1"
elevation(V) from ((thick/2)*(2), 0e-9) to ((thick/2)*(2), -50e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_2halfthickv.txt" format "#x #b #1"
elevation(V) from ((thick/2)*(5), 0e-9) to ((thick/2)*(5), -50e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_5halfthickv.txt" format "#x #b #1"
elevation(V) from ((thick/2)*(10), 0e-9) to ((thick/2)*(10), -50e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_10halfthickv.txt" format "#x #b #1"
elevation(V) from ((spacing/2)*(1/2), 0e-9) to ((spacing/2)*(1/2), -550e-9) export(1750) file "dp_Nd125_t125_S570QW052B00d0_SP110_halfspacv.txt" format "#y #b #1"

elevation(V) from ((-0e-9+spacing*sin(theta)*cos(theta))/tan(theta) - 2.5*spacing, -0e-9+spacing*sin(theta)*cos(theta)) to ((-0e-9)/tan(theta)-1.5*spacing, -0e-9) export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_0p.txt" format "#x #b #y #b #1"
elevation(V) from ((-50e-9+spacing*sin(theta)*cos(theta))/tan(theta) - 2.5*spacing, -50e-9+spacing*sin(theta)*cos(theta)) to ((-50e-9)/tan(theta)-1.5*spacing, -50e-9)
export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_50p.txt" format "#x #b #y #b #1" 
elevation(n_c) from ((-50e-9+spacing*sin(theta)*cos(theta))/tan(theta) - 2.5*spacing, -50e-9+spacing*sin(theta)*cos(theta)) to ((-50e-9)/tan(theta)-1.5*spacing, -50e-9) export(10000) file "dn_Nd125_t125_S570QW052B00d0_SP110_50p.txt" format "#x #b #y #b #1"

export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_150p.txt" format "#x #b #y #b #1" 
elevation(n_c) from ((-150e-9+spacing*sin(theta)*cos(theta))/tan(theta) - 2.5*spacing, -150e-9+spacing*sin(theta)*cos(theta)) to ((-150e-9)/tan(theta)-1.5*spacing, -150e-9) export(10000) file "dn_Nd125_t125_S570QW052B00d0_SP110_150p.txt" format "#x #b #y #b #1"

export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_350p.txt" format "#x #b #y #b #1" 
elevation(n_c) from ((-350e-9+spacing*sin(theta)*cos(theta))/tan(theta) - 2.5*spacing, -350e-9+spacing*sin(theta)*cos(theta)) to ((-350e-9)/tan(theta)-1.5*spacing, -350e-9) export(10000) file "dn_Nd125_t125_S570QW052B00d0_SP110_350p.txt" format "#x #b #y #b #1"

export(10000) file "dp_Nd125_t125_S570QW052B00d0_SP110_500p.txt" format "#x #b #y #b #1" 
elevation(n_c) from ((-500e-9+spacing*sin(theta)*cos(theta))/tan(theta) - 2.5*spacing, -500e-9+spacing*sin(theta)*cos(theta)) to ((-500e-9)/tan(theta)-1.5*spacing, -500e-9) export(10000) file "dn_Nd125_t125_S570QW052B00d0_SP110_500p.txt" format "#x #b #y #b #1"

export(200) file "dp_Nd125_t125_S570QW052B00d0_SP110_alonginc.txt" format "#x #b #y #b #1" 
elevation(n_c) from (-2.0*spacing, 0e-9) to ((-500e-9)/tan(theta)-2.0*spacing , -500e-9) export(200) file "dn_Nd125_t125_S570QW052B00d0_SP110_alonginc.txt" format "#x #b #y #b #1"

summary

report(Q/spacing) report(del_Ec - E_0) end
APPENDIX C

PHOTOLITHOGRAPHY AND ETCH PROCEDURES

Fabrication of circular holes through the top oxide layer on the 3C/4H-SiC mesa sample

Due to the many mesa structures with deep trenches (~12 μm) between mesas, special cautions are needed in spinning a photoresist to have it spread uniformly on the sample surface. Shipley S1818 microposit™ photoresist and Clariant AZ 400K developer are used. Olympus microscope (model ) is used to perform projection type photolithography and the mask used is a thin stainless steel sheet with a circular hole of 0.75 mm in diameter machined.

- Position a dummy rectangular (~3 cm × 3 cm) Si substrate at the center of the spinner chuck.
- Put several drops of photoresist on the Si substrate to cover its whole surface area.
- Spin the photoresist at 5000 rpm and for 30 sec.
- Position the 3C/4H mesa sample (small piece) at the center of the Si substrate.
- Bake on a hot plate at 114 °C and for 2 min.
- Cool down for 1 min.
– Position the (mesa sample/Si substrate) at the center of the spinner chuck.
– Put several drops of photoresist on the mesa sample to cover it completely.
– Spin the photoresist at 1750 rpm and for 10 sec.
– Leave the (mesa sample/Si substrate) on the spinner chuck for 30 sec.
– Bake on the hot plate at 114 °C and for 2.5 min.
– Cool down for 1 min.
– Expose UV light through the mask onto mesas (20:1 reduction) using the full power of the microscope lamp.
– Develop for 40 sec (developer : DI water = 1 : 4).
– Rinse in DI water for 40 sec.
– Bake (sort of hard bake) on the hot plate at 114 °C and for 7 min.

After the lithography steps, the top oxide layer exposed through the circular holes patterned in the photoresist layer is etched by immersing the (mesa sample/Si substrate) in HF (1:5 diluted) for ~1 min, and DI water rinse is followed. Finally, the photoresist is completely removed using acetone with methanol rinse followed.

The photograph in the following page shows the circular holes through the top oxide layer on several mesas made by following these procedures.
exposed 3C epilayer  
mesa covered with top oxide layer
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