Radiation Damage in GaAs and SiC

By

Arno Janse van Vuuren

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DECLARATION:

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I would like to express my sincere thanks to the following people:

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<table>
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<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tr>
<td>BF</td>
<td>Bright Field</td>
</tr>
<tr>
<td>BSE</td>
<td>Back Scattered Electrons</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>DHW</td>
<td>Darwin Howie Whelan</td>
</tr>
<tr>
<td>dpa</td>
<td>Displacements Per Atom</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centred Cubic</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium Arsenide</td>
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<tr>
<td>HTR</td>
<td>High Temperature Reactor</td>
</tr>
<tr>
<td>IBIEC</td>
<td>Ion Beam Induced Epitaxial Crystallisation</td>
</tr>
<tr>
<td>keV</td>
<td>Kilo Electron Volt</td>
</tr>
<tr>
<td>KP</td>
<td>Kinchin and Pease</td>
</tr>
<tr>
<td>LSS</td>
<td>Lindhard, Scharff and Schiott</td>
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<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
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<tr>
<td>MeV</td>
<td>Mega Electron Volt</td>
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<tr>
<td>MPBR or PBMR</td>
<td>Modular Pebble Bed Reactor</td>
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<tr>
<td>NHI</td>
<td>Nano Indentation Hardness</td>
</tr>
<tr>
<td>PKA</td>
<td>Primary Knock-On Atom</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts Per Million</td>
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<tr>
<td>SAD</td>
<td>Selected Area Diffraction</td>
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<tr>
<td>SE</td>
<td>Secondary Electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>SHI</td>
<td>Swift Heavy Ion</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon Carbide</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TDE</td>
<td>Threshold Displacement Energy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TF</td>
<td>Thomas-Fermi</td>
</tr>
<tr>
<td>TRISO</td>
<td>Tri-Isotropic</td>
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SUMMARY

In this dissertation the microstructure and hardness of phosphorous implanted SiC and neutron irradiated SiC and GaAs have been investigated. SiC is important due to its application as a barrier coating layer in coated particle fuel used in high temperature gas cooled reactors. The characterisation of neutron irradiated GaAs has been included in this study in order to compare the radiation damage produced by protons and neutrons since proton bombardment of SiC could in principle be used for out-of-reactor simulations of the neutron irradiation damage created in SiC during reactor operation. The following SiC and GaAs compounds were investigated:

- As-implanted and annealed single crystal 6H-SiC wafers and polycrystalline 3C-SiC bulk material implanted with phosphorous ions.
- As-irradiated and annealed polycrystalline 3C-SiC bulk material irradiated with fast neutrons.
- As-irradiated and annealed single crystal GaAs wafers irradiated with fast neutrons.

The main techniques used for the analyses were transmission electron microscopy (TEM) and nano-indentation hardness testing.

The following results were obtained for the investigation of implanted and irradiated SiC and GaAs:

**Phosphorous Implanted 6H-SiC and 3C-SiC**

- The depth of the P⁺ ion damage was found to be in good agreement with predictions by TRIM 2010.
- Micro-diffraction of the damage region in P⁺ implanted 6H-SiC (dose 5×10¹⁶ ions/cm²) indicates that amorphization occurred and that recrystallisation of this layer occurred during annealing at 1200°C. TEM analysis revealed that the layer recrystallised in the 3C phase of SiC and twin defects also formed within the layer.
Micro-diffraction of the damage region in P⁺ implanted 3C-SiC (dose 1×10¹⁵ ions/cm²) indicates that amorphization also occurred for this sample and that recrystallisation of this layer occurred during annealing at 800°C.

Nano-hardness testing of the P⁺ implanted 6H-SiC indicated that the hardness of the implanted SiC was initially much lower than unimplanted SiC due to the formation of an amorphous layer during ion implantation. After annealing the implanted SiC at 800°C and 1200°C, the hardness increased due to re-crystallisation and point defect hardening.

Neutron Irradiated 3C-SiC

TEM investigations of neutron irradiated 3C-SiC revealed the presence dark spot defects for SiC samples irradiated to a dose of 5.9×10²¹ n/cm² and 9.6×10²¹ n/cm².

Neutron Irradiated GaAs

TEM investigation revealed a high density of dislocation loops in the unannealed neutron irradiated GaAs. The loop diameters increased after post-irradiation annealing in the range 600 to 800 °C. The dislocation loops were found to be of interstitial type lying on the {110} cleavage planes of GaAs. This finding is in agreement with earlier studies on 300 keV proton bombarded and 1 MeV electron irradiated GaAs where interstitial loops on {110} planes became visible after annealing at temperatures exceeding 500 °C. The small dislocation loops on the {110} planes of the neutron irradiated GaAs transformed to large loops and dislocations after annealing at 1000 °C.
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CHAPTER 1

INTRODUCTION

SiC is a material well known for its hardness, excellent radiation resistance, high thermal conductivity, wide bandgap and chemical inertness [Helary (2006), Snead et al. (2007)]. It has applications as a semiconductor (e.g. opto-electronic devices), cutting material and a structural material in fission and fusion reactors. In the case of high temperature gas cooled reactors such as the Pebble Bed Modular Reactor (PBMR), SiC is used as one of the coating layers in the Tri-Isotropic (TRISO) coated particle [Snead et al. (2007)] as shown in Fig.1.1.

![Pyrolytic Carbon 40/1000mm SiC Barrier Coating 35/1000mm Inner PyroCarbon 40/1000mm Porous Carbon Buffer 95/1000mm](image)

**Figure 1.1. Schematic representation of the TRISO coated fuel particle [www.pbmr.co.za].**

During reactor operation, the SiC in the coated particles are exposed to neutron irradiation at elevated temperatures. The neutron irradiation leads to the generation of extended defects such as dislocation loops and voids which could enhance the transport of fission products in the SiC. The TEM study of neutron irradiated SiC is problematic since the irradiated SiC is radioactive and requires a cool down period before it can be handled for analysis. For out-of-reactor experiments, the effects of irradiation damage in neutron irradiated and annealed SiC may be simulated by using proton bombardment without the negative effects of radioactivity. However, in order to design such an experiment, the proton and neutron doses required that will produce the same degree of radiation damage must be determined. In this study, neutron irradiated GaAs was used since extensive data on the radiation damage in proton bombarded GaAs exists in the literature [Gawlik et al. (2001), Neethling and Snyman (1986), Udhayasankar et al. (1999)].
Single crystalline GaAs was irradiated with fast neutrons to a dose of $1 \times 10^{20}$ n/cm$^2$ and subsequently annealed at 600, 800 and 1000°C for 20 min in an argon atmosphere.

Another effect of neutron irradiation is the formation of phosphorous in SiC by the nuclear transmