Hydrogen diffusion and ion implantation in silicon carbide

Martin Janson
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The graph at the top of the cover shows the Si (○) and C (●) atoms of the Si terminated (0001) surface of 4H-SiC.

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Abstract

Secondary ion mass spectrometry (SIMS) has been employed to study the spatial distributions resulting from mass transport by diffusion and ion implantation in single crystal silicon carbide (SiC). By a systematic analysis of this data, fundamental processes that govern these phenomena have been derived.

The acceptor atoms Al and B are known to be electrically passivated by H in SiC. By studying the thermally stimulated redistribution of implanted deuterium (2H) in various acceptor doped structures, it is found that hydrogen forms complexes with the doping atoms, and also interacts strongly with implantation induced defects. A comprehensive understanding of the formation and dissociation kinetics of these complexes has been obtained. The extracted effective capture radius for the formation of 2H-B complexes is in good agreement with that expected for a coulomb force assisted trapping mechanism. The large difference of 0.9 eV in the extracted dissociation energies for the 2H-Al and 2H-B complexes suggests that the atomic configurations of the two complexes are significantly different. Furthermore, by studying the migration behavior of H in the presence of built-in electric fields, it is concluded that all of the mobile H is in the positive charge state in p-type SiC.

A large number of implantations have been performed with respect to ion mass, energy, fluence, and crystal orientation. The electronic stopping cross sections in the low velocity regime for ions with atomic numbers 1 ≤ Z 1 ≤ 15 have been extracted from the ion range distributions. They display both Z 1 -oscillations and a smaller than velocity proportional stopping for ions with Z 1 ≤ 8, in agreement with previous reports for other materials. Furthermore, the degree of ion channeling in various major axial and planar channels of the 6H and 4H-SiC crystal has been explored. Two types of ion implantation simulators have been developed. One based on a statistical, data-base approach, and one atomistic simulator, based on the binary collision approximation (BCA). By fitting BCA simulated profiles to the experimental profiles, detailed information about the electronic stopping and implantation induced damage is extracted. In addition, the vacancy-related damage caused by the implantations has been investigated by positron annihilation spectroscopy (PAS). Two types of implantation induced positron traps have been isolated and are tentatively identified as a Si vacancy (V Si ) and a Si-C divacancy (V Si V C ). The extension of detected V Si is in good agreement with that predicted by BCA simulations, and for implantations with heavier ions V Si are revealed at far greater depths than the mean projected ion range due to deeply penetrating channeled ions.
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II. Electric field assisted migration and accumulation of hydrogen in silicon carbide
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III. Hydrogen-boron complex formation and dissociation in 4H- silicon carbide
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IV. Dissociation of deuterium-defect complexes in ion-implanted epitaxial 4H-SiC
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V. Electronic stopping cross sections in silicon carbide for low-velocity ions with $1 \leq Z \leq 15$
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VI. Channeled implants in 6H silicon carbide
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VII. Effect of crystal orientation and direction on the implant profile of 60 keV Al into 4H-SiC crystals
J. Wong-Leung, M. S. Janson and B. G. Svensson

VIII. Ion implantation range distributions in silicon carbide
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Submitted to J. Appl. Phys. (Nov. 2002)

IX. Vacancy type defect distributions of $^{11}$B-, $^{14}$N-, and $^{27}$Al-implanted 4H-SiC studied by positron annihilation spectroscopy
M. S. Janson, J. Slotte, A. Y. Kuznetsov, K. Saarinen and A. Hallén
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First author
Transient enhanced diffusion of implanted boron in 4H-silicon carbide
M. S. Janson, M. K. Linnarsson, A. Hallén, B. G. Svensson, N. Nordell and H. Bleichner

Dissociation Energy of the passivating hydrogen-aluminum complex in 4H silicon carbide
M. S. Janson, A. Hallén, M. K. Linnarsson, N. Nordell, S. Karlsson and B. G. Svensson

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Precipitate formation in heavily Al-doped 4H-SiC layers  

Incorporation of Hydrogen (1H and 2H) in 4H-SiC during epitaxial growth  
M. K. Linnarsson, U. Forsberg, M. S. Janson, E. Janzén and B. G. Svensson  

The effect of hydrogen diffusion in p- and n-type SiC Schottky diodes at high temperature  

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P. O. A. Persson, L. Hultman, M. S. Janson, A. Hallén, R. Yakimova, D. Panknin and W. Skorupa  

Ion implantation of silicon carbide  

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The nature of the 3838Å-photoluminescence line in 4H-SiC
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Implanted p+n-junction in silicon carbide
A. Hallén, M. S. Janson, J. Osterman, U. Zimmermann, M. K. Linnarsson, A. Y. Kaznetsov,
Y. Zhang, P. O. A. Persson and B. G. Svensson
Submitted to 17th International Conference on the Application of Accelerators in
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Aluminum and boron diffusion in 4H-SiC
M. K. Linnarsson, M. S. Janson, A. Schöner and B. G. Svensson
Author’s contribution to appended papers

I – IV. Planning, sample preparation (except for epitaxial growth and $^2$H-implantation), SIMS measurements, data analysis, computer simulations, and writing of the manuscript.

V, VIII. Planning, part of the SIMS measurements (~20%), data analysis, computer simulations, and writing of the manuscript.

VI. SIMS measurements and writing of the manuscript.

VII. Part of the planning (~50%), SIMS measurements, computer simulations, and part of the writing of the manuscript.

IX. Planning, coordination of sample preparation, part of the PAS measurements, SIMS measurements, data analysis, computer simulations, and writing of the manuscript.
Abbreviations

Acronyms
BC  Bond centered configuration
BCA Binary collision approximation
c-RBS Rutherford backscattering spectroscopy in the channeling mode.
CV  Capacitance versus voltage measurements
DOBS Doppler-broadening spectroscopy
LVM  Local vibrational mode measurements
MARLOWE Implantation simulation code for crystalline targets
MD  Molecular dynamics simulation algorithm
MC  Monte-Carlo simulation algorithm
PAS  Positron annihilation spectroscopy
SIIMPL Implantation simulation code for crystalline targets, developed as a part of this thesis
SIMS Secondary ion mass spectrometry
SPB  Slow positron beam technique
TRIM  Implantation simulation code for amorphous targets
1D  One dimensional
2D  Two dimensional
3D  Three dimensional

Symbols and constants
C  Concentration
D  Diffusion constant
e  Elementary charge
$E_{\text{disp}}$ Displacement energy
$E_d$ Dissociation energy
$E_m$ Migration energy barrier
$E_g$ Electronic energy band gap
$E_b$ Binding energy
$E_0$ Ion implantation energy
F  Particle flux
$\kappa_B$ Bolzmann constant
L  Diffusion length
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_1$</td>
<td>Atomic mass number of implanted ion, scattered particle</td>
</tr>
<tr>
<td>$M_2$</td>
<td>Atomic mass number of target, recoiling atom</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Impact parameter or energy dependence of $S_e$, depending on the context</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature or energy transferred to the recoiling atom in a binary collision, depending on the context</td>
</tr>
<tr>
<td>$R$</td>
<td>Path length of implanted particle</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Projected range of implanted particle</td>
</tr>
<tr>
<td>$S$</td>
<td>Annihilation line-shape parameter, central</td>
</tr>
<tr>
<td>$S_e$</td>
<td>Electronic (in-elastic) stopping cross section</td>
</tr>
<tr>
<td>$S_n$</td>
<td>Nuclear (elastic) stopping cross section</td>
</tr>
<tr>
<td>$S_n^{ZBL}$</td>
<td>Universal nuclear stopping cross section of Ziegler, Biersack, and Littmark [102]</td>
</tr>
<tr>
<td>$\langle m_0 \rangle$</td>
<td>1D mean amplitude of thermal vibrations</td>
</tr>
<tr>
<td>$V_C$</td>
<td>Carbon vacancy</td>
</tr>
<tr>
<td>$V_{Si}$</td>
<td>Silicon vacancy</td>
</tr>
<tr>
<td>$W$</td>
<td>Annihilation line-shape parameter, wing</td>
</tr>
<tr>
<td>$Z_1$</td>
<td>Atomic number of implanted ion, scattered particle</td>
</tr>
<tr>
<td>$Z_2$</td>
<td>Atomic number of target, recoiling atom</td>
</tr>
<tr>
<td>$\Delta E_e$</td>
<td>Electronic energy loss in a binary collision</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of free space.</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Relative dielectric constant</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Annihilation fraction</td>
</tr>
<tr>
<td>$\theta_D$</td>
<td>Debye temperature</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Positron trapping rate</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Jump distance between neighboring lattice sites</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Dissociation frequency</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>Dissociation frequency pre-factor</td>
</tr>
<tr>
<td>$\nu_{lattice}$</td>
<td>Characteristic vibration frequency of the lattice</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Mass density</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Positron lifetime</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>Positron lifetime of undamaged bulk material</td>
</tr>
</tbody>
</table>
Silicon carbide (SiC) is a binary compound whose extraordinary thermal, mechanical and electrical properties makes it the favored material for a wide range of application areas. Excluding its presence in some meteorites there are no (earthly) natural sources for SiC, but it has been synthesized on an industrial level for more than 100 years [1]. Single crystalline SiC wafers became commercially available about 15 years ago, a fact that dramatically increased the scientific and industrial interest for SiC as an electronic material.

SiC is very hard and wear resistant and has – under the name carborundum – been used as an abrasive substance ever since it was first available (e.g. in black sand paper). The combination of extremely high thermal conductivity and thermal stability makes SiC a suitable coating material in various high temperature applications. With the additional property of being a low-Z substance, SiC is further a competitive candidate as a first wall material in fusion plasma devices [2]. The above mentioned properties also make SiC very suitable for micro-fabricated sensor and actuator applications – also known as microelectromechanical systems (MEMS) – intended to function at high temperatures and in highly corrosive or erosive environments [3].

Single crystalline silicon carbide is also a wide band gap semiconductor that can be utilized for electronic and optical applications, as well. A light emitting diode (LED) in SiC was demonstrated already in 1907 [4], and blue LEDs were for a long time considered to be a major market for SiC. The efficiency for these devices is, unfortunately, rather low since SiC has an indirect band gap. The fundamental material advantages of SiC are instead better utilized in electronic applications dealing with high powers, high frequencies, and high temperatures. High power electronics, such as switches and rectifiers used for electronic power regulation, benefit from the exceptional high electric breakdown field and the high thermal conductivity. This will lead to substantially smaller losses in electronic power systems and make costly cooling redundant. Someone has estimated that the full realization of SiC in the power transmission and distribution
infrastructure would save an amount of energy comparable to the capacity of one nuclear power plant in Sweden alone. Furthermore, the saturation velocity for holes and electrons is also very high in SiC, which makes it interesting for RF and microwave transistors. Due to the broad band gap all types of SiC devices could function at high temperatures and this opens new application areas for semiconductor sensors. Examples of this include fast gas sensors operating inside car engines to give greater combustion efficiency and thereby lowering the pollution, and sensors in the heads of drilling equipment. A wide band gap is also favorable for low-noise UV-detectors and commercial SiC UV-detectors are now available.

This thesis deals with fundamental properties of single crystal SiC occurring at an atomic level during processing of the material. The work may be divided into two areas: (a) Hydrogen migration and its interaction with acceptor doping atoms and implantation induced defects. (b) Ion implantation, with an emphasis on properties related to the range distributions of implanted ions and vacancy related implantation induced defects.

The role of hydrogen (H) as an impurity in semiconductors has been studied for about half a century and will most likely continue to inspire researchers of many generations to come. The motivation for this wide attention can be divided in two categories. Hydrogen is the most elementary of all atoms and constitutes therefore a first step towards a fundamental understanding of various phenomena related to impurities in semiconductors, e.g. optical, electrical, and local vibrational properties, and properties related to impurity migration and formation of complexes. The other, more application oriented, driving force is given by the fact that H is a common contaminant in many semiconductor device processing steps, and may even be incorporated into the material for some applications, e.g. in high temperature sensors. H has been found to be highly reactive in semiconductors and can form electrically neutral complexes with defects on the surface, as well as in the bulk of the material. With H present in an operating device, the unintentional passivation of shallow doping atoms can seriously alter the device characteristics. On the other hand, H can also be used as a tool to improve device performance, e.g. in the passivation of interface trapped charge in a MOS capacitor. See Refs. [5] and [6] for further reviews on these subjects.
In SiC epitaxial layers, hydrogen is expected to be a major impurity due to its presence in the epitaxial precursor gases (\( \text{SiH}_4, \text{C}_2\text{H}_6, \text{Al}(\text{CH}_3)_3 \)), and because \( \text{H}_2 \) is used as carrier gas during growth [7]. Indeed, high concentrations of \( \text{H} \) has been observed in both p-type [8, 9] and n-type [10] epitaxial SiC. It has recently been demonstrated that the main source for this H contamination is the \( \text{H}_2 \) carrier gas, and also that the SiC substrate becomes homogeneously filled with H during the epitaxial growth process [11].

The interaction of energetic ions with matter is a scientific field with a history of about 100 years. In the early days this interest was mostly of an academic nature and many experiments were conducted to unravel fundamental aspects of atoms and electronic structures. For example, Rutherford demonstrated already in 1911 the existence, as well as estimated the magnitude of atomic nuclear charges from alpha particle scattering experiments. However, since then numerous practical applications for energetic ions have emerged such as various material synthesis and modification applications, tailoring of surfaces by sputtering and plasma treatments, and different medical applications. Furthermore, Rutherford's experiments have evolved into a broad range of ion beam analysis (IBA) techniques that are today indispensable tools in materials science. The most notable example of material modification is perhaps found in the microelectronics industry, where different beam processing techniques have become central technologies. First of all, ion implantation is an exceptional technique to introduce doping atoms into semiconductors since it in principle allows for a 3D-control of the doping profiles. But there are also several other device processing steps taking advantage of energetic ions. For instance, the damage created by radiation of hydrogen or helium is used for lifetime control in fast switching devices, and in the formation of tunable quantum wells. High dose H implantation is also used to create very thin freestanding layers that are bonded onto isolated substrates, the so-called Smart Cut® process. Furthermore, implantation of oxygen or nitrogen is used in the synthesis of buried isolating layers or islands.

Studies of energetic ions in SiC have primarily originated from two scientific communities: that of fusion reactor plasma devices, where the inner walls would be subjected to bombardment of energetic \(^1\text{H} \) and deuterium \(^2\text{H} \), and that of semiconductor electronics.
1. Introduction

In this thesis, secondary ion mass spectrometry (SIMS) has been employed to study the spatial distributions resulting from mass transport by diffusion and ion implantation in SiC. By a systematic analysis of this data, fundamental processes that govern these phenomena have been derived. Examples of this include the dissociation energies of H-acceptor complexes as well as the electronic stopping cross sections of energetic ions. An ion implantation simulation code has also been developed, that accurately reproduces the experimentally established ion range distributions as a function of ion mass, energy, fluence, and crystal orientation. These simulations have also given information about implantation induced damage and, in particular, of vacancy type defects, which have been further studied using positron annihilation spectroscopy (PAS).

The thesis is organized as follows. Chapter 2 describes the crystal structure and presents some fundamental properties of SiC. The occurrence of polytism and inequivalent lattice sites are covered in some detail. A brief description of doping atoms and various doping techniques is also given. Chapter 3 presents a detailed description of the two measurement techniques utilized in this work, namely SIMS and PAS. The PAS section also includes a literature summary of PAS studies in undamaged and irradiated SiC. Chapters 4 and 5 are intended to give a background and to set the main results of this thesis in a broader context. The chapters give a general description of each subject while most examples are sampled from the bulk of the current work about SiC. Chapter 4 describes hydrogen-acceptor-atom complexes and their formation and dissociation kinetics. The charge state of mobile hydrogen and its affect on migration in external and, especially, internal electric fields is described. Ion implantation is the subject of Chapter 5, which describes the fundamental stopping processes of energetic ions in matter, the occurrence of ion-channeling, and the formation of radiation induced damage in the implanted crystal. Chapter 5 is ended by a brief description of various simulation approaches for ion implantation, and focuses especially on Monte-Carlo simulations within the binary collision approximation. Finally, a summary of the main results of the appended papers is given in Chapter 6.
2 Silicon Carbide

2.1 Crystal structure and fundamental properties

Although SiC is the only stable compound in the Si-C phase diagram it is known to crystallize in up to 200 different configurations, so-called polytypes, each with its own specific set of material properties. The fundamental building blocks of all these polytypes are the tetrahedral bonds between one Si and four neighboring C atoms and vice versa as illustrated in Figs. 2-1 (a)-(b). The interatomic distance between a pair of Si and C atoms is 1.88 Å and the bonds are of ionic type where the electron density is strongly accumulated around the C atom [12, 13]. To understand the occurrence of the different polytypes it is helpful to consider that any SiC crystal can be decomposed into stacked layers of close-packed pairs of Si and C atoms. The fact that the Si-C pairs form hexagonal planes is a consequence of the orientation of the six remaining bonds of each pair [Fig. 2-1(a)]. Starting with one such Si-C layer, a second layer, on top of the first, will be shifted relative the one below in a closed packed manner [Fig. 2-1(b)]. When a third layer is added, there are two possibilities: the layer may either be aligned with the first layer [Fig. 2-1(c)] or aligned with the second layer, but rotated 60° relative to that as demonstrated in Fig. 2-1(d). There are thus three possible positions in the stacking of the hexagonal Si-C layers and they are normally labeled A, B, and C. The atomic positions of the three layer types, projected on the hexagonal plane, are depicted in Fig. 2-2. With this notation the structures of Figs. 2-1(c) and (d) are, from bottom to top,
2. Silicon carbide

Since there is an infinite number of ways to stack these layers, the number of conceivable polytypes is infinite.

It follows from the description above that all SiC crystals may be described by a hexagonal unit cell, but it may not be the smallest conventional one. In addition to hexagonal \((H)\) SiC polytypes there also exist one cubic \((C)\), and several rhombohedral \((R)\) variations. A SiC polytype is usually referred to using the Ramsdell notation, which gives the number of planes in the stacking sequence and the type of unit cell \((H, C, \text{or} \ R)\). For example, a polytype with a stacking sequence \(AB\) is referred to as \(2H\)-SiC, while \(ABC, \ ABAC, \ ABCACB, \text{and} \ ABCACBCABAC\) are \(3C, \ 4H, \ 6H, \text{and}\)  

---

**Figure 2-1** Illustration of the SiC crystal structure by formation of stacked, hexagonal layers of Si-C parirs (a). The positions of the first two bilayers are defined as \(A\) and \(B\) (b), while the third layer has two options, position \(A\) (c) or \(C\) (d).
Hydrogen diffusion and ion implantation in silicon carbide

15R-SiC, respectively. Cubic SiC (3C) is sometimes also referred to as $\beta$-SiC while the hexagonal and rhombohedral polytypes are summed up under the name of $\alpha$-SiC.

Directions and planes in a hexagonal structure are usually given by four Miller indices where the first three relate to the lattice vectors in the hexagonal plane: $a_1$, $a_2$, and $a_3$, and the last to the vector $c$, which is perpendicular to that plane. The $a$ and $c$ vectors are indicated in Fig. 2-2, which also includes the hexagonal $<11\bar{2}0>$ and $<10\bar{1}0>$ directions, as well as the $\{10\bar{1}0\}$ families of directions and planes, respectively. [0001] is the direction that is parallel to the stacking direction, while this direction is equivalent to [111] in the cubic polytype.

The main structural difference between the different polytypes is the periodicity of the lattice, while the interatomic distances are practically identical. It is therefore natural that the main differences are found in the
electronic properties of various SiC polytypes. This is for instance the case for the energy band gap, $E_g$, which has been found to vary between 2.39 eV (3C-SiC) up to 3.33 eV (2H-SiC). Table 2-I lists the lattice parameters, the number of atoms per primitive unit cell, and $E_g$ for the five most relevant SiC polytypes. Another aspect of the SiC crystal is the occurrence of inequivalent lattice sites within the unit cell. This has, for example, the effect that the ionization energies of doping atoms are different for substitution at different lattice sites. One usually makes the distinction between hexagonal and cubic sites depending on the sequence of the neighboring hexagonal planes. In the stacking sequence $ABC$, the Si and C atoms at the $B$ position are cubic, while they are hexagonal for the $B$ position in the $ABA$ sequence. For example, 6H-SiC has three inequivalent lattice sites, one of hexagonal type and two cubic, while 2H- and 3C-SiC consists of only equivalent hexagonal and cubic lattice sites, respectively [14]. The number of inequivalent lattice sites for the primary polytypes are included in Table 2-I.

One consequence of the wide band gap of SiC is the low intrinsic carrier concentration, even at elevated temperatures. As already mentioned this makes SiC a prime candidate for electronic devices operating at high temperatures. The intrinsic carrier concentration is also of great importance for the migration properties of point defects. An impurity may have

### Table 2-I: Lattice constants of the conventional unit cell, number of atoms and inequivalent lattice sites per primitive unit cell, and energy band gap $E_g$ (at 2 K) for the five most relevant SiC polytypes. Data from Refs. [14, 15].

<table>
<thead>
<tr>
<th>SiC polytype</th>
<th>Lattice constants (Å)</th>
<th>Atoms per primitive unit cell</th>
<th>Inequivalent sites</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>$a = 3.08$, $c = 5.048$</td>
<td>4</td>
<td>1</td>
<td>3.330</td>
</tr>
<tr>
<td>3C</td>
<td>$a = 4.349$</td>
<td>2</td>
<td>1</td>
<td>2.390</td>
</tr>
<tr>
<td>4H</td>
<td>$a = 3.08$, $c = 10.050$</td>
<td>8</td>
<td>2</td>
<td>3.265</td>
</tr>
<tr>
<td>6H</td>
<td>$a = 3.08$, $c = 15.079$</td>
<td>12</td>
<td>3</td>
<td>3.023</td>
</tr>
<tr>
<td>15R</td>
<td>$a = 12.691$, $\alpha = 13^\circ 54'$</td>
<td>10</td>
<td>5</td>
<td>2.986</td>
</tr>
</tbody>
</table>
completely different migration barriers and reaction cross-sections depending on its charge state, which in turn depends on the Fermi energy. Figure 2-3 depicts the intrinsic carrier concentrations, $n_i$, as a function of temperature for $3C$, $6H$, $4H$-SiC, and Si. $n_i$ was determined using the effective density of state model with degeneracy factors and effective masses according to Ref. [16], and with a temperature induced bandgap narrowing of $-3.3 \times 10^{-4}$ eV/K [17] for SiC.

Figure 2-3 The calculated intrinsic carrier concentrations, $n_i$, as a function of temperature for $3C$, $6H$, $4H$-SiC, and Si. $n_i$ was determined using the effective density of state model with degeneracy factors and effective masses according to Ref. [16], and with a temperature induced bandgap narrowing of $-3.3 \times 10^{-4}$ eV/K [17] for SiC. These values for $n_i$ only give a rough estimate of the actual intrinsic carrier concentrations, especially for the highest temperatures where the effective masses are energy dependent. However, from Fig. 2-3 it can be seen that the intrinsic carrier concentration is well below the impurity/doping concentrations for the sample/temperature combinations studied in this thesis.

The nearest neighbor configurations are the same for all lattice sites and all polytypes in SiC. This is the reason why properties related to lattice-dynamics, such as the Debye temperature and the bulk modulus, do not differ much between different polytypes [13, 18]. Table 2-II lists some lattice-dynamics properties for $3C$, $4H$, and $6H$-SiC. The corresponding values for C (diamond) and Si are included for comparison.
Table 2-II. Debye temperature $\theta_D$, thermal conductivity $\chi$, acoustic velocity $v$, mean vibration amplitude (1-D) $<u_x>$, bulk modulus $K$, shear modulus $G$, and mass density $\rho$ for Si, diamond and 3C, 4H, and 6H-SiC. The quoted values are valid for 300 K unless otherwise specified.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\theta_D$ (K)</th>
<th>$\chi$ (W/cmK)</th>
<th>$v$ (m/s)</th>
<th>$&lt;u_x&gt;$ (Å)</th>
<th>$K$ (GPa)</th>
<th>$G$ (GPa)</th>
<th>$\rho$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>645$^a$</td>
<td>1.4$^a$</td>
<td>9100$^a$</td>
<td>0.065$^2$</td>
<td>98$^a$</td>
<td>69$^e$</td>
<td>2.33$^f$</td>
</tr>
<tr>
<td>Diamond</td>
<td>1860$^a$</td>
<td>8 ±2$^a$</td>
<td>18330$^a$</td>
<td>0.044$^2$</td>
<td>442$^a$</td>
<td>533$^e$</td>
<td>3.52$^f$</td>
</tr>
<tr>
<td>3C-SiC</td>
<td>1126$^{b}$</td>
<td>3.2$^c$</td>
<td>-</td>
<td>-</td>
<td>219$^{d}$</td>
<td>186$^e$</td>
<td>3.21$^c$</td>
</tr>
<tr>
<td>4H-SiC</td>
<td>1123$^{b}$</td>
<td>3.7$^c$</td>
<td>13730$^{1c}$</td>
<td>-</td>
<td>218$^{d}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>1120$^{b}$</td>
<td>3.6$^c$</td>
<td>13300$^{c}$</td>
<td>0.051, Si$^b$</td>
<td>204$^{d}$</td>
<td>-</td>
<td>3.21$^c$</td>
</tr>
</tbody>
</table>

$^a$Low temperature value, $^b$Calculated from the Debye temperature according to Ref. [19]
$^c$Ref. [20], $^d$Ref.[18], $^e$Ref.[15], $^f$Ref. [13], $^g$Ref.[21], $^h$Ref.[22]

2.2 Doping

Since SiC is a pure group-IV compound it is easily understood that p-type doping is accomplished by group-III atoms, while group-V atoms at substitutional lattice sites become donors. The most commonly used donors are N and P, which have ionization energies varying between 40 and 140 meV, depending on polytype and type of lattice site [14, 23-25]. The N and P ionization energies for comparable lattice sites have been found to be very similar [23-25]. This is rather surprising considering that N substitutes for C [14] while substitutional P has been suggested to reside in the Si sublattice [25, 26], although the preferred site for P is not verified. The acceptors that are currently favored are B and Al, both substituting for Si [14, 27]. These acceptors are rather deep for being “shallow” dopants, ~200 and ~300 meV for Al and B, respectively [14, 28], which means that the ionization at room temperature is far from complete.

There are generally three ways to introduce doping atoms into the material: (i) during the growth process, (ii) by diffusion from the sample surface, and (iii) by ion implantation. Introduction of B, Al, P, and N during epitaxial growth of SiC is now routinely done. Control of the doping can be obtained by varying the ratio between the Si and C containing precursor gases due to the site competition effect between the matrix atoms and the introduced impurities. A high Si/C ratio will promote incorporation of impurities residing at C sites, such as N [26], while a low value facilitates the
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introduction of Al and B [7, 29]. For both Al and B, doping levels far above the solid solubility limit at the growth temperature are attainable using this method [29-31]. The lateral dimensions of an epitaxially doped device may be defined by etching. However, for many applications etched devices cannot be used and it is therefore desirable to develop technique where the doping atoms are introduced in selected areas of the surface. Selective area doping is normally accomplished by diffusion or ion-implantation of the doping atoms through a mask deposited on the sample surface. As opposed to the traditional semiconductor technologies (Si, Ge, GaAs) selective area diffusion has proven to be difficult in SiC due to the very high temperatures (>1700 °C) needed to diffuse sufficient amounts of atoms into the material [32]. These high temperatures bring several problems such as deterioration of the SiC surface [33] and the need to develop new masking techniques [34]. Ion implantation is therefore a more attractive method for SiC, and also adds the advantage of well-controlled vertical doping profiles. Unfortunately, high processing temperatures are also needed after implantation in order to anneal implantation induced defects and to position the implanted atoms into substitutional, electrically active positions. For Al and B post-implantation anneals at ~1600 and ~1700 °C, respectively, are needed to obtain reasonable activation [33, 35-37], while somewhat lower temperatures have been reported for N [37, 38] and P [25], ~1200 and ~1500 °C, respectively. However, ion implantation in SiC is still a technology in its infancy and many problems are still unsolved. For example, the forward voltage drop for a state-of-the-art implanted p-i-n SiC rectifier is often higher than for a corresponding epitaxial device [39]. This is related to difficulties in the electrical activation of the implanted ions, and to the implantation induced damage. In particular, it has been observed that dislocation loops of self-interstitials are formed in the area around the projected range of the implanted ions during the high temperature anneal [40]. However, recent demonstrations involving very high implantation doses and high temperature rapid anneals suggests that these problems are solvable [41, 42].
3 Measurement techniques

3.1 Secondary ion mass spectrometry

Secondary ion mass spectrometry (SIMS) is an extremely powerful technique for quantitative elemental analysis. This is best illustrated by considering the combined performance of SIMS: a possibility of detecting 1 impurity atom out of $10^{11}$ matrix atoms; a dynamic range of up to 6 decades within a single measurement; a depth resolution of just a few atomic layers (per decade of signal); and a lateral resolution better than 1 µm. The history of the SIMS technique can be dated back to the 1930s [43], although it was not until the late 1960s that the first commercial equipment for micro-analysis applications became available [44, 45].
3.1.1 Basic principles

The basic principles for all SIMS techniques are as follows: A beam of primary ions is focused and scanned over a small area on the studied sample (~0.01–0.1 mm²). As the energetic ions – typically in the 0.5 to 20 keV range – hit the target, atoms and molecules are emitted from the topmost atomic layers, a process referred to as sputtering. A small fraction of the sputtered particles becomes ionized (secondary ions) and is accelerated to a few eV up to several keV, depending on the type of instrumentation. The secondary ion beam is finally deflected into a mass analyzer, consisting of some electric and/or magnetic field lens system, where the mass over charge ratio of the ions are determined.

There are mainly three types of SIMS measurement modes: (i) mass spectrum, used for bulk contamination/compositional studies, (ii) depth profiling of impurities, and (iii) lateral imaging of contaminations on surfaces. By combining (ii) and (iii), 3D imaging is also possible. Another way of classifying SIMS distinguishes between static and dynamic SIMS. Static SIMS uses very low primary ion currents and is typically used to study organic molecules adsorbed on surfaces. Ion imaging (iii) is usually classified as static SIMS. Dynamic SIMS, on the other hand, employs high enough currents so that a significant amount of the target atoms is sputtered from the sample during the measurement. This is used for depth profiling.

To gain some insight into the various aspects of the SIMS technique it can be worth-while to consider the following expression for the intensity of detected secondary ions, \( I' \), in a SIMS measurement:

\[
I' = I \cdot S_Y \cdot C \cdot Y \cdot T_Y \cdot D_E .
\]

\( I' \) is the current of primary ions (normally measured just before and/or after each SIMS measurement), \( S_Y \) the sputtering yield (i.e. the number of sputtered particles per impinging primary ion), \( C \) the concentration of the studied species (here relative to the target atomic density), \( Y \) the ionized fraction (yield) of the secondary ion, \( T_Y \) the transmission of the secondary ions through the mass analyzer, and \( D_E \) the efficiency of the detector. It should be mentioned that Eq. (3-1) primarily serves a pedagogic purpose and is not used in the SIMS technique itself.
The sputtering yield is typically in the range of 0.5 to 5 and is mainly a function of the primary ion energy, the projectile and target atomic numbers and masses, the angle of incidence between the ion beam and the target surface normal, and the surface binding energy for the sputtered atoms $U_S$. Provided that $U_S$ is known, $\delta_Y$ can be accurately predicted either by Monte-Carlo simulations within the linear recoil cascade model (see further in Sec. 5.4.1), or by the analytical expressions developed by Sigmund [46]. The ionization yield, on the other hand, is far from being completely understood. $Y$ can vary between $10^{-7}$ up to $10^{-1}$ and is a complex function of various target properties as well as of the primary and secondary ions. A SIMS instrument can be set up for detecting either positively or negatively charged secondary ions, referred to as positive and negative mode, respectively. As a rule of thumb, in positive mode a high ionization yield is expected for atoms or molecules with a low ionization potential, while $Y$ is promoted for particles with a high electron affinity in negative mode. Another important factor for the ionization yield is the work function $\phi$ of a sample. In dynamic SIMS, where the primary ions together with the target atoms form an amorphous surface layer, the choice of primary ion can be used as a tool to modify $\phi$. When negative secondary ions are detected and it is desirable to decrease $\phi$, a primary ion with a low ionization potential should be used. The opposite holds in positive mode, i.e., a bombarding ion with a high electron affinity is desirable. To accomplish this cesium (Cs) is often used as primary ion when detecting negative secondary ions, while oxygen (O) is usually used in positive mode. In positive mode it is even possible to flood additional O over the sample surface to further facilitate the formation of an O rich surface layer and thereby increase $\phi$.

Mainly three types of mass analyzers are used for SIMS: time-of-flight (TOF), quadrupoles, and magnetic sector instruments (see for example Ref.[47]). The mass separation in TOF and sector instruments can act as ion optical systems for the secondary ion beam. This means that ion imaging of the sample surface is possible by detecting the mass-separated particles in an image plane, using a two dimensional multi-channel detector. Another possibility to create a SIMS image is by keeping track of the instant position of the sputtering beam as it is rastered over the surface, similarly to the imaging technique employed in secondary electron microscopy. For this type of imaging the best attainable lateral resolution is
about 0.1-0.2 µm (with gallium primary ions) and is determined by the focus of the primary ion beam. In the former method the resolution is limited by the ion optical system and values of around 0.5 µm can be obtained.

The SIMS measurements presented in this thesis were performed using a magnetic sector instrument of the type Cameca IMS 4f. A principle sketch of the ion optical system for this instrument is shown in Fig. 3-1. The two main parts of the mass analyzer are the electrostatic sector analyzer (ESA) (9 in Fig. 3-1) and the magnetic sector analyzer (MSA) (13). The function of the ESA is to refine the energy of the secondary ions. This has to be done since the kinetic energy of the sputtered particles can be significant in comparison to the acceleration potential between the sample (5) and immersion lens (4). The ESA consists of two toroidal shaped plates biased to create an electric field $E_0$ between the plates. The ion beam is deflected in the field, and the energy $E''$ of the ions passing the energy slit (10) is given by:

$$E'' = 2qr_eeE_0,$$  \hspace{1cm} (3-2)

where $q$ is the ion charge, and $r_e$ the radius of curvature in the ESA. The width of the energy slit sets the energy resolution, which is about 130 eV for a standard measurement. The beam is then focused into the MSA where it is deflected by the magnetic field, $B_0$, and the radius of curvature of the

![Figure 3-1 The ion optical system of a Cameca IMS 4f magnetic sector SIMS instrument. (From the Cameca instruction manual.)](Image)
deflected ions, \( r_m \), is defined by a slit at the exit of the magnet (14). The mass of the ions \( M \) that pass through the slit is then given by

\[
M = \frac{(q r_m B_0)^2}{2E^+}.
\] (3-3)

By combining Eqs. (3-2) and (3-3) the mass of a detected ion in a sector instrument thus becomes

\[
M = \frac{q(r_m B_0)^2}{4r_mE_0}.
\] (3-4)

In principle, it would be possible to adjust \( B_0, r_m, \) and \( E_0 \) (accompanied by \( E^- \)) to set the analyzed mass. In reality, however, \( B_0 \) is the only parameter used to select \( M \). Equation (3-4) also reveals that it is not only the mass of a particle that is detected but rather its \( M/q \) ratio. This means, for example, that \( ^{14}\text{N}^+ \) and \( ^{28}\text{Si}^{++} \) are difficult to separate since they have almost identical \( M/q \) ratios.

Ionized molecules are also emitted in the sputtering process, which means that different particles with equal charge state may be detected for the same \( M \). This is referred to as mass interference. Consider for example the measurement of \( ^{69}\text{Ga}^+ \) in SiC where an interference with the \( ^{12}\text{C}^{28}\text{Si}^{29}\text{Si}^+ \) molecule would occur. Even though the formation and ionization probabilities for such a large molecule are rather small, it would still be a severe problem since the atoms of the molecule are both matrix elements and are therefore abundant in the sample.

However, the mass of two different particles with equal (summed) mass numbers are not exactly identical. This means that it is possible to separate between two interfering masses if the mass resolution \( \Delta M \) in the instrument is high enough. In a sector instrument \( \Delta M \) can be regulated by adjusting the widths of the entrance, energy, and magnet slits of the spectrometer (Fig. 3-1). The mass resolution is usually given as \( M/\Delta M \), a figure that is independent on the analyzed mass [Eq. (3-4)]. In a standard measurement of a Cameca IMS 4f instrument \( M/\Delta M \) is typically \( \sim 300 \) but can be increased to over 10 000. This value is high enough to separate both \( ^{69}\text{Ga}^+ \) from \( ^{12}\text{C}^{28}\text{Si}^{29}\text{Si}^+ \) (\( M/\Delta M > 2480 \)) and \( ^{14}\text{N}^+ \) from \( ^{28}\text{Si}^{++} \) (\( M/\Delta M > 960 \)). It should be mentioned, however, that extremely high resolutions require very
stable measurement conditions, \( M/\Delta M \) above 5000 is normally not practicable. Furthermore, the transmission in the instrument becomes drastically reduced, which can lead to a loss of sensitivity.

The transmission of the mass analyzer \( T_Y \) in Eq. (3-1), depends not only on the mass resolution of the measurement. Due to the loss of ions in the different apertures along the beam line, the highest achievable \( T_Y \) is typically in the order of 0.1. In a standard measurement, however, the transmission is considerably lower since only secondary ions originating from the center of the sputtered crater are analyzed. This is done to avoid ‘memory’ effects from the crater walls. The selection is achieved either by introducing an aperture in an image plane along the beam or by keeping track of the position of the rastered primary beam. Typically, the area from which particles are analyzed is around 5–10% of the total sputtered area.

The last component of Eq. (3-1) is the detector efficiency \( D_E \). Fortunately, the detector is not a limiting factor since single transmitted ions can be detected using an electron multiplier. Hence, \( D_E = 1 \).

It is now possible to make an estimate of the sensitivity limit in a typical measurement using Eq. (3-1). This limit is determined by the acquisition time of each data point, which for depth profiling is typically chosen to \( \sim 1 \) s. This value sets the lower limit of detectable intensity, \( I'_\text{min} = 1 \) s\(^{-1} \). For a standard measurement of say \(^{11}\text{B}\) in SiC the parameters of Eq. (3-1) can be estimated to \( S_Y = 1, Y = 0.01, T_Y = 0.1 \times 0.1, \) and \( D_E = 1 \). With a primary sputtering current of \( I' = 500 \) nA, the detection limit then becomes \( C_{\text{min}} = 3 \times 10^{14} \) cm\(^{-3} \), which translates to a concentration of \( 3 \times 10^{14} \) cm\(^{-3} \). This estimated value is in fact in very good agreement with that observed experimentally in \(^{11}\text{B}\) depth profiling of SiC.

### 3.1.2 General complications

Besides the mass-interference described in the previous section there are several other artifacts that may distort a SIMS measurement. A major limiting factor for the depth resolution is cascade mixing. Cascade mixing occurs since a sputtered atom has normally been relocated several times in the collision cascades (see Sec. 5.3) of the preceding bombarding ions. The average displacement range in these collisions is rather small, \( \sim 10 \) Å, but since each atom is typically displaced around 100 times before it eventually leaves the target, the distance between the original position and the position...
from which an atom is detected can be substantial. For a sample with an ideal delta shaped profile, the cascade mixing will result in an exponential slope of the trailing edge in the measured profile, i.e. the side towards greater depths. For this reason, cascade mixing is quantified in terms of an exponential decay length $\lambda_{CM}$, which primarily is a function of target properties, the energy and angle of incidence of the bombarding ions [48].

As an example, for $^{27}\text{Al}$ in SiC measured with a sputtering beam of 8 keV $\text{O}_2^+$ at an angle of incidence of 40°, $\lambda_{CM}$ has been determined to 25 Å [30].

Another phenomenon which broadens depth profiles is the spontaneous formation of rough surfaces at the bottom of the sputtered craters. In Si sputtered with oxygen this typically occurs after sputtering at depths larger than $\sim 1$ µm. Surface roughening has not been observed in SiC, however.

The interaction between the primary ions and the target will induce a charge in the measured sample. To maintain the accelerating potential of the secondary ions this charge has to be compensated for by a current through the sample holder. If this is inhibited, for instance due to poor conductivity of a sample, a net charge builds up that can change the sample potential by several hundred volts. This is known as sample charging and is a severe problem, not only for measuring insulators, but also for wide band gap semiconductors that contain a high degree of compensating or passivating defects. Examples of this include non-annealed ion implanted samples as well as hydrogenized acceptor doped material. There are several means to avoid sample charging problems. An electron beam can be guided directly into the area of the sputtered crater; a thin gold film deposited on a sample facilitates the transport of electrons from the crater to the sample holder; the sample bias may be altered during a measurement to compensate the change in local potential; negative primary ions ($\text{O}^-$) may be used since the mobility for electrons is normally much higher than for holes. A decrease of the primary ion current, furthermore, gives the induced charge more time to escape the sample. However, in some cases sample charging is so severe that the measurement simply can not be performed.

A modern SIMS instrument is equipped with a ultra high vacuum system with a base pressure in the $10^{-10}$ torr range. However, for some species, especially those that are present in the atmosphere, the sensitivity of the measurement is still limited by the residual content for that species in the instrument. The most problematic species are $^1\text{H}$, $^{14}\text{N}$, and $^{16}\text{O}$ whose
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background concentration levels in a measurement at best can be suppressed to $10^{17}$, $10^{16}$ (in SiC), and $10^{16}$ cm$^{-3}$, respectively. This is, for example, the reason why deuterium ($^2$H), with three decades lower background level than $^1$H, is often preferred the preferred source in experiments where hydrogen diffusion is monitored by SIMS.

For obvious reasons SIMS is classified as a destructive analysis technique. But normally the “destruction” is considered to be confined to the area of the sputtered crater. However, a sample subjected to SIMS analysis may be affected even far away from the crater area. Figure 3-2 shows the $^2$H depth profiles of two pre-hydrogenated samples in a hydrogen diffusion study. The pre-hydrogenated samples have been annealed at 620 $^\circ$C for 30 min (○) and 120 min (●). After the SIMS analysis the 30 min sample was heat treated another 90 min at 620 $^\circ$C and SIMS analyses a second time (▽).

![2H SIMS depth profiles of two pre-hydrogenated B doped SiC samples after annealing at 620 $^\circ$C for 30 min (○) and 120 min (●). After the SIMS analysis the 30 min sample was heat treated another 90 min at 620 $^\circ$C and SIMS analyses a second time (▽).](image)

Figure 3-2: $^2$H SIMS depth profiles of two pre-hydrogenated B doped SiC samples after annealing at 620 $^\circ$C for 30 min (○) and 120 min (●). After the SIMS analysis the 30 min sample was heat treated another 90 min at 620 $^\circ$C and SIMS analyses a second time (▽).
it is related\(^1\) to a recent discovery that substantial amounts of \(^1\)H is incorporated in samples during SIMS analysis [49]. This \(^1\)H was detected, by photo luminescence and SIMS, up to a distance of \(\sim 1\) mm from the sputtered craters. The source for this contamination is most likely residual hydrogen that is adsorbed on apertures in the primary column and become ionized as the primary ions hit the apertures. The ionized \(^1\)H would then be implanted in the sample along with the primary ions. In any case, the results of Fig. 3-2 clearly demonstrate that the continuing use of samples that have been subjected to SIMS analysis can have drastic, unexpected consequences for an experiment.

3.2.3 Complications when measuring depth profiles
In SIMS depth profiling the intensity of the mass separated ions are registered as a function of sputtering time. To convert these profiles to concentration versus depth, two assumptions are commonly made. First that the erosion rate is constant throughout the measurement and, secondly, that the detected intensity is proportional to the concentration of the measured species. Time can then be converted to depth by measuring the depth of the sputtered crater subsequent to the measurement. The concentration-to-intensity proportionality factor is determined by measuring a reference sample with an established content of the studied impurity. For a correct quantification it is necessary that the measurement conditions are stable throughout the analysis and match those of the reference sample. Stability of the primary ion source, sample charging, position of the sample holder, and drift of the high voltage system, especially for high mass resolution analysis, are all factors that may distort a measurement. Fortunately, it is possible to assert the measurement stability by simultaneously detecting species related to matrix elements of the sample. The registered matrix signal in SiC could for example be \(^{30}\)Si. The matrix signal should be constant in the measurements, but for small variations it is possible to use this signal for normalization. However, this

\(^1\) With an additional amount of \(^1\)H incorporated in the surface region, the number of free trapping sites (here boron) for the mobile \(^2\)H would decrease and hence increase the effective \(^2\)H diffusion constant, see Paper I.
type of correction calls for extra care since the error after normalization may in fact increase for some cases when the matrix signal variation is large.

In samples which contain multi-layers of different materials, such as in InP/InGaAsP laser device structures, both the erosion rate and the ionization yield may vary substantially in the different layers of the sample. In this case separate erosion rates and concentration convolution factors have to be used for each type of material in the sample. Such matrix effects may also occur in samples with very high impurity concentrations (>1 atomic %).

However, matrix effects can also be present in samples where the average impurity concentrations is much below this limit due to the formation of precipitates. Figure 3-3 (a) shows the B profiles of an epitaxially grown B doped 4H-SiC structure, as-grown and after an anneal at 1800 °C for 45 min. The B-concentration at the center of the high concentration layers is higher in the annealed than in the as-grown sample. Integration of the profiles suggests that the total amount of B has increased by 35% after the anneal, although no external B have been introduced. The answer to this
mystery can be found in Fig. 3-3 (b), which shows a SIMS 3D-image of the B distribution in the annealed sample of Fig. 3-3 (a). The B distribution in the high concentration region is very inhomogeneous suggesting that B has segregated and formed precipitates during the anneal. The presence of precipitates in a similar sample has been conformed by transmission electron microscopy [50]. The reason for the apparent increase of B can thus be explained by a higher ionization yield for B in a B precipitate compared to that of dilute B in SiC.
3.2 Positron Annihilation Spectroscopy

Positrons have been used to characterize materials since the 1940s. At first positrons were mainly used to examine electronic structures of metals, for example Fermi surfaces, but since the late 1960s when it was discovered that the annihilation properties are sensitive to imperfections in a crystal, the study of crystal defects has been the dominating use for positrons in materials science.

3.2.1 Basic principles

Figure 3-4 demonstrates the fundamental principles of the positron annihilation measurement technique. An energetic positron that is injected into a sample becomes thermalized typically within a few ps time. The positron then starts to migrate in a random fashion until, after some characteristic lifetime $\tau$, it annihilates with an electron and produces two collinear 511 keV $\gamma$-quanta. 511 keV is the mass equivalent energy of an electron (or positron) at rest, but since the momentum of the electron – as opposed to the thermalized positron – is not negligible, a small Doppler-
shift, $\Delta E = p_z c/2$, is added to the annihilation energy. Here $p_z$ is the electron momentum component in the direction of the $\gamma$-rays, and $c$ is the speed of light. In a positron annihilation energy spectrum this Doppler-shift results in a Doppler-broadening of the 511 keV line, which thus carries information of the electronic environment at the annihilation site. The characteristic lifetime as well as the magnitude of the Doppler-broadening are highly material dependent and constitute the core of the two main positron annihilation spectroscopy (PAS) measurement modes: positron lifetime spectroscopy and Doppler-broadening spectroscopy (DOBS).

A positron that diffuses in a perfect crystal is highly delocalized but if it encompasses an open volume defect in the crystal, for instance a vacancy or vacancy agglomerate, the positron may become localized, or trapped, at the defect site where it remains until it annihilates or dissociates from the trap. The binding energy of the positron to a vacancy defect is normally high enough ($\sim$1 eV) so that the probability for dissociation within the positron lifetime is negligible. However, since the electronic configuration around a vacancy defect is radically different compared to that of the undamaged lattice, the lifetime, as well as the Doppler-shift, will differ from the respective bulk values. The mean electronic density in a vacancy is smaller than in a perfect crystal, which results in an increased lifetime for a trapped positron. The Doppler-shift, on the other hand, will be reduced, since the localization of the positron to the center of the vacancy will decrease the probability for annihilation with a high momentum core-electron, in favor of the valance electrons surrounding the defect. The Doppler-broadening spectrum of a damaged sample will therefore be sharper than the one obtained from an undamaged sample.

Vacancy concentrations as low as $10^{15}$-$10^{16}$ cm$^{-3}$ can be detected by PAS. This high sensitivity is due to the large volume that is covered by the migrating positrons before they annihilate. For a sample with a low concentration of positron trapping sites, the effective diffusion length $L$ is typically in the 200 nm range, which means that a very large number of potential vacancy sites are probed by each positron. In semiconductors, the charge-state of a defect is also of great importance for the detection limit. A negatively charged defect will naturally have a greater capture cross-section for a passing positron than a neutral or positively charged defect. This usually means that n-type material is preferred to p-type when studying defects at low-concentrations in semiconductors by PAS.
Positrons may also be trapped at negatively charged non-open volume defects, for instance ionized acceptors in semiconductors. These trapping sites are referred to as “shallow positron traps”, since the positron binding energy to these traps is normally so low that trapping is only observed at temperatures far below 300 K. Shallow traps have very similar lifetime and Doppler-broadening characteristics as bulk material, but can drastically limit the effective positron diffusion length. This implies that the existence of shallow traps can lead to severe misinterpretations of an experiment, especially regarding the concentration of detected defects.

In most PAS experimental set-ups, the positrons, $\beta^+$, are generated from the decay of $^{22}$Na:

$$^{22}\text{Na} \rightarrow ^{22}\text{Ne} + \beta^+ + \nu_e + \gamma,$$  \hspace{1cm} (3-5)

where the 1.27 MeV $\gamma$ quantum can be used as a start signal in lifetime measurements. $\nu_e$ is a neutrino. The energy spectrum of the emitted positrons is rather broad with a mean value around 100 keV and a maximum around 550 keV. Positrons at these energies can create defects in the lattice. This is, however, usually not a problem for the investigation itself, since the number of created defects is much too small to be detected by PAS even in a very long lasting experiment. The broad energy spectrum leads to a large variation in projected range for the injected positrons with a mean value typically around 100 µm. This means that only bulk properties can be studied with positrons obtained directly from a $^{22}$Na source. However, when the area of interest is located in the vicinity of the sample surface, such as in ion implantation studies, the positron energy must be moderated. This is accomplished by first thermalizing the fast positrons after which they are accelerated to a desired energy. Since the positron energy can be varied during a measurement, information of the depth distribution of the studied defects can be obtained. PAS measurements employing moderated positrons are commonly referred to as slow-positron-beam (SPB) measurements.

Moderation can be accomplished using a thin <100> tungsten foil, although this has the drawback that only a small fraction of the fast positrons injected into the moderator is emitted with a thermal energy distribution. Normally, moderator efficiencies are in the $10^{-4}$ range. Due to this low efficiency the activity of the positron source must be substantially increased to avoid unrealistically long measurement times. Unfortunately,
this increased activity means that the correlation between the “start” \( \gamma \) quantum emitted in the \(^{22}\text{Na}\) decay, and the “stop” \( \gamma \) of the annihilation is lost due to overlapping events. As an affect, conventional lifetime measurements are not possible using slow positrons. SPB lifetime measurements can, however, be accomplished with the help of a beam chopper. These systems are unfortunately rather complex and only a few setups have been built.

### 3.2.2 Lifetime measurements

In positron lifetime measurements individual lifetimes from several million annihilation events are collected to compose a so-called lifetime spectrum \( N(t) \), which is the derivative of the lifetime decay spectrum \( D(t) \). Figure 3-5 shows the lifetime spectra of an as grown epitaxial 6H-SiC sample together with a sample that has been irradiated with 2 MeV electrons to a dose of \( 3 \times 10^{17} \text{ cm}^{-2} \) at 300 K [51]. For a sample with \( k \) types of positron trapping centers the lifetime spectrum will be composed of \( k+1 \) lifetime components, \( \tau_i \), and corresponding intensity components, \( I_i \),

\[
N(t) = -\frac{dD(t)}{dt} = \sum_{i=1}^{k+1} I_i \exp\left(-\frac{t}{\tau_i}\right). \tag{3-6}
\]

With no trapping centers in a sample \( N(t) \) will only have one component, equal to the bulk lifetime \( \tau = \tau_b \). For the case of partial trapping at defects (with no detrapping) the first component will be smaller than \( \tau_b \) while the other components reflect the lifetimes of the individual positron traps. When all injected positrons annihilate at defect sites, known as saturation
trapping, \( N(t) \) reduces to \( k \) components that correspond to the lifetimes of the defects, again assuming no detrapping. The lifetime intensities depend primarily on the concentrations of the different defects. In principle it is possible to obtain both the lifetimes and the concentrations of all defects in a sample from a single lifetime spectrum. The deconvolution of a lifetime spectrum is, however, a very delicate procedure, especially if the spectrum has more than two components. This can for instance lead to diverging results for similar samples observed by different research groups, as exemplified in Sec. 3.2.5. Therefore, it can sometimes be necessary to use the average lifetimes,

\[
\tau_{av} = \sum I_i \tau_i ,
\]

when comparing lifetime spectra obtained by different groups. \( \tau_{av} \) naturally carries less information than the convoluted components, but is much less sensitive to the numerical treatment.

One major advantage of positron lifetime spectroscopy is the fact that the lifetimes of the bulk and various defect configurations can be reasonably well predicted using computational \textit{ab initio} methods. This is very helpful for the identification of a defect whose positron lifetime has been experimentally established.

### 3.2.3 Doppler-broadening measurements

Figure 3-6 shows the normalized Doppler-broadening spectrum of an ion implanted 4\( H \)-SiC sample together with one obtained from virgin material. The spectrum of the implanted sample is narrower than that of the reference sample indicating the presence of open volume defects, as discussed above. Doppler-broadening spectra are usually quantified by the line-shape parameters \( S \) and \( W \), defined as

\[
S = \int_{-E_s}^{E_s} I_{\nu}(511 \text{keV} + E) dE
\]

\[
W = \pm \int_{\pm E_{\nu}}^{\pm E_{\nu}} I_{\nu}(511 \text{keV} + E) dE
\]
where \( I_N \) is the normalized Doppler spectrum intensity after subtraction of the background noise signal. The limits for the \( S \) parameter are chosen symmetrically around, and close to the 511 keV line to provide information of annihilations with low momentum, valance electrons. As a rule of thumb the limits should be chosen to give \( S \approx 0.5 \) for a perfect crystal, which typically translates to a value for \( E_S \) in the 1 keV range. The \( W \) parameter is defined to describe annihilations with the high momentum core electrons of the annihilation site. The boundaries, \( E_{W1,2} \), should be chosen to give as little correlation with the \( S \) parameter as possible, but without sacrificing too much signal dynamics. Typical values for \( E_{W1} \) and \( E_{W2} \) are 3 and 7 keV, respectively. The \( W \) integral may be performed on both sides of the 511 keV line to maximize the data usage, although this implies a very careful compensation for the highly unsymmetric background level, which can be seen in Fig. 3-6. There are no standards for the choice of \( S \) and \( W \) integration limits, nor for the background reduction, which again means that it is difficult to compare results obtained by different research groups. A standard would perhaps not be very meaningful anyway, since the Doppler-spectra themselves also may differ from system to system, mainly due to the resolution of different detectors. To minimize this problem, \( W \)
and $S$ are frequently given as normalized to their corresponding values for undamaged bulk crystals, i.e., $S/S_{b}$ and $W/W_{b}$.

Each type of annihilation site, bulk crystal, sample surface, or various positron traps, has a characteristic Doppler-broadening spectrum with a corresponding $(S, W)$ state. The Doppler-broadening spectrum obtained in a measurement is a superposition of all annihilations in the sample, and the main advantage of quantifying spectra according to Eq. (3-8) is that the extracted $S$ and $W$ parameters are the superposition of all the individual line-shape parameters:

$$S(E) = \eta_{b}(E)S_{b} + \eta_{s}(E)S_{s} + \sum_{d} \eta_{d}(E)S_{d},$$

$$W(E) = \eta_{b}(E)W_{b} + \eta_{s}(E)W_{s} + \sum_{d} \eta_{d}(E)W_{d},$$

$$\sum_{\zeta} \eta_{\zeta} = 1,$$  \hspace{1cm} (3-9)

where the subscripts $b$, $s$, and $d$ represents bulk, surface, and the different defect annihilation sites. $E$ is the energy of the impinging positrons. The fraction $\eta_{\zeta}$ of the positrons that will annihilate at each state $\zeta$ is determined by the positron implantation profile, the positron migration due to diffusion and drift, the defect concentrations, and the corresponding positron trapping (and detrapping) rates. Figure 3-7 shows the normalized $S$ and $W$ parameters as a function of the positron energy from a SPB-DOBS measurement of an 18 keV $^{11}$B implanted SiC sample together with the one from a virgin sample. The top of the graph gives the expected mean positron implantation range, $R_{p}^{+}(E)$, for SiC. For the highest energies, $S$ and $W$ are close to the bulk values in both samples, but as the energy decreases, bringing the implanted positrons closer to the sample surface, $S$ and $W$ gradually increase and decrease, respectively. The behavior of the reference sample is understood by considering the dependence of $R_{p}^{+}(E)$ on the fraction of implanted positrons that can diffuse back to the surface instead of annihilating in the bulk. In fact, this type of back-diffusion experiment of virgin samples can be performed to extract the positron diffusion constant, which in this case was determined to $D_{+} = 7 \text{ cm}^{2}/\text{s}$. In the implanted sample the appearance of implantation induced vacancy type defects is revealed around $E \approx 2 \text{ keV}$ as a distinct maximum and minimum in $S$ and $W$, respectively. This energy translates to
a projected range for the implanted positrons of 30 nm, in good agreement with the predicted projected range for vacancies created by 18 keV $^{11}$B in SiC [Paper IX].

As opposed to the lifetime measurements, the characteristic annihilation properties of individual defects ($S_d$, $W_d$) can not be directly determined from a DOBS measurement. To still make the identification of the defect states possible, $S(E)$ and $W(E)$ can be depicted in a $S$ versus $W$ diagram. When only two types of annihilation states are present for a range of positron implantation energies, the $S$ and $W$ will form a straight line-segment between the two states in the $S(W)$ plot. This result is obtained directly from Eq. (3-9) assuming two annihilation sites, and with the annihilation fractions $\eta$ changing as a function of positron energy. As a consequence, an annihilation state may be identified at the point where two line segments meet. This is exemplified in Fig. 3-8, where a defect state $t_1$ in a series of implanted SiC samples (see Paper IX for details) has been identified at ($S/S_b = 1.060, W/W_b = 0.85$). Between the bulk state ($S/S_b = 1, W/W_b = 1$) obtained for the highest positron energies (see Fig. 3-7), and the defect state $t_1$, occurring for positron energies giving $R_{p^+}(E)$ in the high concentration damage area, the positrons only annihilate in the bulk or at

![Figure 3-7 Annihilation line shape parameters $S$ and $W$ as a function of implanted positron energy for a virgin ($\bullet$), and an 18 keV $^{11}$B implanted ($\square$) 4H-SiC sample. The upper scale shows the projected range of the implanted positrons. The solid lines represent simulated spectra with defect profiles according to Fig. 3-10.](image-url)
the $t_1$ defect. At lower energies positrons also annihilate at the sample surface, but for these energies annihilation only takes place at $t_1$ or at the surface, giving a straight line between the $t_1$ defect and the surface annihilation state. Fig. 3-8 also includes the $S$ and $W$ from a virgin sample. Here no defects are present and annihilation only takes place in undamaged bulk material or at the sample surface, thus forming a line between those states. Together with the implanted samples a closed triangle is formed in the $S(W)$ plot. At the corners of this triangle all positrons annihilate at a single site, i.e. $\eta_c = 1$.

$S$ versus $W$ plots can also be used to monitor the transformation of defects in a sample, for example in isochronal, $S/W = S/W(T)$, or isothermal, $S/W = S/W(t)$, annealing studies. It should also be mentioned that straight lines may occur in a $S(W)$ plot with more than two defects present. For example when different defect states are positioned on the same line or when two out of three states preserve their respective annihilation fraction independent of $E$. To accurately determine a $(S, W)$ defect state, many different samples should be used, which all give saturation trapping for the same $S$ and $W$ values.

![Figure 3-8](image_url) Normalized $S$ versus $W$ plot for a series of implanted (*), implanted and etched (+, ▶), and virgin (◀) 4H-SiC samples. For details, see Paper IX.
The identification of an established \((S, W')\) defect state with a specific defect configuration is considerably more problematic than for positron lifetimes. Calculations of the \(W'\) parameter for defects have been performed, but so far agreements to the experimental values have only been qualitative – at best. However, some clues to the identity of a defect state can be obtained from the high momentum, core electron part of a Doppler-broadening spectrum. Different atoms have different electronic shell structures and it is therefore possible to obtain information about the chemical surrounding of a positron trap. To accomplish this the background noise level has to be substantially reduced compared to a standard single detector DOBS measurement. This can be accomplished using a two-detector setup, a so-called coincidence measurement, which unfortunately is a very time consuming technique, since most of the detected annihilation data is discarded. This technique can be used to identify the sublattice of a vacancy in a compound material, or a vacancy-impurity complex. For details of the coincidence measurement technique, see for example Ref. [52].

### 3.2.4 Extraction of defect profiles

In the previous section it was shown that features in the \(S(E)\) and \(W'(E)\) profiles could be related to features of the defect profile by considering the projected range of the implanted positrons. By simulating the implantation, migration, and trapping of the positrons it is also possible to gain a more detailed picture of defect distributions from SPB-DOBS measurements. The extraction of defect profiles is performed by a least square fit procedure of Eq. (3-9) to the experimental spectra. This is a rather complex iterative process where it can be difficult to assert the uniqueness of a particular solution.

The first step in this process is to determine the different \((S, W')\) annihilation states that are present in the sample. This can for example be done using an \(S(W')\) plot as described above. The \(S\) and \(W'\) versus \(E\) spectra are then simulated by calculating the annihilation fractions at each site, \(\eta_\zeta\), as a function of positron energy. The annihilation fractions are synonymous to the flux of positrons that annihilate at each state, \(F_\zeta\), normalized to the total positron flux injected into the sample, \(I_0\), i.e., \(\eta_\zeta = F_\zeta / I_0\). The total flux of positrons annihilating in undamaged material:
Hydrogen diffusion and ion implantation in silicon carbide

\[ F_b = \int_0^\infty \frac{Cdx}{\tau_b}, \]  

(3-10)

where \( C \) is the concentration of positrons at depth \( x \) from the sample surface. With no detrapping of positrons, the annihilation flux at a defect \( d \) is similarly given by

\[ F_d = \int_0^\infty \mu_d C_d dx, \]  

(3-11)

where \( C_d \) is the defect concentration profile, and \( \mu_d \) is the corresponding trapping coefficient. Typical values for \( \mu_d \) at 300 K are in the \( 10^{-9} \)–\( 10^{-7} \) cm\(^3\)/s range depending on type of defect and its charge state [52]. The flux of positrons annihilating at the surface can be determined considering the surface boundary condition, or by using the conservation constraint for \( \eta \) in Eq. (3-9). The problem is thus reduced to determining the positron concentration profiles for each positron implantation energy. This is accomplished by solving the steady state transport equation for positrons, see Appendix A for details.

The positron implantation profile \( I_p(x, E) \) is usually approximated by a so-called Makhov distribution which originally was developed for describing electron penetration [52, 53]. The distribution is a function of the target density \( \rho \), as well as a number of empirical parameters. A set of parameters has been extracted that gives reasonable accuracy for most materials although it is preferable to use Makhov distributions that have been specifically developed for the studied material. The accuracy of an extracted defect profile can never be better than the precision of the \( I_p(E) \) profiles. The positron implantation profiles are unfortunately rather broad, which limits the spatial resolution of the extracted defect profiles. The range straggling of \( I_p \) is typically of the same magnitude as the projected range. This is illustrated in Fig. 3-9, which depicts the predicted positron profiles in SiC for energies up to 40 keV.

Once the annihilation fractions \( \eta\zeta(E) \) have been determined, the \( S(E) \) and \( W(E) \) profiles can be calculated from Eq. (3-9). The simulated spectra are compared to the experimental ones and, after modification of the defect profiles, the procedure is repeated until a satisfactory agreement is obtained.
3.2 Measurement techniques – PAS

In these iterations all factors that affect the simulated spectra can be used as fitting parameters, but it is important to keep the number of free parameters to a minimum. This also includes the number of parameters that describe the defect distributions, which therefore are typically given as simple box shaped profiles. With a large number of fitting parameters it is always possible to obtain good fits to the experimental spectra, but usually on the expense of the physical relevance of the solution.

There are a number of available program packages dedicated to the extraction of defect profiles from SPB measurements, for instance the VEPFIT code [54]. For this thesis, however, a new code has been developed, written in the high level mathematical programming language MATLAB. The heart of any such code is the swift and accurate solving of the positron transport equation. An effective algorithm that accomplishes this is given in Appendix A.

Figure 3-7 includes the simulated $S(E)$ and $W(E)$ spectra that provided the best fits ($S$ and $W$ simultaneously) to the experimental data. For the reference sample, no defects were included in the simulations, and a positron diffusion constant of 7 cm$^2$/s was obtained from the fit. For the $^{11}$B implanted sample two defects were postulated [Paper IX], and the

\[ \rho_{SiC} = 3.21 \text{ g/cm}^3. \]

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Positron implantation profiles in SiC}
\caption{Positron implantation profiles in SiC predicted using Makhov distributions with stopping parameters as determined for Si [53] combined with the density of SiC, $\rho_{SiC} = 3.21$ g/cm$^3$.}
\end{figure}

Figure 3-9
corresponding profiles provided by the simulation are shown in Fig. 3-10. The defect profiles in Fig. 3-10 are given in positron trapping rates, $\kappa_d$, (right axis) as a function of depth. $\kappa_d$ is the product of the concentration of a defect, $C_d$, and its specific trapping constant, $\mu_d$, i.e.,

$$\kappa_d = \mu_d C_d.$$  

The concentration scale of Fig. 3-12 (left axis) is connected to the $\kappa_d$ scale to via Eq. (3-12), assuming a trapping coefficient for both defects of $\mu_d = 2 \times 10^{-8}$ cm$^3$/s. This is a typical value for neutral positron traps in semiconductors [52]. For comparison, Fig. 3-10 also includes the distribution of silicon vacancies, $V_{Si}$, produced in ballistic collisions during the $^{11}$B implantation as predicted by Monte Carlo BCA simulations, which are described in Sec. 5.4.1. For more details about the experiment shown in Fig. 3-10, see Paper IX.

Figure 3-10 Positron trapping rate profiles $\kappa_t$ (right scale) of defect $t_{1}$ (solid line), and $t_{3}$ (dashed line) obtained from least square fits of simulated PAS spectra to the experimental data of the 18 keV $^{11}$B implantation shown in Fig. 3-7. The concentration axis (left) is connected to the $\kappa_t$ axis by the relation $\kappa_t = \mu_d C_d$, where $C_d$ is the concentration of the defect and $\mu_d$ is set to $2 \times 10^{-8}$ cm$^3$/s$^1$. The $V_{Si}$ profile (histogram) determined by BCA simulations is also included for comparison. For more details see Paper IX.
3.2.5 PAS measurements in SiC

An increasing number of experimental as well as theoretical PAS studies of bulk and irradiated SiC has been published over the past 5–6 years. Starting with undamaged, virgin material the experimental bulk lifetime, $\tau_b$, is typically determined to be 142 ps with just a few ps in variation between different research groups and different types of SiC material [51, 55-59]. This value is in good agreement with the one obtained in different computational efforts: Brauer et al. give $\tau_b = 141$ ps [56], while Staab et al. obtained a somewhat lower value, $\tau_b = 131$ ps [60].

Considerably greater variations have been found for the positron diffusion constant, $D_+$, determined from SPB back-diffusion experiments as described in the previous section. A compilation of experimentally and theoretically extracted $D_+$ in as-grown SiC is presented in Table 3-I. The lowest values, around 0.3 cm$^2$/s, are a great deal smaller than the highest experimental values, 3−7 cm$^2$/s, as well as the theoretically estimated value of 4 cm$^2$/s. The two lowest quoted $D_+$ values were both obtained from substrate material, as opposed to epitaxial SiC used in the other experiments. Therefore, it seems reasonable that the large variation in $D_+$ is related to the crystalline quality and impurity content, which are known to be significantly higher and lower, respectively, for epitaxial compared to substrate SiC. For instance, Polity et al. [58] has reported the existence of a shallow positron trap in as grown 6H-SiC doped with N to a concentration of $5.4 \times 10^{17}$ cm$^{-3}$ (the type of material was not given although the doping level suggests that substrate material was used). The positron binding energy of this trap was determined to 170 meV, which means that it is fairly stable at 300 K. The presence of this defect in a back-diffusion experiment performed at 300 K would hence limit the diffusion length of the positrons, which would explain the material dependence of the extracted $D_+$. The identity of this shallow trap has not been asserted but it is most likely not related to an ionized acceptor, which is expected to have a significantly lower binding energy [61]. Furthermore, the defect was found to be very thermally stable but did eventually anneal out at a temperature of 1740 K [58]. This gives further support for the assumption that the shallow trap is not related to a doping atom.
TABLE 3-I Compilation of experimental and theoretical positron diffusion constants \( D_+ \) in undamaged SiC. The experimental \( D_+ \) are calculated from \( D_+ = L^2/\tau_b \), where the effective diffusion lengths \( L \) are determined from back-diffusion SPB experiments with an assumed mean positron implantation projected range of \( R_{p+}^{++} = 40E^{1.6/3.2} \) (nm). \( \tau_b \) was set to 140 ps for all \( D_+ \).

<table>
<thead>
<tr>
<th>( D_+ ) [cm(^2)/s]</th>
<th>Material</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>6H-SiC, substrate, n-type</td>
<td>Brauer et al. [62]</td>
</tr>
<tr>
<td>0.3 – 0.8</td>
<td>4H-SiC, substrate, semi-insulating</td>
<td>Beling et al. [63]</td>
</tr>
<tr>
<td>1.4</td>
<td>3C-SiC, epitaxial, n-type, ( 3 \times 10^{16} ) cm(^3)</td>
<td>Uedono et al. [64]</td>
</tr>
<tr>
<td>1.8</td>
<td>6H-SiC, epitaxial, n-type, ( 5 \times 10^{15} ) cm(^3)</td>
<td>Kawasuso et al. [51]</td>
</tr>
<tr>
<td>2.4</td>
<td>3C-SiC, epitaxial on Si, n-type, ( 1 \times 10^{16} ) cm(^3)</td>
<td>Itoh et al. [65]</td>
</tr>
<tr>
<td>2.9</td>
<td>6H-SiC, epitaxial, n-type, ( 1 \times 10^{17} ) cm(^3)</td>
<td>Barthe et al. [66]</td>
</tr>
<tr>
<td>4.5</td>
<td>6H-SiC, epitaxial, n-type, ( 3.5 \times 10^{15} ) cm(^3)</td>
<td>Uedono et al. [67]</td>
</tr>
<tr>
<td>7(^{a})</td>
<td>4H-SiC, epitaxial, n-type, ( 5 \times 10^{15} ) cm(^3)</td>
<td>Janson et al. [Paper IX]</td>
</tr>
</tbody>
</table>

Theoretical

| 3.6–4.3 | 3C-SiC | Panda et al. [68] |

\(^{a}\)This value was obtained with \( R_{p+}^{++} = 27.5E^{1.7/3.2} \) (nm). A value of 10 cm\(^2\)/s was obtained using the same \( R_{p+}^{++}(E) \) as used by the other authors.

A large number of irradiation studies have been performed in SiC. Unfortunately, no consensus regarding the characteristics of the various annihilation centers or their identification has so far been achieved. This is illustrated in Table 3-II, which shows a literature summary of annihilation parameters (\( \tau, S, W \)) in electron, proton, and heavier ion irradiated SiC. All irradiations represented in Table 3-II were performed at 300 K, with the exceptions of the electron irradiated samples of Polity et al. (e) and Puff et al. (f) performed at 4 K and 77 K, respectively. Lifetimes are given both as average lifetimes \( \tau_{av} \) [Eq. (3-7)] and, when decomposed spectra were published, as lifetime components with corresponding intensities. \( S \) and \( W \) are given normalized to the respective bulk values.
### TABLE 3-II
Compilation of experimental lifetimes $\tau$ and Doppler-broadening line-shape parameters $S$ and $W$ in irradiated SiC. For decomposed lifetime spectra, average lifetimes, $\tau_{av}$, are given first, followed by the lifetime components with corresponding intensities in brackets. $S$ and $W$ are given normalized to the bulk values $S_b$ and $W_b$, respectively, which are given in brackets. The type of vacancy ($V_C$ or $V_S$ related) determined from the high-momentum part of the Doppler-broadening spectra in coincidence measurements is given in the $W$ column.

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>$\tau$ [ps] (intensity)</th>
<th>$S/S_b$ ($S_b$)</th>
<th>$W/W_b$ ($W_b$)</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrons</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230–350 keV</td>
<td>153 –</td>
<td>(V$_C$ related)</td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>500 keV</td>
<td>176 –</td>
<td>–</td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>800 keV, 1.1$\times 10^{18}$ cm$^{-2}$</td>
<td>$\tau_{av} = 161$ 158 (95%) 210 (5%)</td>
<td>1.015 (0.4415) 0.973 (0.0514) (V$_C$ related)</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td>1 MeV, 1.1$\times 10^{18}$ cm$^{-2}$</td>
<td>$\tau_{av} = 158$ 76 (27.7%) 189 (72.3%)</td>
<td></td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>2.2 MeV, 6$\times 10^{16}$ cm$^{-2}$</td>
<td>$\tau_{av} = 188$ 160 (72%) 260 (28%)</td>
<td>1.030 (0.419)</td>
<td></td>
<td>d</td>
</tr>
<tr>
<td>2 MeV, 3$\times 10^{17}$ cm$^{-2}$</td>
<td>194 (~100%)</td>
<td>1.033 (0.434) 0.86 (0.0034) (V$_S$ related)</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>2 MeV, 10$^{18}$ cm$^{-2}$ (4K)</td>
<td>$\tau_{av} = 195$ 178 (61%) 222 (39%)</td>
<td>– –</td>
<td></td>
<td>e</td>
</tr>
<tr>
<td>2 MeV, 10$^{18}$ cm$^{-2}$</td>
<td>$\tau_{av} = 178$ 220 (50%)</td>
<td>1.029 (0.4415) 0.938 (0.0514)</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td>2.5 MeV, 10$^{19}$ cm$^{-2}$, (77 K)</td>
<td>$\tau_{av} = 207$ 143 (31.0%) 236 (69.0%)</td>
<td>1.045 (-) –</td>
<td></td>
<td>f</td>
</tr>
<tr>
<td>1–3 MeV</td>
<td>210 –</td>
<td>(V$_S$ related)</td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>10 MeV, 1.2$\times 10^{17}$ cm$^{-2}$</td>
<td>$\tau_{av} = 213$ 160 (47%) 260 (53%)</td>
<td>1.050 (0.419) –</td>
<td></td>
<td>d</td>
</tr>
</tbody>
</table>
Hydrogen diffusion and ion implantation in silicon carbide

**TABLE 3-II continued from previous page.**

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>( \tau ) [ps] (intensity)</th>
<th>( S/S_b ) ((S_b))</th>
<th>( W/W_b ) ((W_b))</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Protons</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 MeV, ( 10^{16} ) cm(^{-2} )</td>
<td>( \tau_{av} = 209 ) 144 (33.5%) 242 (66.5%)</td>
<td>1.047 (–) –</td>
<td>–</td>
<td>f</td>
</tr>
<tr>
<td>12 MeV, ( 8 \times 10^{16} ) cm(^{-2} )</td>
<td>210 (100%)</td>
<td>1.058 (0.4415) 0.870 (0.0514) ((V_S)) related</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>150 keV, ( 4 \times 10^{16} ) cm(^{-2} )</td>
<td>–</td>
<td>1.063 (0.453) 0.855 (0.0416)</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td><strong>Heavier ions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( N_2^+ ), 100 keV, ( 1 \times 10^{13} ) cm(^{-2} )</td>
<td>215</td>
<td>1.059 (0.459) –</td>
<td>–</td>
<td>h</td>
</tr>
<tr>
<td>( Al^+ ), 100 keV, ( 1 \times 10^{13} ) cm(^{-2} )</td>
<td>219</td>
<td>1.058 (0.459) –</td>
<td>–</td>
<td>h</td>
</tr>
<tr>
<td>( P^+ ), 200 keV, ( 1 \times 10^{13} ) cm(^{-2} )</td>
<td>223</td>
<td>1.067 (0.457) –</td>
<td>–</td>
<td>h</td>
</tr>
<tr>
<td>( Ge^+ ), 200 keV, ( 1 \times 10^{13} ) cm(^{-2} )</td>
<td>( \tau_{av} = 210 ) 235 (80%)</td>
<td>– –</td>
<td>–</td>
<td>i</td>
</tr>
<tr>
<td>( Ge^+ ), 200 keV, ( 1 \times 10^{14} ) cm(^{-2} )</td>
<td>( \tau_{av} = 234 ) 220 (92%) 400 (8%)</td>
<td>1.068 (0.474) –</td>
<td>–</td>
<td>i</td>
</tr>
<tr>
<td>( Xe^+ ), 124 MeV and neutron irradiation</td>
<td>225 (plateau in dose-study)</td>
<td>– –</td>
<td>–</td>
<td>j</td>
</tr>
<tr>
<td>( Al^+, N^+, B^+ ), as implanted and etched samples</td>
<td>–</td>
<td>( S_{st1} = 1.060 ) ( W_{st1} = 0.850 ) (0.480) (0.0326)</td>
<td>k</td>
<td></td>
</tr>
<tr>
<td>( Ge^+ ), 200 keV, ( 1 \times 10^{14} ) cm(^{-2} )</td>
<td>( \tau_{av} = 234 ) 220 (92%) 400 (8%)</td>
<td>1.068 (0.474) –</td>
<td>–</td>
<td>i</td>
</tr>
</tbody>
</table>

\(^a\)Rempel et al.[69], \(^b\)Arpiainen et al.[57], \(^c\)Kawasuso et al.[51, 70], \(^d\)Dannefaer et al.[55], \(^e\)Polity et al.[58], \(^f\)Puff et al.[59, 71], \(^g\)Barthe et al.[66], \(^h\)Uedono et al.[64, 72], \(^i\)Brauer et al.[56, 62], \(^j\)Girka et al.[73], \(^k\)Janson et al.[Paper IX]
For the heavier ion implantations where only Doppler-broadening data was published, only results are quoted where either the shape of the $S(E)$ and $W'(E)$ profiles, the dose development, or an $S(W')$ plot suggests that the $S$ and $W'$ originate from saturation trapping at one defect. The type of vacancy ($V_c$ as opposed to $V_{Si}$ or $V_cV_{Si}$), determined by comparing experimental and theoretical high-momentum parts of the Doppler-broadening spectra, are given in the $W'$ column for experiments using the coincidence measurement technique.

Table 3-II gives a good illustration for the difficulty of decomposing lifetime spectra in a reproducible way. For example, compare the lifetime components obtained from the 800 keV electron irradiation of Arpiainen et al. [57] to that at 1 MeV reported by Kawasuso et al. [70]. While Arpiainen et al. obtained two components of 160 and 210 ps, Kawasuso et al. extracted the corresponding lifetimes to 76 and 189 ps. On the other hand, the average lifetimes of the two groups are quite similar, 161 and 158 ps, which suggests that the difference in the decomposed values are not due to the irradiations or the used materials, but rather to the decomposition itself.

Out of the many different lifetime components represented in Table 3-II, mainly two groups are possible to isolate: (i) (158 ±5) ps [55, 57, 69] and (ii) (218 ±8) ps [57, 58, 62, 64, 69, 72, 73]. Coincidence measurements, theoretical lifetimes (see below), and the electron energy dependence all support the assignment of the (158 ±5) ps annihilation center to the $V_c$. On the other hand, the identification of the (218 ±8) ps defect has raised some diverging opinions. Arpiainen et al. [57] have identified their 210 ps defect to a $V_{Si}$ while Brauer et al. [62], Polity et al. [58], Uedono et al.,[64, 72], and Ling et al. [74] suggest that their 215-232 ps defects originate from the $V_{Si}V_c$ divacancy. This latter view is shared by Kawasuso et al. who ascribe their 189-194 ps lifetime positron trap to the $V_{Si}$ [51, 70]. One important contribution to this identification is the finding that the 232 ps [74] and 222 ps [58] lifetimes are thermally stable up to 1400°C in agreement with an expected very high stability for the $V_{Si}V_c$ divacancy [75].

The $(S, W')$ states of the samples with saturation trapping at one defect also seem to fall into two groups: (i) $t_1 = (1.059 ±0.001, 0.86 ±0.01)$ [57, 64, 66, Paper IX], which was identified as a $V_{Si}$ by Arpiainen et al. [57], and (ii) $t_2 = (1.0685 ±0.0015, 0.82)$ [62, 72, Paper IX], identified as $V_cV_{Si}$ by Brauer et al. [62]. By comparing the radiation conditions for these samples, one inconsistency may be found: The 100 keV Al+, 1×10^{15} cm^{-2} implanted
sample from Uedono et al. gives an $S$ value of 1.058, close to the $t_1$ defect, while an equally implanted sample reported in Paper IX gives a value of $S = 1.070$, i.e. that of $t_2$. It is likely that the difference between $t_1$ and $t_2$ ($\Delta S = 0.010$) is too small to be accurately separated in the measurements of two different research groups. It is important to point out, however, that two different defects exist around $t_1$ and $t_2$, as shown in Paper IX, although the absolute values (even after normalization) may shift somewhat in different systems. The $(S, W)$ state for the $V_C$ may be determined from the 800 keV electron irradiated sample [57]: $(S, W)_{VC} = (1.013, 0.979)$, assuming a 5% contribution from $t_1$ in the experimental values.

As already mentioned, theoretically determined lifetimes play an important role in the identification of positron defects, and the above quoted assignments were mainly done by comparing the experimental lifetimes to calculated ones. Table 3-III shows a compilation of theoretically determined positron lifetimes and binding energies, $E_b$, for free positrons and for positrons trapped in various intrinsic defect configurations of SiC. The calculations show only small differences ($\leq 3$ ps) between different polytypes and nonequivalent defect configurations of the same defect. The quoted data are average values when more than one structure for each defect was presented. The calculations from Staab et al. [60] take the lattice relaxation around the defects into account, while it is not considered in the works from Brauer et al. [56, 76]. Staab et al. have also shown that the $V_C$ on the one hand and the $V_S$ and $V_S V_C$ on the other, have significantly different signatures in the high momentum part of the Doppler-broadening spectra, while the predicted difference between $V_S$ and $V_S V_C$ is most likely too small to be resolved experimentally.

By considering all the experimental and theoretical data described above, a least-common-denominator model for the positron annihilation properties of the simplest intrinsic defects in SiC may be formulated. Table 3-IV lists the mean values of the identified experimental lifetimes, which are compared to the corresponding mean values of the two theoretical contributions [56, 60]. It is interesting to note that the average experimental values are systematically $\sim 10$ ps higher than the corresponding theoretically values for all defects. The Doppler-broadening line-shape parameters for $V_S$ and $V_C V_S$ in Table 3-IV are from Paper IX, since it is the only source to quote both $S$ and $W$ parameters for both defects.
3.2 Measurement techniques – PAS

TABLE 3-III  Calculated positron lifetimes $\tau$ and binding energies $E_b$ for bulk SiC and for different intrinsic defect configurations. The calculations show only small differences ($\leq 3$ ps) between different polytypes and nonequivalent defect configurations of the same defect. The quoted data are average values when more than one structure for each defect was presented. The calculations from Staab et al. [60] take the lattice relaxation around the defects into account while it is not considered in the works from Brauer et al. [56, 76].

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$\tau$ [ps]</th>
<th>$E_b$ [eV]</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk</td>
<td>131</td>
<td>0</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>141</td>
<td>0</td>
<td>b</td>
</tr>
<tr>
<td>$V_C$</td>
<td>137</td>
<td>+0.08</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>153</td>
<td>-0.26</td>
<td>b</td>
</tr>
<tr>
<td>$V_{Si}$</td>
<td>194</td>
<td>-2.0</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>193</td>
<td>-2.4</td>
<td>b</td>
</tr>
<tr>
<td>$V_{C}V_{C}$</td>
<td>161</td>
<td>-0.58</td>
<td>b</td>
</tr>
<tr>
<td>$V_{Si}V_{C}$</td>
<td>215</td>
<td>-2.6</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>214</td>
<td>-3.0</td>
<td>b</td>
</tr>
<tr>
<td>$V_{Si}V_{Si}$</td>
<td>196</td>
<td>-2.6</td>
<td>b</td>
</tr>
<tr>
<td>$2-V_{Si}V_{C}$</td>
<td>254</td>
<td>-3.5</td>
<td>b</td>
</tr>
<tr>
<td>$3-V_{Si}V_{C}$</td>
<td>286</td>
<td>-4.3</td>
<td>b</td>
</tr>
<tr>
<td>$4-V_{Si}V_{C}$</td>
<td>321</td>
<td>-4.9</td>
<td>b</td>
</tr>
</tbody>
</table>

$^a$Staab et al. [60], $^b$Brauer et al. [56]

TABLE 3-IV  Positron annihilation properties of bulk and intrinsic defects in crystalline SiC. The experimental lifetime values $\tau_{exp}$ represent mean values of identified lifetimes obtained from the literature, while the corresponding theoretically determined values $\tau_{theory}$ are average values from the works of Staab et al. [60] and Brauer et al. [56]. $\Delta \tau$ gives the difference between the experimental and theoretical values, $\Delta \tau = \tau_{exp} - \tau_{theory}$. The Doppler-broadening line-shape parameters for $V_C$ are from Arpiainen et al. [57] (after compensation for the 5% contribution from $V_{Si}$), while the $V_{Si}$ and $V_{C}V_{Si}$ values are from Paper IX.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$\tau_{exp}$ [ps]</th>
<th>$\tau_{theory}$ [ps]</th>
<th>$\Delta \tau$ [ps]</th>
<th>$S/S_{b}$</th>
<th>$W/W_{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk</td>
<td>142$^{a,b,c}$</td>
<td>136</td>
<td>6</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$V_C$</td>
<td>157$^a$</td>
<td>145</td>
<td>12</td>
<td>1.013</td>
<td>0.979</td>
</tr>
<tr>
<td>$V_{Si}$</td>
<td>202$^b$</td>
<td>194</td>
<td>8</td>
<td>1.060</td>
<td>0.850</td>
</tr>
<tr>
<td>$V_{C}V_{Si}$</td>
<td>223$^c$</td>
<td>214</td>
<td>9</td>
<td>1.070</td>
<td>0.820</td>
</tr>
</tbody>
</table>

$^a$Refs [55, 57, 69]  
$^b$Refs. [51, 57]  
$^c$Refs. [58, 62, 72, 74]
Hydrogen migration and complex formation in semiconductors

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Hydrogen (H) is a highly reactive species in semiconductors and can drastically alter the electrical properties of a device. Surface dangling bonds as well as doping impurities have been found to be passivated by the formation of electrically neutral complexes with H. The study of hydrogen in semiconductors is not only driven by an academic curiosity for the subject, but is also motivated by the possibility of actively modifying the material and by the fact that H is a common contaminant in many device processing steps. This chapter describes the nature of hydrogen-acceptor complexes in semiconductors and the reaction kinetics related to their formation and dissociation. Furthermore, the difficulty of determining the diffusion constant for mobile H is discussed as well as the H charge state and its implication on the migration behavior in the presence of doping gradients.
4.1 Hydrogen-acceptor complex

The existence of a passivating H-acceptor complex was first suggested in 1983 by Sah and co-workers [77] who studied the decrease in net charge carrier concentration in B-doped silicon (Si). Further evidence for the H-B complex in Si (H-B:Si) was given later that year by Pankove et al. [78]. The concept of an electrically neutral complex between a shallow acceptor and a H atom is easy to comprehend considering the “missing” electron of the acceptor and the un-paired 1s electron of H. Pankove et al. [78] suggested a simple model for the configuration of the H-B:Si complex where the H atom is directly attached to a Si atom, near the bond center site between the Si and the B atoms, and where the B relaxes towards the plane of the three neighboring Si to form a three-fold coordinated B-Si$_3$ system. This model was later supported by the local vibrational mode (LVM) properties of the complex [79], as well as by total energy \textit{ab initio} calculations [80]. The probability for the formation of a H-acceptor complex is further enhanced by the fact that H has been found to exist in a positive charge state in most p-type semiconductors (see further in Sec. 4.2.1). This means that (i) the ionized acceptor will exert a long range coulomb attraction force on the migrating H$^+$, and (ii) no third particle, electron or hole, is involved in the formation of the complex. Since 1983, a large number of experiments for a wide range of acceptor-semiconductor combinations have been performed to verify the existence, and to determine the dissociation energies of the complexes. In all of these experiments H has been found to form a passivating complex with the acceptor.

4.1.1 Formation kinetics

In an experiment where a H-acceptor complex is to be investigated, H is typically introduced in the surface region of the sample using a hydrogen plasma or low energy H$^+$ ion implantation. If the temperature during the hydrogen treatment is sufficiently high for the H atoms to migrate, but not high enough to dissociate the H-acceptor complexes, a layer of fully passivated acceptors gradually develops deeper and deeper into the sample. If the complex formation can be described by the theory of diffusion limited reactions [81], the leading front of the passivated layer becomes exponential with the exponential slope $\alpha$ given by [Paper I]:
where $X_0$ is the initial acceptor concentration and $R$ is the effective reaction radius of the H-acceptor complex. This type of H-acceptor complex formation is exemplified in Fig. 4-1, which shows the deuterium ($^2$H) depth profiles determined by SIMS in three B-doped 4H-SiC epitaxial layers that have been implanted by 10 keV $^2$H$^+$ and then annealed at 460 °C for 30 min. The validity of Eq. (4-1) is qualitatively confirmed directly by studying the leading fronts of the out-diffused $^2$H profiles exhibited in Fig. 4-1: steeper exponential slopes are observed for samples with higher B-doping. By extracting $\alpha$ from a large number of B doped samples annealed at 460 °C, an experimental effective reaction radius for the $^2$H-B complex in SiC at this temperature was determined to $R_{\text{HB:SiC}} = (21 \pm 4)$ Å [Paper I]. This relatively large capture radius suggests that the trapping mechanism involves a long range coulomb attraction between the B$^-$ and the mobile H$^+$. As a first approximation, this coulomb force assisted reaction radius $R_c$ is often estimated as the distance $r$ between the mobile H$^+$ and the ionized acceptor $X^-$, where the coulomb potential energy loss $V$ equals the thermal energy,

$$V_{r=R_c} = \frac{e^2}{4\pi \varepsilon R_c} = k_B T.$$ (4-2)
4.1 Hydrogen-acceptor complex

Here $e$ is the elementary charge, $\varepsilon = \varepsilon_r \varepsilon_0$ the dielectric constant, $k_B$ Boltzmann’s constant, and $T$ the absolute temperature. Eq. (4-2) originates from the theory of recombination in gases [82] and the direct adaptation to solid state diffusion has not been thoroughly investigated. For example, one might question the value of $1 \times k_B T$ to represent the thermal energy. On the other hand, the Dulong and Petit value of $3 k_B T$ would certainly be too high considering that these experiments are conducted at temperatures far below the Debye temperature $\theta_D$ of the material. An effect that is not included in Eq. (4-2) is the screening of the coulomb potential by free carriers in the semiconductor. A simple way to include screening is to use a modified potential, $V_{\text{scr}} = \frac{e^2}{4\pi\varepsilon r}(\exp(-q_0 r) - 1)$ [83], where the reciprocal screening length $q_0$ for a free carrier gas of density $n$ is given by $q_0 = \sqrt{\frac{e^2 n}{\varepsilon k_B T}}$. The screening effect will thus shift $R_c$ to lower values and depends primarily on the doping concentration. This is demonstrated in Fig. 4-2, which compares $R_c$ using the un-screened and the screened potentials as a function of carrier concentration for SiC at 460 °C, and for Si at 25 °C and 80 °C, respectively.

Only a few experiments have been conducted where the effective capture radius for a H-acceptor complex has been determined. However, the approximate $R_c$ of Eq. (4-2) has proven to be in surprisingly good agreement with the limited number of experimental $R$ values. This is visualized in Fig. 4-3 which shows the experimental values of $\varepsilon R_c$ (where $\varepsilon$ is the relative dielectric constant) as a function of temperature for $^1$H-B:Si at 25 °C [84] and 80 °C [85], and for $^2$H-B:SiC at 460 °C [Paper I]. The material

![Figure 4-2 The effective reaction radius $R_c$ for a positively and negatively charged pair, satisfying the relation $V_{\text{net}} = k_B T$, as a function of carrier concentration for an un-screened (dashed lines) and a screened potential (solid lines) for SiC at 460 °C, and for Si at 25 °C and 80 °C, respectively.](image-url)
Hydrogen diffusion and ion implantation in silicon carbide

independent \( \varepsilon R_c = e^2/(4\pi \varepsilon_0 k_B T) \) is drawn as a solid line in Fig. 4-3 and the good agreement to the experimental data gives support for the general \( T^{-1} \) dependence of \( R \) and, to some extent, the choice of \( 1 \times k_B T \) in Eq. (4-2). One contributing reason for this is given by the fact that coulomb screening is not expected to play a substantial role in any of the above experiments. The acceptor concentrations in both Si experiments were \( 1.4 \times 10^{15} \text{ cm}^{-3} \) [84, 85], while the \( r_{HB:SiC} \) value was determined with a total acceptor concentration of \( 1-7 \times 10^{17} \text{ cm}^{-3} \) [Paper I]. The calculated \( R_c \) using the screened potentials, as determined from Fig. 4-2, all fall within the given accuracy for each experimental \( R \).

4.1.2 Dissociation kinetics

Once a complex has formed it may dissociate to its original components provided that sufficient energy is transferred to the complex. This energy barrier for dissociation is commonly referred to as the dissociation energy, \( E_d \), and is usually taken as the sum of the binding energy of the complex, \( E_b \), and the migration energy (or enthalpy) of the mobile H, \( E_m \). \( E_b \) is here defined as the energy difference between a crystal system with a H and an acceptor well separated from each other, and the system where the pair has formed a complex. \( E_m \) is the energy barrier between two neighboring H lattice sites, separated by the jump distance \( \lambda \). However, if the formalism
4.1 Hydrogen-acceptor complex

with an effective capture radius is to be maintained, \( E_d = E_b + E_m \) does not hold exactly since the potential energy of a H atom after dissociation is lower than \( E_b \) by the amount of the coulomb potential at \( r = R_c \). With \( R_c \) given by Eq. (4-2), the dissociation energy then becomes:

\[
E_d = E_b + E_m - k_B T
\]  

(4-3)

Figure 4-4 shows the schematic total potential energy as a function of the separation \( r \) for a H-acceptor pair with \( E_b = 1.6 \text{ eV}, E_m = 1 \text{ eV} \), (i.e. with \( E_d = 2.5 \text{ eV} \) at 730 K). These values are chosen to correspond to the \(^2\text{H-B} \) complex in SiC, as discussed below. The unscreened coulomb potential (dashed line) as well as the reaction radius \( R_c \) for SiC at 730 K (Eq.(4-2)) are also included. The magnitude of the thermal energy \( k_B T \) at 730 K is indicated in the upper left corner.
The dissociation energy can be established experimentally by determining the temperature dependence of the dissociation frequency $\nu$ for the complex, which is expected to follow the Arrhenius equation:

$$
\nu = \nu_0 \exp(-E_d/k_B T). 
$$

(4-4)

$\nu_0$ is the so called attempt frequency and is closely related to the characteristic oscillation frequency of the lattice $\nu_{\text{lattice}}$. One way to define $\nu_{\text{lattice}}$ is to weight each vibration mode of the lattice, $\omega_k$, with the energy of that mode,

$$
\nu_{\text{lattice}} = \frac{1}{2\pi} \langle \omega \rangle = \frac{1}{2\pi} \sum_k \omega_k^2 \hbar \langle n \rangle 
$$

(4-5)

Here $\langle n \rangle$ is the Planck distribution function, and $\hbar$ the reduced Planck constant. Numerical integration of Eq. (4-5) with the dispersion relation given by the Debye approximation typically yield values for $\nu_{\text{lattice}}$ around $10^{13}$ s$^{-1}$. However, a H$^+$ that has just been released from an acceptor has a higher probability to be (re-) captured than a H$^+$ at a random position in the crystal. To account for this, a correlation factor, $f < 1$, is introduced: $\nu_0 = f \nu_{\text{lattice}}$. Ideally, $f$ only depends on geometrical entities (e.g. $R_c$, $\lambda$, and the crystalline structure) but can only be determined by numerical simulations.

Two classes of experiments have been employed to determine $\nu(T)$ for H-acceptor complexes. In the most common method, pre-hydrogenated samples are thermally annealed in the presence of a strong electric field supplied by a reversed biased Schottky contact. The H$^+$ atoms, released from complexes, are then swept out of the depletion region by the applied field. With the concentration of mobile H$^+$ greatly reduced in this region, recapture of H$^+$ can be neglected and the concentration of complexes, [HX], is reduced according to the first order rate equation: $\partial[HX]/\partial t = -\nu [HX]$. The drawback of this method is that the electric field may influence the trapping/dissociation kinetics and that it also has to be shown that the recapture of H can be neglected. A typical example of such a reverse bias experiment is given in Fig. 4-5, which shows the capacitance-voltage (CV) depth profiles of the net acceptor concentration at 530 K in pre-hydrogenated $\alpha$H Al doped SiC using a reverse bias of 5 V [86]. The acceptor concentration in the near surface region is seen to increase as a
function of time as the $^2$H-Al complexes gradually dissociate, while the released $^2$H$^+$ is swept deeper into the sample. This results in decreasing acceptor levels outside the space charge region, which in this case reaches a depth of $\sim$2 µm. In this experiment the dissociation energy of the $^2$H-Al:SiC complex was estimated to $E_d = (1.75 \pm 0.1)$ eV.

The second class of experiments exploit the fact that the mass transport of H in a trap rich material is entirely limited by the trapping and dissociation processes, as long as the concentration of complexes dominates over the concentration of mobile H$^+$ and there are with no electric fields present. With the total concentration of H substantially lower than the acceptor concentration, $X_0$, the effective (or apparent) diffusion constant $D_{\text{eff}}$ can be shown to follow [Paper I]:

$$D_{\text{eff}} = \frac{V}{4\pi R X_0}.$$  \hspace{1cm} (4-6)

The dissociation frequency can then be calculated from the experimentally determined $D_{\text{eff}}$, provided that the acceptor concentration and the effective capture radius $R$ of the complex are known. Figure 4-6 shows how an originally delta-shaped $^2$H profile at the edge of a buried Al doped SiC epitaxial layer is redistributed as a function of time at a temperature of 350 °C [Paper I]. The $^2$H of the annealed samples has formed Gaussian-shaped profiles indicating that the $^2$H diffusion obeys Fick’s law with a constant diffusion coefficient. By determining $D_{\text{eff}}$ from a wide set of samples, and with $R = R_c$ in Eq. (4-6), the dissociation energy for the $^2$H-Al:SiC complex was determined to $E_d = (1.61 \pm 0.02)$ eV [Paper I]. This value is in
reasonably good agreement with the less precise value determined using the reversed biased Schottky method. For the system $^1$H-B:Si, Zundel and Weber have employed the two different experimental procedures in two independent studies [85, 87], and obtained practically identical dissociation energies for that complex.

The dissociation of H-acceptor complexes has proven to be very well-behaved systems in the sense that the extracted dissociation frequencies usually exhibit Arrhenius temperature dependencies for all measured $\nu$, covering a range of up to 5 decades. This is shown in Fig. 4-7 where the extracted $\nu$ for $^2$H-Al:SiC and $^2$H-B:SiC closely follow straight lines in the Arrhenius plot over the more than three orders of magnitude covered by the experimental values. This means that $E_d$ and $\nu_0$ can be determined to a high degree of accuracy and this has been done for a wide number of acceptors in Si [85], GaAs [88-90], and SiC [Paper I]. Figure 4-7 includes the fitted Arrhenius equations determined in these experiments. With the exception of the $^1$H-Mg complex in GaAs, all extracted pre-exponential $\nu_0$ fall in the range $10^{13}$ to $10^{14}$ s$^{-1}$, with an experimental uncertainty of typically $\pm$ 50-90%. A good correlation between the experimental $\nu_0$ and the lattice vibration frequency can be viewed as an evidence that the activation energy obtained from the Arrhenius fit is identical to the dissociation energy of the complex. The extracted dissociation energies for the $^1$H-Al, $^1$H-Ga, and $^1$H-In complexes in Si all give the same value $E_d = (1.42 \pm 0.02)$ eV [85], which is only slightly higher than that for the complex with the smallest acceptor, $^1$H-B:Si, $E_d = (1.28 \pm 0.03)$ eV [85]. All of these H-acceptor complexes are
4.1 Hydrogen-acceptor complex

expected to have the near bond centered (BC) configuration, where the interaction between H and Si is stronger than that between H and the acceptor [85]. This explains why all these different complexes have so similar dissociation energies.

In GaAs the $^{1}$H-Si, $^{1}$H-C, $^{1}$H-Zn, and $^{1}$H-Be complexes also exhibit very similar dissociation energies, $E_d = (1.2–1.4 \pm 0.1)$ eV, where $E_d$ for the As site group-IV acceptors (Si and C) are somewhat higher (~0.2 eV) than for the group-II acceptors occupying a Ga site (Zn and Be) [88, 89]. These complexes have also been found to have a BC configuration and the difference in $E_d$ of the two groups can be qualitatively understood considering that H has been shown to bond primarily to the Ga atom in the former, but to the acceptor in the latter case [91]. The $^{1}$H-Mg complex in GaAs provides the exception to the above pattern, not primarily due to the lower dissociation energy, $E_d = (0.90 \pm 0.03)$ eV, but mainly due to the five decades lower pre-exponential $\nu_0$ [90]. This different behavior could perhaps be related to the observation that the $^{1}$H-Mg complex, in contrast to the above complexes, do not have a BC-configuration [92]. The

Figure 4-7  Arrhenius plot of the extracted dissociation frequencies for the $^{2}$H-Al (●) and $^{2}$H-B (■) complexes in 4H-SiC [Paper I]. Solid lines are least square fits of Arrhenius equations to the experimental data. Also included are the corresponding Arrhenius equations extracted for a variety of $^{1}$H-acceptor complexes in Si (dashed lines) Ref. [85], and GaAs (dotted lines) Refs. [88, 89, 91].
Hydrogen diffusion and ion implantation in silicon carbide

The H-acceptor dissociation energies in 4H-SiC are found to be higher than those in Si and GaAs. As already mentioned, $E_d = (1.61 \pm 0.02)$ eV for $^3$H-Al:SiC, but the $^3$H-B complex is found to be even more stable: $E_d = (2.51 \pm 0.04)$ eV [Paper I]. The authenticity of these values is supported by the fact that although $E_d$ differs by almost 1 eV, the extracted pre-exponentials, $\nu_0$, are almost identical for the two complexes (Fig. 4-7) and fall just below the characteristic lattice frequency of the SiC lattice, $\nu_{\text{lattice}} = 1.6 \times 10^{13}$ s$^{-1}$ [Paper I]. A difference of 0.9 eV in $E_d$ suggests that the configuration of the two complexes in SiC are significantly different. Unfortunately, no local vibrational mode data has yet been published to reveal the atomic configurations of these complexes. On the other hand, in a recent ab initio study by Aradi et al., the energetically most favorable configurations for the $^1$H-Al and $^1$H-B complexes in 4H-SiC were calculated [93]. For the $^1$H-B complex they found that the H atom is positioned at a BC site, forming a strong bond to the C atom [Fig. 4-8 (a)], similar to the H-acceptor configurations in Si and GaAs. In contrast, the most stable configuration for $^1$H-Al was found with the H at an antibonding site according to Fig. 4-8 (b). This could be qualitatively understood considering that the H atom can not fit into the BC site in the dense, closed packed SiC lattice when the B atom was substituted by the larger Al acceptor. Furthermore, the binding energies, $E_{\text{b}}$, of the $^1$H-B and $^1$H-Al complexes were calculated to 1.6 eV and 0.7 eV, respectively. These theoretical findings are convincingly supported by the experimental results since the difference between the calculated $E_{\text{b}}$ are identical to the difference
between the empirically extracted $E_d$, in agreement with Eq. (4-3). By combining the experimental and theoretical results, a migration barrier for H in 4H-SiC of $E_m = E_d - E_b + k_B T \approx 1$ eV can be estimated. This value for $E_m$ should, however, be treated with some care since the absolute errors in the calculated $E_b$ are expected to be relatively large, as pointed out by Deák et al. [94].

### 4.2 Migration of hydrogen

According to Fick’s law [95] the net flux of atoms $A$ in random motion, $F_r$, is proportional to the negative concentration gradient of $A$, where the proportionality constant is identical to the diffusion coefficient, $D$, i.e. in the one-dimensional case: $F_r = -D \frac{\partial [A]}{\partial x}$. (Brackets denote concentration values of $A$.) The atomic flux originating from the drift of particles $A$ of charge $q$ in an electric field $E$, $F_d$, can also be shown to be proportional to $D$: $F_d = qD/(k_B T)E[A]$, due to Einstein’s relation between mobility and diffusivity. The gradient of the sum of the two fluxes gives the differential equation governing diffusion and drift

$$\frac{\partial [A]}{\partial t} = D \left( \frac{\partial^2 [A]}{\partial x^2} - \frac{q}{k_B T} \frac{\partial (E[A])}{\partial x} \right), \quad (4-7)$$

where $D$ has been assumed to be independent on concentration. For an atom with an interstitial diffusion mechanism, typical for small atoms like hydrogen, the diffusion constant is given by

$$D = D_0 \exp(-E_m/k_B T) \quad (4-8)$$

where the pre-exponential is only weakly temperature dependent and normally falls in the range of $D_0 = \frac{\lambda^2 v_{lattice}}{2}$. The migration energy, $E_m$, can be determined by establishing the temperature dependence of $D$. However, the intrinsic diffusion constant for hydrogen $D^0$ has proven to be very difficult to measure at temperatures below ~1000°C. There are mainly two reasons for this: (i) The solid solubility for isolated H in semiconductors is very low, typically much below the sensitivity limit for any quantitative analysis method. (ii) In experiments where H is monitored, either by direct techniques (e.g. SIMS) or by indirect methods (e.g. CV-measurements), the overwhelming majority of the detected H appear in the form of complexes.
such as H-acceptor pairs or H$_2$ molecules. As a consequence, the mobility of H detected at temperatures below $\sim$1000°C is limited, not by $D^H$, but by the formation and dissociation properties of the dominating H-defect complex, as exemplified by Eq. (4-6). This independence of $D^H$ can be visualized considering that the average time between de-trapping and re-trapping of H, i.e. the time that is determined by $D^H$, is negligible compared to the average lifetime of a complex.

Typically, $D^H$ can only be determined as the product $D^H[H]$ [Paper I] and since [H] is normally not accessible, only a lower limit for $D^H$ can be established. In order to determine $D^H$ by monitoring the H migration, the concentration of H must exceed that of the complexes. If $\nu$, $R$, and $D^H$ are known (or can be reasonably estimated) the relation

$$\frac{[H]}{[HX]} = \frac{\nu}{4\pi R D^H[X]}, \quad (4-9)$$

may be used to determine the minimum temperature $T_{\text{min}}$ needed [Eqs. (4-3), (4-4), (4-8), and (4-9)] to fulfill the criterion $[H]/[HX] > 1$. Here X is a point defect that forms a complex, HX, with a hydrogen atom. This temperature is usually very high as shown by the following example. For SiC with an Al concentration, $A_{\text{lo}}$, of $10^{19}$ cm$^{-3}$, $\nu$ and $R$ as determined in Paper I, $E_m = 1$ eV, and with an assumed $D_0$ of 0.01 cm$^2$/s, $T_{\text{min}}$ becomes 1500°C. (In this example $[H]_{\text{tot}} = [H] + [HAl]$ is assumed to be considerably lower than the concentration of Al so that $[X] = A_{\text{lo}}$ in Eq. (4-9).) However, at this temperature the diffusion length $L = \sqrt{D_t}$ becomes much too large for reasonable annealing times $t$, to be determined by any conventional surface technique such as SIMS or CV-measurements. The experimental difficulty of determining $D^H$ at temperatures below $T_{\text{min}}$ is illustrated by the fact that only one experiment has been conducted at these temperatures ($^1$H in B doped Si at 300 K) where the extracted diffusion constant is believed to represent the diffusivity of the mobile H atoms [84].

### 4.2.1 Charge state

The migration of H in semiconductors is further complicated by the fact that H has been shown to occur in different charge states depending on the Fermi level position. The occurrence of a positive charge state for mobile H in p-type Si was experimentally discovered in 1985 by Tavendale et al. [96]. By monitoring the active acceptor profile in pre-hydrogenated B
doped Si under a reversed biased Schottky contact, they could conclude that H, released from H-B complexes, drifted along the applied field as a positively charged species. A few years later, Tavendale et al. [97] and Zhu et al. [98] simultaneously published evidence that H migrates as H\(^{+}\) in n-type Si. A positive and a negative H charge state has also been found in GaAs [88] while for SiC, only H\(^{+}\) has been clearly demonstrated so far [86]. These experimental findings are in good agreement with computational ab initio studies, which have predicted both a donor and an acceptor level for isolated H in many semiconductors. In Si [99], GaAs [100], GaN [101], and 4H-SiC [93] a so called negative-U behavior has been predicted for H, which in this case means the H is transferred from a positive directly to a negative charge state (+/-) as the Fermi level rises in the band gap. For 3C-SiC, on the other hand, a small stability window for H\(^{0}\) has been suggested [94].

4.2.2 Migration in the presence of doping gradients
The migration of charged H will not only be affected by externally applied electric fields, as illustrated in Fig. 4-5, but also by internal fields that arise due to gradients in the doping [Paper II]. This effect is demonstrated in Fig. 4-9 (a), which shows the SIMS profiles of three pre-hydrogenated SiC samples annealed for 30–60 s at 650, 750, and 850 °C, respectively. The epitaxially grown samples contain three buried Al doped regions and a homogenous B background doping. The \(^2\)H SIMS profiles are compared to two sets of computer simulations of the diffusion experiment in which complex formation and dissociation with the Al and B in the layers have been taken into consideration. If drift of \(^2\)H\(^{+}\) in the field generated by the gradients in the Al profile is excluded in the simulations the agreement to the SIMS profiles is poor, as demonstrated in Fig. 4-9 (b). On the other hand, when drift of \(^2\)H\(^{+}\) is taken into account [Fig. 4-9 (c)], the simulated and the experimental profiles are in much better agreement. For more details about this experiment, see Paper III.

When comparing the simulated profiles of Figs. 4-9 (b) and (c) it can be seen that one effect of the internal electric fields is to delay the spreading of \(^2\)H into the sample, i.e. reducing the effective diffusion length. This effect could therefore be used to study diffusion at higher temperatures than otherwise imposed by the depth range of the measurement technique and \(L(T,\delta)\), as discussed above. This possibility was proposed in Paper II as a
way to determine $D^H$ using SIMS. $^2$H diffusion at 900 °C in a similar structure as that in Fig. 4-9 was also demonstrated in this paper. However, it could later be shown (see the example above) that at 900 °C the concentration of $^2$H-Al complexes is expected to clearly dominate that of the diffusing $^2$H$^+$ for an Al concentration of $10^{19}$ cm$^{-3}$. This means that the $^2$H diffusion observed at 900 °C in Paper II was not limited by $D^H$, a possibility that was also suggested the paper.

Another effect of internal electric fields is that the concentration of mobile $^2$H$^+$ in equilibrium will not be homogenous through a sample, but will, instead, follow the profile of the acceptors [Appendix B]. When the acceptor, X, that gives rise to the built-in electric field also is the main trapping center for the hydrogen, it can be shown that the measured profile of the total (chemical) hydrogen concentration, $[H]_{tot}$, will have a quadratic dependence of the corresponding acceptor profile, $X_0$ [Appendix B]:

$$[H]_{tot} = k(X_0 - [H]_{tot})^2,$$  \hspace{1cm} (4-10)
where \( k \) is a proportionality constant. If the internal field would not have been considered, the corresponding expression to Eq. (4-10) would be linear.

The analytically deduced dependence of Eq. (4-10) is experimentally demonstrated in Fig. 4-10 (a), which shows the SIMS profiles of \(^2\text{H}\) and B in a 4H-SiC B doped staircase structure, implanted with 20 keV \(^2\text{H}\) and annealed at 800 °C for 4 h. The box-shaped profile of the \(^2\text{H}\) suggests that a state close to equilibrium has been reached, and it is clearly seen that the \(^2\text{H}\) concentration dependency is stronger than proportional to the B concentration. To determine this dependency, the \(^2\text{H}\) concentration inside the B staircase is plotted versus \([\text{B} - 2\text{H}]\) in Fig. 4-10 (b). A least squares fit of a power function to the experimental data gives: \([2\text{H}] \propto ([\text{B}] - [2\text{H}])^{1.9}\), in close agreement with Eq. (4-10). Besides from elucidating the effect of doping gradients on the migration of charged species, this result also shows that practically 100% of the mobile H are in the positive charge state under the investigated conditions. This result agrees with the predicted position of

Figure 4-10 (a) \(^2\text{H}\) (solid line) and B (dotted line) SIMS depth profiles of a \(^2\text{H}\) implanted and 800 °C for 4 h annealed 4H-SiC sample with a buried B staircase structure. (b) shows the same data as in (a) but plotted as \(^2\text{H}\) versus \([\text{B} - 2\text{H}]\). A least squares fit of a power function (solid line) reveals an almost quadratic dependence of \([\text{B} - 2\text{H}]\) on \(^2\text{H}\).
the (+/−) level in the upper half of the 4H-SiC band gap [93], a conclusion that could not have been obtained from reverse bias experiments.
Ion implantation is a process that is widely used in the manufacturing of semiconductor electronic devices. Furthermore, energetic ions are also used in various material analysis techniques. In these applications it is of great importance to be able to predict the distribution, the energy loss, and the damage created by the implanted ions. This chapter describes the fundamental processes of the stopping of energetic ions in matter, how it is affected by the crystal orientation, and how damage is created by the ions in the target. A brief description of ion implantation simulations is given at the end of the chapter.
5.1 Stopping power

The retarding forces acting on an energetic ion in matter are commonly treated in terms of stopping powers, $dE/dR_i$, i.e. the differential kinetic energy loss with respect to the distance $R_i$ traveled by the ion. The stopping cross section $S$ is related to the stopping power via

$$S = 1/N (-dE/dR_i),$$

where $N$ is the atomic density of the target. With this definition the total path length $R$ of an impinging ion with initial energy $E_0$ is given by integration,

$$R = \frac{1}{N} \int_0^{E_0} \frac{dE}{S}. \quad (5-1)$$

The implanted ion looses its energy by displacing the target atoms in elastic collisions and by exciting the target electrons, referred to as nuclear stopping ($S_n$) and electronic stopping ($S_e$), respectively. These two processes can in most applications be regarded as being independent of each other and the total stopping cross section is thus the sum of the two, $S = S_n + S_e$.

The stopping power is strongly dependent on the kinetic energy $E$ of the ion. This is demonstrated in Fig. 5-1 which shows the energy dependence of $S_n$ and $S_e$ for $^{14}$N in SiC. At low energies nuclear stopping dominates, but as the ion velocity increases the cross section for elastic collisions decreases.

**Figure 5-1** The energy dependence of the nuclear stopping ($S_n$, broken line) and electronic stopping cross section ($S_e$, solid line) for $^{14}$N in SiC. The Fermi velocity $v_F$, and the Thomas-Fermi velocity $v_{TF}$ are shown as vertical solid and dotted lines, respectively. $S_n$ is equal to that predicted by Ziegler et al. [102], while $S_e$ is the expression from Paper V, experimentally verified up to $\sim v_{TF}$. 
5.1 Ion implantation – stopping power

and the electronic stopping becomes the major stopping force. The magnitudes of $S_n$ and $S_e$ are also functions of ion type and of the target properties and, while $S_n$ can be determined to a high degree of accuracy by theoretical means, empirical corrections are usually needed to predict $S_e$.

5.1.1 Nuclear stopping, $S_n$

All collision processes that result in kinetic energy transfer from the implanted ion to the target nuclei are included in the nuclear stopping power. This means that the nuclear scattering can be fully described by a potential between the ion $I$ and $j$ target atoms, $V_1 = V(r_1, Z_1, r_1, Z_1, r_2, Z_2, ...)$, where $r_x$ is the position of the nucleus of ion/atom $x$. Fortunately, this many-body potential can, to a high degree of accuracy, be replaced by the sum of interatomic potentials between pairs of atoms

$$V_1 = \sum_j V(r, Z_1, Z_j), \quad (5-2)$$

where $r = |\vec{r}_1 - \vec{r}_j|$ is the interatomic distance. For head-on collisions, repulsion between the positive nuclei of the colliding atoms is the dominating scattering mechanism and the interatomic potential can be approximated by the electrostatic potential between the positive charges of the ion and the target atom nuclei, $V' = Z_1 Z_2 e^2 / 4 \pi \varepsilon_0 r$, where $e$ is the elementary charge and $\varepsilon_0$ the permittivity of free space. This type of scattering, known as Rutherford scattering, results in large angle deflections and light ions may even be deflected $>90^\circ$ from a target with heavier atoms (Rutherford backscattering). However, the probability for Rutherford scattering is very small for energetic ions and for the vast majority of the ion-target collisions, the interatomic potential will be considerably reduced, mainly due to the electronic screening of the two nuclei.

Numerous approaches have been used to calculate interatomic potentials. In the simplest methods, the electronic charge distribution is fixed and the different contributions to the potential are calculated independently as a function of the interatomic distance $r$. A more sophisticated way is to use self-consistent ab initio calculations, but these methods require considerably more computer power. Ziegler, Biersack and Littmark calculated the interatomic potentials for a wide number of atomic pairs using fixed Hartree-Fock charge-distributions [102]. They generally found good agreements to both self-consistent calculations and to experimental data.
The especial usefulness of their results is that they managed, with reasonable accuracy, to “compress” all their calculated potentials to a single analytical expression, often referred to as the universal interatomic potential

$$V_U = \frac{Z_1 Z_2 e^2}{4 \pi \varepsilon_0 r} \Phi_U \left( \frac{r}{a_U} \right),$$ (5-3)

where the universal screening function $\Phi_U(x)$ and the screening length $a_U(Z_1, Z_2)$ are fitting formulas [102].

When the interatomic potentials between the ion and the target atoms are known, the energy transfer from the ion to the target atoms can be determined. In principle, this could be done by evaluating the motion of all $N$ atoms in a system, determined by $N$ potentials such as that in Eq. (5-2), as a function of time. This type of calculations, usually referred to as molecular dynamics (MD) simulations, are very time consuming and are today mostly used for studying phenomena related to individual ion-target interactions. A great simplification is made by only considering the collision between two atoms at a time. This is the so-called binary collision approximation (BCA) and is valid for ion energies typically above a few 100 eV [102]. The geometry for a collision between two atoms is shown in Fig. 5-2. An ion $M_1$ with velocity $v_0$ (energy $E$) is deflected by a target atom $M_2$, whose position relative the $M_1$ trajectory is defined by the so-called impact parameter $p$, which is the smallest distance between $M_2$ and the trajectory of $M_1$ before the collision. In the collision, $M_1$ and $M_2$ are deflected asymptotically towards trajectories with angles relative to the original $M_1$ trajectory, $\theta$ and $\phi$, respectively, and the kinetic energy $T$ is transferred from $M_1$ to $M_2$. The equations that relate $\theta$, $\phi$, and $T$ to $M_1$, $M_2$, $p$, $E$, and
5.1 Ion implantation – stopping power

$V(r)$ were originally derived by J.J. Thomson in his work on electrical conductivity [103], but are equally relevant to scattering of two atoms:

$$\phi = \int_0^r \frac{pd\tau}{r^2} g^{1/2} , \quad g = 1 - \frac{V(r)}{E_c} \left( \frac{p}{r} \right)^2 , \quad (5-4a)$$

$$\tan \theta = \frac{M_2 \sin 2\phi}{M_1 - M_2 \cos 2\phi} , \quad (5-4b)$$

$$T = E \frac{4M_1M_2}{(M_1 + M_2)^2} \cos^2 \phi , \quad (5-4c)$$

where $E_C = E/(1 + M_1/M_2)$. $r_0$ is the so-called apsis of collision, which is the smallest interatomic distance $r$ in the collision and can be determined from the equation:

$$g(r_0) = 0 . \quad (5-4d)$$

With the final assumption that the ion reaches the asymptotic trajectory between consecutive collisions, the nuclear stopping cross section can be determined for a given interatomic potential using Eq. (5-4)

$$S_n(E) = \lim_{E \to \infty} T(E) \delta(E) dp = \pi \sigma(E) dp . \quad (5-5)$$

Using their universal potential, Ziegler et al. could extract a corresponding universal nuclear stopping cross section, $S_n^{ZBL}(E, Z_1, M_1, Z_2, M_2)$ [102]. Fig. 5-1 shows the $S_n^{ZBL}$ prediction for $^{14}$N in SiC and the typical features of $S_n(E)$ can be qualitatively understood as follows. For low ion energies (or ion velocities) the target atom will have time to move away from the approaching ion at an early stage in the collision. As the ion velocity increases the colliding atoms will get closer to one another, resulting in an increased (highest) potential during the collision and therefore an increased $T$ and $S_n$. At some velocity, the interaction time in the collision becomes the limiting factor in the impulse taken up by the target atom. Eventually, this results in a decreasing stopping power as a function of ion energy.
5.1.2 Electronic stopping

In semiconductor processing, ion implantations with energies up to several hundred keV are normally used. Except for the lightest ions, these energies translate to ion velocities that are considerably lower than the average velocity of the target valence electrons, i.e. the Fermi velocity \( v_F \). The Fermi velocity is normally in the same order of magnitude as the Bohr velocity \( v_0 \), which equals \( 2.19 \times 10^8 \) cm/s or 25 keV/amu. In this low velocity regime the target electrons induce a friction-like force on the ion and \( S_e \) is thus anticipated to be proportional to the ion velocity \( v \). Around 1960, two theories for this low velocity electronic stopping were presented: that of Lindhard and Scharff [104, 105], and that of Firsov [106]. In the Lindhard and Scharff model, the inelastic energy loss is given as a mean stopping cross section,

\[
S_e^{LS} = \frac{8\pi\hbar^3}{m_e^2} \frac{Z_1^{7/6}Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{3/2}} v,
\]

where \( m_e \) is the electron mass, and \( \hbar \) the reduced Planck constant. Firsov’s model, on the other hand, gives the energy loss per collision, \( \Delta E_e \), depending on the impact parameter \( p \)

\[
\Delta E_e^F = \frac{0.35m_e^2}{\hbar} \left[ 1 + \frac{(Z_1 + Z_2)^{5/3}}{1.6(Z_1 + Z_2)^{1/3} \rho/a_0} \right] v, \tag{5-7}
\]

where the Bohr radius \( a_0 = \hbar^2/(m_e e^2) \approx 0.53 \text{ Å} \). Integration of Eq. (5-7) [similar to Eq. (5-5)] shows that the Firsov model gives comparable stopping to \( S_e^{LS} \) for \( Z_1 \approx Z_2 \), but higher values when \( Z_1 \) and \( Z_2 \) differ considerably. Generally \( S_e^{LS} \) has proven to be in better agreement to experimental data [105]. However, the form of Eq. (5-7) with an impact parameter dependent electronic energy loss has proven to be useful in Monte-Carlo BCA simulations, where the energy loss is evaluated for each collision, as discussed in Sec. 5.4.1.

Both Eqs. (5-6) and (5-7), as well as later theoretical work [107], predict a strict velocity proportionality for the low-velocity stopping, i.e. \( S_e \propto E^p \), with \( p = 0.5 \). (\( p \) is used for both the impact parameter and for the \( S_e \) energy dependence due to convention.) However, systematic deviations from velocity proportionality have been observed [102, 108-110, Paper V]. Figure
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Figure 5-3 Exponent $p$ for the low velocity electronic stopping, $S_e \propto E^p$, as a function of the ion atomic number $Z_1$. The SiC data are from Paper V while the carbon data are obtained from Refs. [108, 109].

5-3 shows the experimental $S_e$ energy dependencies $p$ as a function of $Z_1$ in C [108, 109] and SiC [Paper V]. The extracted $p$ show a very similar dependency on $Z_1$ in both materials, with $p < 0.5$ for $Z_1 \leq 9$ and $p > 0.5$ for $13 \leq Z_1 \leq 15$. These deviations from velocity proportionality should not be confused with those discussed in Ref. [105] for very low ion velocities. No theoretical work has yet been presented that accounts for these observations of the low velocity electronic stopping.

Relatively soon after the publications of Eqs. (5-6) and (5-7) it was experimentally revealed that $S_e$ did not exhibit the monotonic $Z_1$ dependence predicted by those models. This is exemplified in Fig. 5-4 which shows experimental $S_e/\nu$ values as a function of $Z_1$ for C [108] and SiC [Paper V], together with the corresponding $S_e/\nu$ of Eq. (5-6). The experimental $S_e$ for both C and SiC were extracted at a velocity of $0.41 \nu_0$. Typically, local maxima in $S_e$ are found at $Z_1 = (6-8)$ and $(17-18)$, while corresponding minima are located at $Z_1 = (11-13)$ and $(30-32)$ [19, 108, 111, Paper V]. These features are referred to as $Z_1$-oscillations and have been attributed to the electronic structure of the impinging ions. Similar behavior of $S_e$ is also seen as a function of target material, i.e. $Z_2$-oscillations [112, 113]. Many contributions have been devoted to the theoretical understanding of these phenomena [107, 114, 115]. In Ref. [107] the stopping power of an electron gas for slow ions was studied using density-functional formalism (DTF), and in these \textit{ab initio} calculations the $Z_1$-oscillations for slow ions ($\nu < \nu_0$) appeared in a natural way. In Fig. 5-4 we
have included their $S_e/\nu$ values of an electron gas with a density of $4.0 \times 10^{23}$ cm$^{-3}$, which is close to the valence electron density of both SiC and C. The DFT calculations show a distinct maximum at $Z_1 = 7$ and a deep minimum around $Z_1 = 12$, in close agreement to the experimental data. Quantitative agreement to the experimental data is reasonable up to $Z_1 \approx 6$, but for higher atomic numbers the theory clearly underestimates the inelastic stopping. This observation, as well the observed higher stopping in SiC compared to that in C, demonstrates the importance of the core electrons for the low velocity electronic stopping. In this context it is interesting to note that the DFT prediction of the $Z_1$ behavior were considerably better when compared to the electronic stopping for ions implanted in axial channeling directions in Si [107]. This agrees with the fact that the influence of the core electrons on $S_e$ is strongly reduced for channeled ions, as further discussed in Sec. 5.2.

For ion velocities larger than $v_T$, the ion is gradually stripped off its electrons and at velocities well above the Thomas-Fermi velocity, $v_{TF} = \nu_0 Z_1^{2/3}$, the ion will move as a bare nucleus through the target. At these energies the stopping rapidly decreases as a function of velocity (Fig. 5-1) according to the theory of Bethe and Bloch [116, 117],

![Figure 5-4 Ratio of electronic stopping and ion velocity $S_e/\nu$ as a function of the ion atomic number $Z_1$. The SiC values from Paper V (●) and the C stopping (○) from Ref. [108] are obtained at a velocity of $0.41\nu_0$. The experimental data are compared to the $S_e/\nu$ values of an electron gas with a density of $4 \times 10^{23}$ cm$^{-3}$ (×) calculated using Density Functional Theory (DFT) [107]. The Lindhard-Scharff (LS) values for SiC and C are shown as solid and broken lines, respectively.](image-url)
5.1 Ion implantation – stopping power

\[ S_e^{BB} = \frac{4\pi Z_1^2 e^4}{m_e v^2} Z_2 L_S, \quad (5-8) \]

where \( L_S \) is the so-called stopping number. For \( v > 2m_1Z_1 \) the stopping number can be approximated by the Bethe formula \( L_{Bethe} = \log(2m_e v^2 / I_e) \) [116], where \( I_e \) is the mean excitation energy typically on the order of \( I_e \approx 10Z_2 \) eV.

In the energy range between the low and high velocity regimes, around the maximum of \( S_e \) located just above \( v_{TF} \), prediction of \( S_e \) is complicated mainly due to the partial stripping of the ion. In the velocity range between \( v_T \) and \( v_{TF} \) the stopping cross section will increase (relative to an unstripped ion) due to the higher effective charge of the ion seen by the target electrons (Fig. 5-1). Although some work has been devoted to this regime [118, 119] a quantitative theory describing the electronic stopping power for low and high mass ions, from low to high velocities is still missing. For a recent review of electronic stopping powers see Ref. [110]

5.2 Ion Channeling

The stopping powers discussed in the previous section are valid for implantations where the ion follows a “random” trajectory through the target, so that all possible impact parameters are sampled in the collisions, i.e. \( d\sigma/d\rho = 2\pi\rho \) [Eq. (5-5)]. This is always true for ions implanted in amorphous targets but not necessarily in crystals, where rows of atoms in highly symmetrical axial or planar directions form channels through the material. When an ion is injected into such a high symmetry direction it will be steered towards the center of the channel since the atoms along the “channel wall” form a more or less continuos potential \( V_{CH} = V_{CH}(\rho_{CH}) \), where \( \rho_{CH} \) is the perpendicular distance between the ion and a row of atoms in the channel. Due to this continuos potential the ion will start an oscillating movement along the channel, as sketched out in Fig. 5-5. This effect is referred to as ion channeling and was first discovered about 40 years ago in experiments, which revealed strong crystal orientation dependencies on sputtering yields, ion ranges, and backscattering yields [19]. The increased ion range, and the related reduced sputtering yield, is explained by the fact that the nuclear stopping power for an ion with a channeling trajectory is considerably reduced, since close encounters are
effectively avoided. Furthermore, the electronic stopping power for channeled ions will also be reduced since the average electron density is lower in the center of a channel.

An ion that has started a channeling trajectory may be scattered out of the channel again, referred to as dechanneling of the ion. Dechanneling in a defect free crystal happens when the transverse energy for the ion $E_\perp = \alpha^2 E + V_{CH}(\rho_{CH})$ exceeds a critical value $E_{\perp\text{crit}}$, where $\alpha$ is the angle between the instantaneous ion trajectory and the channel wall, see Fig. 5-5. With $E_\perp > E_{\perp\text{crit}}$ the ion comes too close to the target atoms for stable channeling to continue. The initial $E_\perp$ will increase during the oscillating movement since the gradient of $V_{CH}$ along the channel direction can not be fully neglected. This is especially true when thermal lattice vibrations are considered; Lindhard has shown [120] that the rate of increased transverse energy, with respect to the propagation $x$ along the channel direction, depends on the mean vibrational amplitude $<u_x>$ as $<dE_\perp/dx> \propto <u_x>^2$.

The thermal vibrations have furthermore been suggested to limit the value of $E_{\perp\text{crit}}$ according to the relation $E_{\perp\text{crit}} = V_{CH}(<u_x>)$ [19]. Dechanneling is also very sensitive to defects in the lattice, especially to interstitial type defects. This property has been exploited in the widely used measurement technique Rutherford backscattering spectrometry in the channeling mode (c-RBS), which provides near surface disorder information of a sample. c-RBS is typically used for studying depth profiles of displaced atoms after ion implantation and for determining the lattice site location of heavy doping atoms in semiconductors.

The ion-channeling effect plays an important role for the range distribution of implanted atoms in crystalline semiconductors. The detailed shape of a
given implantation profile is a complex matter and depends on the target structure and temperature, implantation direction, ion mass, energy, fluence, and flux. Figure 5-6 shows the (normalized) SIMS depth profiles of nine implantations of 60 keV $^{27}$Al, each in a different direction relative to the 4H-SiC crystal. The implantations were performed under low dose conditions, i.e. the damage produced by the previously implanted ions has not significantly affected the dechanneling probability for the subsequent ions. Three of the implantations were performed parallel to major axial directions [Fig. 5-6 (a)], while the remaining implants were performed at tilt angles 8-10° off a major axis. Four of the latter implantations were tilted in a major planar channel [Fig. 5-6 (b)], while the remaining two were tilted toward low symmetry directions [Fig. 5-6 (c)]. All profiles exhibit a peak at a depth of 0.07 µm, which coincides with the expected projected range for a corresponding random implant. This shows that a significant fraction of the Al beam becomes dechanneled close to the sample surface in all implantations. The range of the (detected) deepest penetrating ions as well as the fraction of channeled ions differ markedly between the various directions.

Figure 5-6 | Normalized range profiles of nine 60 keV Al implantations at 300 K for different axial (a), planar (b), and low symmetry (c) directions of 4H-SiC (see Paper VII for experimental details). All implantations were performed under conditions where no dose dependence of the profiles was observed.
A qualitative understanding for the axial and planar channeling demonstrated in Fig. 5-6 can be obtained by studying the atomic sequence encountered by an ion in the different beam directions. Figure 5-7 shows the Si and C atoms of the 4H-SiC crystal projected onto a plane perpendicular to each of the directions of the implantations represented in Fig. 5-6. The most open of the different directions is the [1120] projection.

Figure 5-7 The Si (○) and C (●) atoms of the 4H-SiC crystal projected on a plane perpendicular to various high and low symmetry directions of the crystal. The directions correspond to those of the 60 keV implantations in Fig. 5-6.
explaining the deep penetration as well as the large channeling fraction of that implantation. The smaller channeling fraction of the [11\overline{2}3] implantation compared to that along [0001], also seems to make sense considering the higher surface density of atoms for the [11\overline{2}3] projection. On the other hand, the openings of the [11\overline{2}3] channels are larger than for [0001], which should give a lower electronic stopping and therefore deeper penetration, in agreement with the observation in Fig. 5-6 (a). Furthermore, the widths of the open planar channels for the off-axis directions in the (11\overline{2}0) and (0001) planes [Figs. 5-7 (d) and (e)] are clearly larger than those for the two off-axis projections in the (10\overline{1}0) plane [Figs. 5-7 (g) and (h)], in good qualitative agreement with the observed planar channeling behavior demonstrated in Fig. 5-6 (b). The implantations in the (10\overline{1}0) planar channels provide identical profiles to the corresponding off axis implantations in the low symmetry (random) directions [Fig. 5-6 (c)], which shows that no significant channeling occurs in the (10\overline{1}0) plane.

The tails of the profiles in Fig. 5-6 (c) reveal that a small fraction of the implanted ions can penetrate deep into the material also for implantations where the initial direction of the ions do not coincide with a main axial or planar direction. This is explained by the fact that an ion with a random trajectory may be scattered into a channel due to multiple collisions during

![Figure 5-8](image)

**Figure 5-8** MC-BCA simulated ion positions (dots) (relative to the initial position at the sample surface) of 3×10⁴ 60 keV ²⁷Al ions implanted in 4H-SiC in a ‘random’ 8° off [0001] direction (solid line).
the ion path. Figure 5-8 shows simulated ion positions (relative to the initial position at the sample surface) of $3 \times 10^4$ 60 keV $^{27}$Al ions implanted in 4H-SiC in a “random” 8° off [0001] direction, corresponding to the off [0001] experimental profile in Fig. 5-6 (e). The implantation direction is indicated in Fig. 5-8 as a straight line. The distribution of the ions form a drop-like shape, pointing towards the [0001] direction, which demonstrates that the deep tail of ion distributions of implantations with a random off [0001] direction mainly originate from ions that have been scattered into the [0001] channel in the stopping process. For further details of the simulations, see Sec. 5.4.1.

In semiconductor processing one usually strives to minimize ion channeling since implantation in a channeling direction prevent formation of shallow/abrupt junctions and would make the processing much more difficult to control. Tilting the wafer relative to the beam towards a random direction far from any significant channel, normally ensures minimum channeling conditions. For example, in Si technology a tilt angle of 7° is normally used [121]. For implantation of (0001) hexagonal SiC, the beam is often oriented perpendicular to the wafer surface, defining the tilt angle by the off axis cut of the wafer. The results presented in Fig. 5-6 show that this method works fine for wafers cut towards [11\overline{2}0], like the ones manufactured currently by Cree Inc. [122], while (0001) SiC wafers which are cut towards [10\overline{1}0], as those from Sterling Semiconductor [123], should be tilted relative to the beam to avoid channeling in the (11\overline{2}0) plane (see further Paper VII). However, channeling can never be totally avoided, as demonstrated above, and when very shallow doping profiles are desired it may be necessary to perform the implants at very large tilt angles to minimize the ion momentum directed into the sample.

For materials like SiC and other compound materials, where the damage created by the implanted ions constitutes a severe problem, the use of channeled implants suggests an interesting possibility. Since the electrons in the target take up a relatively greater part of the kinetic energy of an impinging ion in a channeling direction, the damage created will be less compared to a standard random implantation with the same dose. Monte-Carlo simulations have predicted that the damage introduction rate for channeled implants in $<0001>$ 6H-SiC is about half of that for a random implant [124].
### 5.3 Implantation induced damage

As the kinetic energy of an implanted ion is gradually transferred to the target, damage is created in the lattice. In a conductor or a semiconductor, this damage mainly originates from elastic collisions between the ion and single target atoms, although complex many-body phenomena, such as localized melting [125] and even simultaneous coherent displacements of atomic planes [126], are also known to occur. When the transferred elastic energy $T$ in a binary collision [Eq. (5-4)] exceeds a certain threshold value, the target atom is displaced from its lattice position, thus creating a Frenkel pair, i.e. a self-interstitial and a vacancy. This energy barrier, usually referred to as the displacement energy, $E_{\text{disp}}$, is strongly anisotropic and can vary substantially for different materials, but is usually found to be in the 15–100 eV range. $E_{\text{disp}}$ can be experimentally determined by monitoring the minimum energy needed for creating defects by electron irradiation [127]. In recent years $E_{\text{disp}}$ has also been estimated theoretically using MD-simulations. In SiC, experimental results suggest the values $E_{\text{disp}}^{\text{Si}} = 35$ eV and $E_{\text{disp}}^{\text{C}} = 20$ eV for average displacement directions [127], where the value for Si displacements is less well established than that for C. Various theoretical studies seem to support these values [128, 129], although some controversy on the subject still remains [129].

A displaced atom recoils away from the primary ion trajectory with an energy of $T - E_b$, where $E_b$ is a binding energy in the range of 1-2 eV. For collisions with small impact parameters, this recoiling energy can be substantial and the atom, also referred to as the secondary ion, has enough energy to travel far from its original position, displacing other atoms along its path. In this way a stochastic cascade of defects is created by each implanted ion. This is exemplified in Fig. 5-9, which shows the BCA-simulated damage cascade created by a single 100 keV Al ion in 4H-SiC. The mean number of Frenkel pairs created in a cascade depends primarily on the mass of the implanted ion. In SiC the average number of silicon vacancies, $V_{\text{Si}}$, created by a 200 keV $^{1}\text{H}^+$ ion is only 7, while 200 keV ions of $^{4}\text{He}$, $^{11}\text{B}$, $^{27}\text{Al}$, and $^{75}\text{As}$ result in 60, 250, 600, and 900 $V_{\text{Si}}$, respectively. The energy of the implanted ion, on the other hand, has a relatively moderate influence on the amount of damage produced. This can be understood considering that the implantation energy is usually significantly...
higher than the energy that gives the maximum nuclear stopping cross section (Fig. 5-1). This means that a further increase in implantation energy will only give a small increment to the total energy deposited in elastic collisions. For $^{27}$Al in SiC, the $S_n$ maximum appears around 10 keV and the mean number of $V_{Si}$ per primary ion for Al implants at energies 1, 10, 100, 1000, and 10 000 keV are 6, 60, 360, 1100, and 1800, respectively. For the distribution of the damage, however, the energy is an important parameter. (The above calculations were performed by Monte-Carlo BCA simulations with the full cascade damage algorithm, as described in Sec. 5.4.1.)

Implantation related defects are not limited to the elementary point defects described above, i.e. self-interstitials and vacancies. Both vacancies and interstitials can form complexes with one another and with impurities in the crystal. The formation and annealing kinetics of implantation related defects is, however, a very complex affair. Non-elementary defects may be formed in the ps time scale of the damage cascade evolution and thermalization process. Complex defects may also be formed during the course of the entire implantation when the sample as a hole is in an excited state with an abundance of electron-hole pairs and phonons. It is also known that a substantial part of the produced Frenkel pairs, around 95% in Si, annihilate during a typical implantation [130]. Furthermore, the
formation of certain defects is greatly enhanced if the ion is implanted in an already defected area, so-called overlapping cascades. Damage recovery and formation of tertiary defects also occur during post-implantation treatments, for instance thermal annealing. It is therefore obvious that different combinations of implantation conditions such as ion mass and energy (size and density of damage cascades), implantation dose (probability for overlapping cascades), dose rate (time for annealing of defects between potentially overlapping cascades), and implantation temperature (migration, formation, and dissociation of the defects) have a significant influence, not only on the number, but also on the types of defects that are generated.

The influence of implantation dose on the nature of created defects is illustrated in Fig. 5-10, which shows the Doppler-broadening line shape parameter $W/W_b$ as a function of implantation dose for 100 keV Al implantations at 300 K in 4H-SiC. The positron annihilation events were registered using a 3 keV positron beam to obtain the same projected range for the positrons as for the implanted Al. Indicated are also the $W/W_b$ values for the $t_1$ and $t_2$ defects as well as the expected amorphization dose threshold, a-SiC. The solid line is just a guide to the eye.

Figure 5-10 Normalized Doppler-broadening line shape parameter $W/W_b$ as a function of implantation dose for 100 keV Al implants at 300 K in 4H-SiC (●). The positron annihilation events are registered using a 3 keV positron beam to obtain the same projected range for the positrons as for the implanted Al. Indicated are also the $W/W_b$ values for the $t_1$ and $t_2$ defects as well as the expected amorphization dose threshold, a-SiC. The solid line is just a guide to the eye.
the dose is further increased \( W/W_0 \) rapidly decreases indicating the formation of larger vacancy clusters. This decrease coincides with an amorphization of the implanted SiC, which c-RBS experiments have shown to be fully developed at a dose around \( 10^{15} \text{ cm}^{-2} \) for 100 keV Al at 300 K [131, 132].

This dose-dependence on the type of dominating defect is related to the probability for damage cascades to overlap during the implantation. To show this, three sets of MC-BCA simulations were performed where the final 3D-positions of all created Frenkel pairs was registered. A number of Al ions were randomly implanted over a surface area of 1000×1000 Å² to give the corresponding implantation doses \( 10^{12}, 10^{13}, \) and \( 10^{14} \text{ cm}^{-2} \). Figure 5-11 shows the \( V_{\text{Si}} \) created in a thin square segment, with sides of 400 Å and a thickness of 20 Å, in the vicinity of the projected range of the damage profiles (exemplified in Fig. 5-9). For the \( 10^{12} \text{ cm}^{-2} \) implant [Fig. 5-11 (a)], the \( V_{\text{Si}} \) form well separated groups, which means that the probability for cascades to overlap is low if defect migration is negligible. On the other hand, when the implanted dose is increased by a factor of 10 [Fig. 5-11 (b)] it is no longer possible to distinguish individual groups of defects, which means that the cascades are very likely to overlap in the implant. For the \( 10^{14} \text{ cm}^{-2} \) implant [Fig. 5-11 (c)], the \( V_{\text{Si}} \) are almost evenly distributed throughout the sample segment. The simulations thus suggest that the dominating vacancy related defect (t2) seen in the \( 10^{13}–10^{14} \text{ cm}^{-2} \) implanted samples are formed due to overlapping damage cascades, while such defects are not seen in the \( 10^{12} \text{ cm}^{-2} \) implant. This interpretation also agrees with
the identification of $t_1$ as an elementary point defect ($V_{Si}$) and $t_2$ as a complex (divacancy).

5.4 Simulation of ion implantation

The access to precise and efficient process simulators has become vital in modern semiconductor technology in order to decrease the development time and cost for new types of devices. To simulate ion implantations two different approaches can be used depending on the purpose of the simulation: (i) simulators based on physical models of the ion stopping processes or (ii) a purely statistical approach where the simulated profiles are constructed from a large data bank of experimental distributions. The latter type of simulators are based on the fact that most ion range depth profiles can be represented – to a high degree of accuracy – by their first to fourth order distribution moments, $R_p$, $ΔR_p$, $γ$, and $β$, using Pearson frequency distribution functions [133, Paper VIII]. The main advantage of the statistical simulators is the instantaneous execution time. Depth profiles of multiple energy implantations can thus be readily and precisely simulated by interpolation between established distribution moments, providing that the amount of experimental data is sufficient. The usefulness of this type of simulation is exemplified in Fig. 5-12, which depicts the SIMS profile of an 8-fold multiple energy $^{11}$B implantation in SiC together with a simulation of the implant using Pearson distributions. The interpolated distribution moments of the simulated profiles are from Paper VIII. The execution time of a corresponding simulation using a physically based approach would typically be on the order of several hours.

However, the use of statistical simulators is strictly limited to cases where sufficient experimental data exists, and it does not provide any information of the damage profiles or collision events. This can be accomplished by simulating the stopping process of the implanted ions. There are mainly two types of physically based simulators: molecular dynamics (MD) simulations, and simulators based on the binary collision approximation (BCA). The MD algorithm, briefly described in Sec. 5.1.1, is the most accurate, but is currently too demanding for studying more than individual ion-target interactions. For the normal user, with limited computer resources, simulators based on the BCA approximation are mostly used and are also most often sufficient.
In this thesis both statistical and BCA based simulators have been explored. A lengthier description of the former approach is given in Paper VIII, while the latter is described in the following section.

5.4.1 Monte-Carlo BCA simulations
In the following, a relatively detailed description of a simulation algorithm based on the binary collision approximation is presented. This algorithm is a so-called Monte-Carlo (MC) method, which means that the simulated distributions are the sum of a large number of individual ion trajectories, each affected by a set of random numbers. An alternative to the MC-BCA method is the BCA algorithms employing the Bolzmann transport equations [134]. However, since this method only allows amorphous targets and since the increasing computer power makes MC-BCA simulations attainable for the everyday user, it is rarely used nowadays. The first MC-BCA computer programs were presented already in the early 1950s but most BCA codes of today stem from the algorithms described by Robinson et al. in the mid 1970s [135, 136], i.e. those implemented in the MARLOWE simulation code. A few years later Biersack and Haggmark presented the widely spread TRIM code [137], which was especially designed to decrease the computer execution time. Other reasons for the popularity of the TRIM package (or SRIM, as it is called today) are the inclusion of an extensive library of empirical stopping data for a large number of ion-target

![Figure 5-12](https://via.placeholder.com/150)

Figure 5-12 SIMS (dotted line) and Pearson simulated (solid line) depth profiles of an 8-fold $^{11}$B implantation in 4H-SiC, with ion energies ranging from 25 to 300 keV. The individual simulated profiles for each energy are included as thin broken lines. The energy dependent distribution moments used in the Pearson functions have been extracted from Paper VIII.
combinations [102], and that it is extremely user friendly. However, one of the sacrifices that was made to increase the computer efficiency is that TRIM can only handle amorphous targets. TRIM has become a more or less standard tool for ion implantation and this has, for example, led to an underestimation of the range of implantation induced damage in some studies [138, 139]. Considering the enormous increase in computer power since TRIM was first developed, this rather severe limitation is no longer needed. Today there exists many different MC-BCA codes for crystalline targets, for example MARLOWE, Crystal-TRIM [140], KING-IV [141], and SIIMPL [this thesis], but none of these have been able to match the accessibility, the user friendliness, and the large empirical data bank of TRIM. One challenging task for the ion implantation simulation community would be to make simulations of crystalline targets an option within the TRIM package.

Basic principles
The MC-BCA algorithm is event driven, which in this case means that the ion trajectory is determined by consecutive binary collisions, as opposed to MD simulations where the ion path is discretized in time. The event driven propagation of a MC-BCA ion trajectory is demonstrated in Fig. 5-13 (a). An ion at position \( I \) is heading towards the target atoms \( A, B, \) and \( C \). The target atom of the next binary collision is the one which is closest to the ion (projected on the ion velocity vector and in front of it) and that has an impact parameter \( p \) which is smaller than a certain maximum value \( p_{\text{max}} \). In

![Figure 5-13](image-url) Geometry for the subsequent collisions between an ion \( I \) and the target atoms \( A, B, \) and \( C \) in a MC-BCA simulation with a maximum impact parameter of \( p_{\text{max}} \). The target atoms remain at their respective lattice positions in (a) while a random displacement has been added to the lattice position of \( A \) after it has been chosen as a collision partner, bringing \( A \) to a position \( A' \) that is closer (b) or further away (c) from \( I \).
Fig. 5-13 (a) this is atom $A$ since $p > p_{\text{max}}$ for atom $C$, and $B$ is further away from $I$ than $A$. The value of $p_{\text{max}}$ should be chosen large enough so that collisions with $p > p_{\text{max}}$ have a negligible effect on the ion trajectory, but not too large since the number of collisions per unit path length in a simulation increases as $p_{\text{max}}^2$. Typical values for $p_{\text{max}}$ are 2-3 Å. Once the collision partner is found the ion is moved forward a distance $\Delta r$ to the asymptotic point of the collision $I'$ (see also Fig. 5-2) and the nuclear kinetic energy loss $T$, and scattering angles $\vartheta$ and $\phi$, are calculated by solving Eq. (5-4). After subtraction of the electronic energy loss (see below) the procedure is repeated – the next collision in Fig. 5-13 (a) would be with atom $B$ at $I''$ – until the ion energy falls below some lower limit value, typically in order of a few eV, where the ion is considered to be stopped. When simulating range distributions, a large number of ions is followed from a randomly chosen position at the target surface until they are stopped. For a target with an ideal lattice, i.e. no thermal vibrations or damage, it is only the start position that involves any random numbers in a simulation.

The bottlenecks of MC-BCA codes are typically the algorithms that search for the next collision partner and the solution of the scattering integral, Eq. (5-4a). While earlier codes solved the scattering integral by some time-consuming numerical method, one of the main achievements of the TRIM code was an effective treatment of the problem, i.e. the so-called Magic Formula [102, 137]. However, with the increasing memory resources of modern computers, the scattering integral is fastest solved by employing a 2D look-up interpolation scheme [142].

The MC-BCA simulations presented in this thesis have been performed using a new code for crystalline targets, developed as a part of this work. The program has named SIIMPL (simulation of ion implantation) and in this version, the scattering integral has been solved using the Magic Formula with the universal interatomic potential [102].

**Electronic Stopping**

The electronic energy loss is subtracted from the ion energy in each collision. This energy loss can either be treated as a conventional stopping force, i.e. $\Delta E_e = N S_e \Delta r$, or, as originally proposed by Firsov [106], as a function of the impact parameter [Eq. (5-7)]. This latter approach is preferable and physically motivated since experiments have shown that the electronic stopping is less for channeled ions than for ions with a “random”


5.4 Ion implantation – simulation

The most commonly used form of an impact parameter depending electronic stopping is that of Oen and Robinson [136]

\[ \Delta E_e^{OR} = ANS_e \exp(-sp/a), \]

(5-9)

where \( s \) is a constant originally set to 0.3, but is usually treated as a fitting parameter, and \( a = a(Z_1, Z_2) \) is a screening length. \( A = A(p_{\text{max}}, s, a) \) is a normalizing constant, which ensures that the average stopping cross section of Eq. (5-9) for a random trajectory is equal to \( S_e \). The dependence of the \( s \) parameter in \( \Delta E_e^{OR} \) on the range profile of a 60 keV Al implantation in the [1123] direction of 4H-SiC is depicted in Fig. 5-14. One simulation is performed with no impact parameter dependence \( (s = 0) \), and three with \( s \) set to 0.3, 0.5, and 0.7, respectively. All simulations give the same projected range for ions that never entered a channel at the surface (the random peak at 0.07 \( \mu \)m), which shows that the normalization parameter \( A \) in Eq. (5-9) has been accurately determined. The differences in penetration depth for the deepest channeled ions are, on the other hand, substantial. The best fit to the experimental profile among these values is given for the simulation with \( s \) set to 0.5.

Figure 5-14 Normalized SIMS profile (thick solid line) of a 60 keV Al implantation into the [1123] direction of 4H-SiC. MC-BCA simulations (histograms) of the implantation with the \( s \) parameter of the Oen-Robinson electronic stopping expression set to 0, 0.3, 0.5, and 0.7 are also included. The mean electronic stopping in the simulations is from paper V.
Thermal vibrations
As already mentioned in Sec. 5.2, thermal vibrations of the target atoms are an important factor for the dechanneling of channeled ions and should therefore be included in MC-BCA simulations of crystalline targets. In the MARLOWE code, vibrations of the atoms are treated in such a way that the collision partner is first located assuming a frozen lattice. A random 3D-displacement with a Gaussian distributed amplitude and a standard deviation of $\sqrt{3} \langle u_\alpha \rangle$ is thereafter added to the lattice position, after which the impact parameter and point of collision are recalculated (see Table 2-II for typical values of $\langle u_\alpha \rangle$ at 300 K). However, this treatment brings problems that may be difficult to circumvent. Figure 5-13 (b) illustrates a situation where the thermal displacement has brought the atom from lattice position $A$ to a position $A'$, closer to the ion. This means that if the scattering angle in the collision with $A$ is small, the ion, now at $I'$, may collide with atom $A$ a second time. This effect was, however, taken into account and could be avoided [135]. What was not considered is the situation where the thermal displacement brings the atom further away from the ion [Fig. 5-13 (c)], which also gives rise to severe problems. In this case, when the ion is moved to the position $I'$, there is a probability that the collision with atom $B$ never occurs, irrespective of the impact parameters for the collisions. For a channeled ion, i.e. with a trajectory almost parallel to the atomic rows, the probability for this to happen is substantial since the projections on the ion path of the lattice positions of two atoms at opposing sides of the channel then can be very close. This is for example the case for the atoms $A$ and $B$ in Fig. 5-13.

Unfortunately, there is no easy way to solve this latter problem. Instead, it would be better to add the displacements to the lattice positions first and then search for the collision partners. Naturally, the displacements can then not be extracted using random numbers since they would have to be the same for the same atom position each time it is evaluated, to avoid the above mentioned problems. However, by replacing the random numbers by a rapidly – relative to the distance between neighboring atoms – oscillating function that is a function of the laboratory lattice position $|r|$ only, seemingly uncorrelated lattice vibrations can be accomplished. In this way the problems of the MARLOWE model are avoided since the positions of the atoms are not changed after a collision partner has been found. Appendix C presents an effective algorithm that produces these “quasi
random” numbers as a function of $|r|$. This vibration model will be referred to as the SIIMPL algorithm below.

The reason why this problem, to our knowledge, has not been noted previously is most likely due to the fact that it is more or less cancelled by another algorithm in the MARLOWE code, which is intended to solve a completely different problem, namely the simultaneous collision algorithm. This algorithm was introduced since Robinson and Torrens suggested that the standard BCA treatment may introduce an instability for ions with a channeling trajectory, if the distance between subsequent binary collisions is too small. Instead they proposed a quasi many-body treatment of the problem where the momentum transfer in each of these binary collisions should be linearly subtracted from the ion momentum and the then ion moved directly to the most distant of these “simultaneous” collisions [135]. However, this point has never been properly investigated, although it would be possible with today’s computational resources using MD-simulations. One consequence of the simultaneous collision model is the cancellation of the above mentioned neglect of collisions in the treatment of the thermal vibrations.

The effect of the missing collisions in the MARLOWE thermal vibration algorithm and the role of the simultaneous collision algorithm are illustrated in Fig. 5-15, which shows the simulated range profiles of a 100 keV implantation into the [001] direction of a single cubic test target with a

![Figure 5-15](image)

**Figure 5-15** Two sets of simulations of 100 keV X ions ($Z = 15$ and $M = 30$) into the [001] directions of a single cubic test target X, using the MARLOWE (broken lines) and SIIMPL (solid lines) algorithms for thermal vibrations. No vibrations are included in (a) while the mean atomic 1D-displacement $<u_x>$ is set to 0.01 Å in (b) and (c). For the simulations in (c) the simultaneous collision algorithm has been used. Both sets of simulations were executed using the SIIMPL code.
lattice parameter of 2 Å. Both the ion and target atoms are of a test species X, which has been defined with atomic number 15 and mass 30. The simulations using the two different thermal vibration algorithms are both executed using the SIIMPL code. In Fig. 5-15 (a) simulations are performed with a frozen lattice and the profiles of the MARLOWE and SIIMPL algorithms are practically identical. However, when a very small vibration is included, \(<\mu> = 0.01\) Å, [Fig. 5-15 (b)] the simulated profile using the MARLOWE vibration algorithm becomes considerably more shallow, while the SIIMPL profile does not differ significantly from the simulations of a frozen lattice. The SIIMPL result seems to make more sense considering the small amplitude of the vibrations. Figure 5-15 (c) shows the simulated profiles with the same small lattice vibration as in Fig. 5-15 (b), but now also including the simultaneous collision algorithm in both simulations. Again both algorithms produce very similar profiles, but with even less dechanneling compared to the frozen lattice simulations in Fig. 5-15 (a). These results clearly demonstrate that the MARLOWE treatment of thermal vibrations leads to a significantly overestimated dechanneling rate and that this artifact is cancelled by the inclusion of the simultaneous collision algorithm. As a consequence, these results also put some major question marks around the proposed limitations of the BCA treatment caused by simultaneous collisions.

**Damage and dose dependence**

The calculation of ballistic damage profiles, i.e. of mono vacancies and interstitials produced in the binary collisions, is a relatively straightforward procedure in MC-BCA simulations. If the energy transferred from the ion to the target atom in a collision \(T\) exceeds the displacement energy \(E_d\) for that species (see Sec. 5.3), the ion trajectory of the recoiling secondary atom is treated in the same way as the implanted, primary ion. Since there is no time dependence in the MC-BCA scheme and hence no correlation between the recoils, the trajectories of the secondary ions and the subsequent generations of recoils that they may produce, can be performed one at a time after the primary ion trajectory has been completed. This method is usually referred to as the full damage cascade algorithm. A simpler way to determine damage profiles is the Kinchin-Pease model, which states that the interstitial and vacancy concentration profiles are proportional by a factor of \(0.4/E_d\) to the distribution of energy deposited in nuclear collisions by the primary ion [102]. This is a much faster method.
since the recoiling trajectories are not simulated, but it is less accurate especially for compound targets. Full damage cascade calculations must also be employed to demonstrate effects like the small forward shift of the interstitial relative to the vacancy profiles [143].

If the crystal damage reaches high enough concentrations during an implantation, the trajectories of the subsequently implanted ions may be seriously affected. This dose-effect can be seen as a saturation of channeling tails in ion range profiles, since atoms displaced by the implantation (in the following called interstitials) gradually “fill” the channels of the crystal and hence enhance the dechanneling rate. Examples of this type of dose dependent range profiles in SiC can be found in Papers VI and VII. A simple way to include this phenomenon in MC-BCA simulations is to evaluate the probability of the next collision to be a collision with an implantation induced interstitial atom. This probability $P$ is often [140, 144, Paper VI] evaluated as

$$P = c_a N_I / N,$$  \hspace{1cm} (5-10)

where $N_I$ is the local density of interstitials provided by the simulation. $c_a$ is a semi empirical parameter, which among other things include recombination, clustering, and the scattering efficiency of the point defects. $P$ is then compared to a random number, which decides if the collision is to be with an interstitial instead of a lattice atom. The collision with an interstitial atom could in principle be done by defining the position of the interstitial in the unit-cell, but it is more commonly treated as a collision with a randomly positioned target atom. In the MARLOWE code this is accomplished by a random rotation of the crystal before the collision, while the SIIMPL code randomly positions the target atom in a cylinder in front of the ion, which has a radius $p_{\text{max}}$ and a length $L_{\text{cyl}} = 2(\pi p_{\text{max}}^2 N)^{-1}$. The same models can also be used for simulations of amorphous targets or amorphous surface layers.

However, by evaluating $P$ according to Eq. (5-10) the dose dependence for ions with a channeling trajectory will not be unambiguously treated in the simulation, which is explained in the following. Since the interstitial atoms are assumed to be randomly distributed in the target, it follows that the average path length between collisions with the interstitial atoms, $<\Delta r_I>$, should be,
Hydrogen diffusion and ion implantation in silicon carbide

\[
<\Delta r> = \left(\pi p_{\text{max}}^2 N_i\right)^{-1},
\]  

(5-11)

for all types of ion trajectories. In the BCA simulations, \( <\Delta r> \) will be given by

\[
<\Delta r> = \frac{<\Delta r>}{P},
\]

(5-12)

where \( <\Delta r> \) is the average path length between subsequent binary collisions with the target atoms. For an ion with a random trajectory, \( <\Delta r> \) is given by

\[
<\Delta r_{\text{rand}}> = \left(\pi p_{\text{max}}^2 N_i\right)^{-1},
\]

(5-13)

which shows that the simulated \( <\Delta r> \) [Eq. (5-12)] for a random path ion becomes identical to Eq. (5-11) with \( P \) evaluated according to Eq. (5-10). However, for an ion with a channeling trajectory, Eq. (5-13) is no longer valid due to the ordered movement of the ion relative the lattice, and \( <\Delta r> \) will thus differ from the value stipulated by Eq. (5-11). Simulations have shown that depending on the value of \( p_{\text{max}} \), \( <\Delta r> \) for a channeled ion can differ up to about 30% compared to \( <\Delta r_{\text{rand}}> \). This has the effect that the dechanneling rate caused by implantation induced damage is over- or underestimated by the same amount. One way to overcome this problem is to instead evaluate \( P \) as:

\[
P = c_p N_i <\Delta r_{\text{loc}}> \pi p_{\text{max}}^2,
\]

(5-14)

where \( <\Delta r_{\text{loc}}> \) is a local value, determined during the simulation and updated typically every 50 collisions. In this way, Eq. (5-11) will always hold. In SIIMPL, \( P \) is evaluated according to Eq. (5-14).

**Simulation examples**

A critical test for a simulation code is to examine its ability to handle implantations in various high symmetry directions of a crystal. This has been done using the SIIMPL code for the 9 different alignments of the dose-independent 60 keV Al implantations in 4H-SiC, presented earlier in Sec. 5.2 and in Paper VII. The simulated and experimental profiles are shown in Fig. 5-16. The labels, (a)-(i), of the panels in Fig. 5-16 correspond to those in Fig. 5-7. Two parameters have been adjusted in these simulations: the \( \lambda \) parameter of the \( \Delta E_{\text{c,OR}} \) expression (Eq. 5-9), and the thickness, \( L_\alpha \), of an amorphous surface layer. The introduction of this type of layer is a standard procedure in this kind of simulations [145-148] and
has been physically motivated to represent a native oxide on the sample surface. However, $L_a$ is usually treated as a fitting parameter in the simulations in order to obtain a correct channeling fraction. The average electronic stopping, $S_e$, is the one extracted in Paper V. The simulated profiles are found to be in good agreement with the experimental ones for all directions. This is quite remarkable considering the large variation of the experimental profiles, which is clearly demonstrated in Fig. 5-6, and the fact that the same set of parameters was used in all simulations to accomplish an overall best fit, namely $s = 0.52$ and $L_a = 8 \, \text{Å}$. 

Figure 5-16 Normalized SIMS (solid lines) and MC-BCA simulated (histograms) profiles of nine 60 keV Al implantations in different axial (a-c), planar (d-e, g-h), and low symmetry (f, i) directions of 4H-SiC (see paper VII for experimental details). The simulations are performed using SIIMPL with the $s$ parameter in the Oen-Robinson electronic stopping model set to 0.52, and with an amorphous surface layer of 8 Å thickness to obtain an overall best fit for all simulations. The average $S_e$ is the one determined in Paper V.
Figure 5-17 shows the simulated dose dependence for the above described 60 keV Al implantations in the [0001] (a) and [1123] (b) axial directions of 4H-SiC, where $c_a$ has been adjusted to obtain best possible fits to the experimental SIMS profiles. These simulations use slightly different values of $s$ and $L_a$ than those above, to give the best possible fit for the dose-independent profiles in each direction. For the [0001] implants of Fig. 5-17 (a), $c_a$ was set to 0.6. This value is interestingly enough very close to the value obtained for a 1.5 MeV Al implantation in the [0001] direction of 6H-SiC, using a different MC-BCA code [Paper VI]. For the [1123] implants, on the other hand, best fits were obtained using $c_a = 0.25$ [Fig. 5-17 (b)]. This difference in observed in the extracted $c_a$ parameters may be caused by the fact that the interstitial defects are not randomly distributed, as assumed in the simulations, but have fixed positions in the lattice and therefore affect the ions differently in different crystal channels. It may therefore be possible to gain information of the position of the defects in the crystal from this type of profiles, using a more refined model for the interstitial type defects in the simulations.
6. Summary of results

The main body of the results presented in this summary stem from the appended articles, but some results refer to co-authored papers that have not been included in this thesis (Refs. [86], [149], and [150]) and to previously unpublished results presented in the preceding chapters.

Hydrogen (H) has been found to form electrically neutral complexes with the acceptors B and Al in SiC [149, 150]. By studying the redistribution of H during thermal anneals in a large number of pre-hydrogenated samples, a comprehensive understanding of the formation and dissociation kinetics of these complexes have been obtained. An effective capture radius for the formation of $^2$H-B complexes at 460 °C has been determined to $R_{\text{HB}} = (21 \pm 4) \text{ Å}$ [Paper I]. This value is in good agreement with that expected for a Coulomb force assisted trapping mechanism. Furthermore, the dissociation energies, $E_d$, for the two complexes have been determined and the large difference between the extracted values, $(2.51 \pm 0.04) \text{ eV}$ for $^2$H-B and $(1.61 \pm 0.02) \text{ eV}$ for $^2$H-Al, suggested that the atomic configurations of the two complexes are significantly different [Paper I]. This conclusion was later supported in an ab-initio computational study by Aradi et al. [93], who also quantitatively reproduced the observed difference in $E_d$ between the two complexes.

The migration of H under a reverse bias Schottky contact has revealed that H is present as H$^+$ in p-type SiC [86]. By studying the H redistribution in samples containing large doping gradients, the influence of internal electric fields on the H migration could be revealed [Papers II-III]. It was demonstrated that drift of H$^+$ has to be accounted for when gradients in the doping profile are present, although the original intention to use this effect to determine the intrinsic H diffusion constant was not successful (see Sec. 4.2.2). On the other hand, the effect of the built-in electric fields on the H migration was exploited in another experiment to reveal that practically 100% of the mobile H are in the positive charge state in p-type acceptor doped material [Sec. 4.2.2]. This result also agreed with the ab initio predicted position of the negative-U (+/−) level for H in the upper half of the 4H-SiC band gap [93].
The first published one of the appended papers, Paper IV, presents a study of the out-diffusion of implanted $^2\text{H}$ during thermal anneals at temperatures $\geq 1000 \, ^\circ\text{C}$. It was found that the amount of implanted $^2\text{H}$ decreased according to first order kinetics, and that the depth profiles could be well represented by computer simulations assuming trapping and detrapping of mobile $\text{H}$ at implantation induced defects. A dissociation energy for the process of $\sim 5 \, \text{eV}$ was extracted and the trapping centers were tentatively assigned to a Si-vacancy, $V_{\text{Si}}$.

A large number of “random” direction implantations of $^1\text{H}$ up to $75\,\text{As}$ have been performed at energies ranging from a few keV up to several MeV. The implantations were analyzed by SIMS and the first to fourth order distribution moments of the range profiles were determined. With additional range data obtained from the literature a vast library of implantation range distributions in SiC was assembled. In Paper V, this data are used to extract the low velocity electronic stopping cross sections, $S_e$, for $^1\text{H}$, $^2\text{H}$, $^7\text{Li}$, $^{11}\text{B}$, $^{14}\text{N}$, $^{16}\text{O}$, $^{27}\text{Al}$, and $^{31}\text{P}$. It was found that the $S_e$ behavior in SiC is in good qualitative agreement with the low-velocity $S_e$ behavior previously reported in carbon. This includes the so-called $Z_1$-oscillations ($Z_1 = \text{ion atomic number}$) and the energy dependence of the stopping, which was found to be smaller than the square root (i.e. smaller than being proportional to the ion velocity) for ions with $Z_1 \leq 8$. The main importance of the results presented in Paper V is perhaps that it presents stopping data which can be used in various implantation simulators to give accurate predictions for ion implantation in SiC. The range data were also used, in Paper VIII, to create an empirical implantation simulator for SiC, using Pearson frequency functions. This was accomplish by fitting analytical functions to the extracted distribution moments as a function of implantation energy, which then could be used as a compact look-up scheme for an implantation of a certain energy.

A series of implantations in high symmetry directions of $4\text{H}$- and $6\text{H}$-SiC has also been performed to study the effect of ion channeling as a function of implantation direction, dose, ion mass, and energy. The results presented in Papers VI and VII can be used as a guide in the choice of tilt angles for SiC wafers during implantation in order to minimize the channeling effect, but serves primarily the purpose as standards for atomistic simulation models of ion implantation. By fitting simulated implantation profiles to the depth profiles of these aligned implantations, detailed information about
6. Summary of results

electronic stopping and damage accumulation can be extracted [Papers VI and VII, and Sec. 5.4.1].

A new Monte-Carlo binary collision approximation simulation code for ion implantation in crystalline targets has been developed. The code is named SIIMPL (simulation of ion implantation) and include several updated algorithms, as partly described in Sec. 5.4.1. The SIIMPL code has been employed for the results presented in Papers V, VII, VIII, and IX. Simulations of the implantations performed in Paper VII are further presented in Sec. 5.4.1. It should be noted, however, that the simulations presented in Paper VI were performed using another MC-BCA code.

The last of the appended papers, Paper IX, presents a study where PAS measurements have been undertaken to study the vacancy type defect distributions of $^{11}$B-, $^{14}$N-, and $^{27}$Al-implanted 4H-SiC. The Doppler-broadening line-shape parameters of two types of radiation induced point defects were established and tentatively identified as $V_{Si}$ and $V_{C}V_{Si}$ (see also Sec. 3.2.5). Paper IX further demonstrates that the implantation induced defects detected by PAS at considerably greater depths than the mean projected range of the implanted ions, $R_p$, were primarily caused by ion-channeling during the implantations. This effect has previously been reported by other groups for SiC and also for other implanted materials, but it was not concluded whether it was caused by diffusion of implantation-induced defects from the region around $R_p$, or, as shown in Paper IX, by deeply channeled ions.
Acknowledgements

First of all I would like to express my gratitude towards my supervisor Anders Hallén. He had the difficult task of keeping me on reasonable track during this sometimes bumpy journey, and also to direct me back to earth when needed. I am also greatly in debt to my co-supervisor Margareta Linnarsson for patiently introducing me to the SIMS technique and for everyday discussions. Bengt Svensson has a great responsibility for the existence of this thesis. It was his inspiring lecturing in a solid state theory course (a course I was later to teach in) that first brought my attention to this research field, and it was also Bengt who accepted me as a Ph.D. student at the FTE laboratory. Bengt is further acknowledged for numerous interesting discussions and for his always careful proof reading of my manuscripts.

Experimental physics is to a high degree a collective effort. This thesis is a good illustration of this, considering that the appended papers are authored by a total of 12 people. This number increases to an astonishing figure of 62 when the authors of the papers that were not included in this thesis are also counted. All of my co-authors are greatly acknowledged, but I would like to send special thanks to Jonatan Slotte at the Helsinki University of Technology (HUT), especially for his patient understanding regarding the difficulties we encounter with the implantations for the PAS experiments. Furthermore, I am also most grateful to Jennifer Wong-Leung for being a terrific host and for enduring the impossible work-load I laid upon her during my stay at the Australian National University in Canberra (ANU).

Many of the experiments presented in this thesis would not have been possible without the unique epitaxially grown SiC structures, which were supplied by Nils Nordell, Stefan Karlsson, Adolf Schöner, and Andrey Konstantinov. Thank you all. Furthermore, I am also grateful to Erik Danielsson and to my room-mate, Uwe Zimmermann, for their assistance with the ICP etchings. Uwe is also highly appreciated for, among many things, his proof reading of this thesis and for putting up with my music over the past five years.
The FTE laboratory (now MSP) has been an inspiring place to work at. It has especially been a privilege to work in such an international environment; individuals from 18 different nations have been part of the FTE staff ever since I first started my masters project, 6 years ago. All of you are greatly acknowledged for contributing to the relaxed atmosphere at FTE.

Finally, I would like to direct my gratitude to Ulf Karlsson for his active concerns regarding my academic future on the other side of this thesis.

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Martin Janson

Stockholm, February 2003
Appendix A: Solution of the positron transport equation at steady state

This appendix outlines a precise and computer efficient method to solve the 1D positron transport differential equation at steady state,

\[ \frac{d}{dx} \left( D_+ \frac{dC}{dx} \right) - \frac{d}{dx} \left( \mu_+ E_f C \right) - \frac{C}{\tau_b} - \sum_d \mu_d C_d C + I_p = 0 \,, \quad (A1) \]

where \( D_+ \) is the positron diffusivity, \( C \) the concentration of positrons at position \( x \), \( \mu_+ \) the positron mobility in an electric field \( E_f \), \( \tau_b \) the positron bulk lifetime, \( C_d \) the concentration of positron trapping centers with trapping coefficients \( \mu_d \), and \( I_p \) the positron generation (implantation) term.

The solution generally follows the one published by van Veen et al. for the VEPFIT code [54], but since an attempt to implement their solution failed – most likely due to some printing error in Table 2 of Ref. [54] – a correct treatment is given in the following. This solution also permits gradients in the electric field, which was not allowed in the one given by van Veen et al.

Formulation of problem

Introducing Einstein’s relation for the mobility, \( \mu_+ = D_+ e E_f / k_B T \), where \( e \) is the elementary charge, \( k_B \) the Boltzmann constant, and \( T \) the absolute temperature, and assuming a constant \( D_+ \), Eq. (A1) may be rewritten as

\[ \frac{d^2 C}{dx^2} - \alpha \frac{dC}{dx} - \beta C = -\gamma \,, \quad (A2) \]

\[ \alpha = e E_f / (k_B T) \,, \]

\[ \beta = ( \sum \mu_d C_d + 1/\tau_b ) / D_+ \, dE_f / dx \, (e/k_B T) \,, \]

\[ \gamma = I_p / D_+ \,. \]

Note that the last term in the \( \beta \) expression has been omitted in the VEPFIT code [54], which will generate an erroneous solution in the presence gradients in the electric field.

Two boundary conditions for the surface (\( x = x_0 \)) are considered. The first condition assumes that the surface acts as a perfect sink for the positrons:
Appendix A: Solution of the positron transport equation at steady state

\[ C_{x=x_0} = 0 \]  \hspace{1cm} (A3)

The second type is a so-called radiative boundary condition that states that the flux \( J \) is proportional, by a factor \( -\Lambda \), to the concentration of positrons at the surface

\[ J_{x=x_0} = -\Lambda C, \]  \hspace{1cm} (A4a)

which, including diffusion and drift, at the surface can be written as

\[ \frac{dC}{dx_{x=x_0}} = (\alpha + \Lambda/D_+) C . \]  \hspace{1cm} (A4b)

The surface boundary condition is usually treated as a fitting parameter when simulating a SPB measurement. The deep boundary \((x = x_N)\) should be chosen deep enough so that \( I = E_f = 0 \) and \( C_d = C_{d, x=x_N} \) for \( x > x_N \). In that case the deep boundary condition can be written [54]

\[ \frac{dC}{dx_{x=x_N}} = -\sqrt{\beta C} \]  \hspace{1cm} (A5)

**Numerical solution**

The problem is discretized into \( N \) segments between \( x_0 \) and \( x_N \) so that the approximation \( \nabla \alpha = \nabla \beta = \nabla \gamma = 0 \) can be made in each slab. Equation (A2) can then be solved for each slab \( i \)

\[ C_i(x) = A_i \exp(d_i^+ x) + B_i \exp(d_i^- x) + \frac{\gamma_i}{\beta_i} \]  \hspace{1cm} (A6)

with \( d_i^\pm = \alpha_i/2 \pm \sqrt{\alpha_i^2/4 + \beta_i} \). The \( 2N \) coefficients \( A_i \) and \( B_i \) are determined by enforcing continuity for the neighboring \( C_i(x) \) and \( dC_i/dx \) \((x)\), and with the boundary conditions of Eqs. (A3) \(-(A5)\). Introducing the variables \( c_i = C_i \ (x = x_i) \) and \( c_i' = dC_i/dx \ (x = x_i) \) the problem can be reformulated as

\[ M c = b, \]  \hspace{1cm} (A7)

where \( M \) is a tri-diagonal matrix of size \( N \times N \), and \( c \) and \( b \) are vectors of length \( N \).
The elements of \( \mathbf{M} \) and \( \mathbf{b} \) are given in Table A1. \( c_i' \) can be determined once \( c_i \) has been solved from Eq. (A7):

\[
\begin{align*}
c_i' &= \left( c_{i-1} - f_i c_i - g_i \right) / e_i \quad (i = 2 \ldots N) \\
c_1' &= e_1 c_2' + f_1 c_2 + g_1'
\end{align*}
\] (A8a)

where \( e_i, e_i', f_i, f_i', g_i, \) and \( g_i' \) are defined in Table A-I. Once Eq. (A7) has been solved, \( \mathbf{A}_i \) and \( \mathbf{B}_i \) in Eq. (A6) may be determined from the \( c_i \) and \( c_i' \) elements.

### Table A-I. Elements of matrix \( \mathbf{M} \) and vector \( \mathbf{b} \) in equation \( \mathbf{M} \mathbf{c} = \mathbf{b} \) where \( \mathbf{c} \) are the discretized positron concentrations at \( x_i, c_i = C_0 x_i \).

<table>
<thead>
<tr>
<th>( i )</th>
<th>( m_{i-1} )</th>
<th>( m_i )</th>
<th>( m_{i+1} )</th>
<th>( b_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2 \ldots N-1 )</td>
<td>(-1/e_i )</td>
<td>( f_i + e_{i+1}' )</td>
<td>( f_i' + g_i )</td>
<td>( l_i = g_i / e_i )</td>
</tr>
<tr>
<td>( 1 ) ((C_x = x_0 = 0))</td>
<td>( \uparrow )</td>
<td>( \uparrow )</td>
<td>( \uparrow )</td>
<td></td>
</tr>
<tr>
<td>( 1 ) ((J_x = x_0 = -\Lambda))</td>
<td>(-f_i - L_0 f_i' + e_2' )</td>
<td>( \uparrow )</td>
<td>( l_i = g_i / e_i )</td>
<td></td>
</tr>
<tr>
<td>( N )</td>
<td>(-1 )</td>
<td>( f_N - e_N \sqrt{\beta_N} )</td>
<td>(-)</td>
<td></td>
</tr>
</tbody>
</table>

\[
L_0 = (\alpha_0 + \Lambda/D) / \epsilon, \quad l_i = \frac{e_{i+1}'}{e_{i+1}} g_{i+1} - g_{i+1}'
\]

\[
e_i = \frac{h_i^+ - h_i^-}{d_i^+ - d_i^-}, \quad f_i = \frac{h_i^+ h_i^+ - d_i^+ h_i^-}{d_i^+ - d_i^-} \quad g_i = \frac{d_i^+ - d_i^- - d_i^+ h_i^- + d_i^- h_i^+}{d_i^+ - d_i^-} \quad \gamma_i
\]

\[
e_i' = \frac{d_i^+ h_i^+ - d_i^- h_i^-}{d_i^+ - d_i^-}, \quad f_i' = \frac{1}{d_i^+ - d_i^-} \left( h_i^+ - h_i^- \right) d_i^+ d_i^- \gamma_i, \quad g_i' = \frac{1}{d_i^+ - d_i^-} \left( h_i^+ - h_i^- \right) d_i^+ d_i^- \gamma_i
\]

\[
h_i^\pm = e^{-d_i^\mp (x_i - x_{i-1})}, \quad d_i^\pm = \frac{\alpha_i}{2} + \sqrt{\frac{\alpha_i^2}{4} + \beta_i}
\]
Appendix B: Steady-state H profiles in the presence of doping gradients and trapping

In the presence of an internal electric field, \( E(x) \), generated by gradients in the doping profile, the steady-state concentration of mobile H\(^+\) is not homogeneous. This is realized by setting \( \partial[H^+]/\partial t = 0 \) in Eq. (4-7) (with \( A \equiv H^+ \)), which gives the steady state solution for H\(^+\), relative to the H\(^+\) concentration at some point \( x_0 \), as

\[
\frac{[H^+]_{x_0}}{[H^+]_{x_0}} = \exp \left[ \frac{q}{k_B T} \int_{x_0}^{x} E(x') dx' \right].
\]  

(B-1)

It can be seen that this ratio follows the corresponding ratio for holes and the ratio of \([H^+]\) between two points \( x_1 \) and \( x_2 \) – where the local doping gradient is negligible – will therefore follow the ratio of the uncompensated and non-passivated ionized acceptors, \( N_{A^-} \):

\[
\frac{[H^+]_{x_1}}{[H^+]_{x_2}} = \frac{N_{A^-_x_1}}{N_{A^-_x_2}}.
\]  

(B-2)

When the acceptor, X\(_x\), that gives rise to the built-in electric field also is the main trapping center for the mobile H\(^+\), the concentration of H-X complexes at steady-state [Eq. (4-8)],

\[
[HX] = \frac{4\pi RD^1}{v} [X][H^+],
\]  

(B-3)

will not be directly proportional to the acceptor concentration, which would be anticipated if the H concentration is homogenous. Instead a quadratic dependence on \([X]\) is expected. For a system where \([H]\_tot = [HX]\), i.e. \([H^+] \ll [HX]\), and with \( N_{A^-} = [X] = X_0 - [HX] - [H^+] = X_0 - [H]\_tot\), Eqs. (B-2) and (B-3) give the total concentration of H at equilibrium

\[
[H]_{tot} = k(X_0 - [H]\_tot)^2,
\]  

(B-4)

where \( X_0 \) is the total, chemical concentration of the acceptor atom, and \( k \) is a proportionality constant. In Eq. (B-4) it has also been assumed that \([H^+] \ll X_0 - [H]\_tot\). This is always true when \([H^+] \ll [HX]\) except for the case
of saturation trapping, where $[HX] = X_0$. For the case where $[H_{tot}] \ll X_0$, the measured total H concentration will exhibit a pure quadratic dependence on the acceptor concentration.
Appendix C: Quasi random number algorithm for the thermal vibration model

This appendix outlines an algorithm that generates a random-like number sequence for neighboring lattice sites of a crystal and that is a function of the lattice position \( R \) only. The algorithm is used in the new thermal vibration model of MC-BCA simulators described in Sec. 5.4, and is designed to be as computer efficient as possible considering that it will be evaluated a large number of times for each collision of the simulation. This is accomplished by creating a 64 bit variable \( R \) that expresses the distance from \( R \) to some reference point in the laboratory system, for example \([0,0,0]\). The last 10 bits of \( R \) will have a random-like behavior when evaluated for neighboring \( R \) and still give enough information for the current purpose.

Below follows an example of how this algorithm can be implemented in the programming language C. The above described variable \( R \) is assumed to have already been calculated. The last ten bits of \( R \) are shifted to become the highest bits of the mantissa in the union variable \( X.QR \). The exponent of \( X.QR \) is set to 0, which means that \( X.QR \) becomes a number between 1 and \((2 - 2^{-10}) \approx 1.999\).

```c
#define BITSHIFT 10
// BITSHIFT = (32-1-11 - N), 64 bit float, IEEE standard 754
// N = number of lowest bits that are shiftest to the
// highest bits, here N = 10 -> BITSHIFT = 10

union QR_union {
    double QR; // 64 bit double
    unsigned int i[2]; // 32 bit integer
    // i[0] == lo byte of QR
    // i[1] == hi byte of QR
};
union QR_union X;
X.QR = R;
X.i[1] = (0x3ff00000 | ((X.i[0]«BITSHIFT) & 0x0000ffff));
```

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References

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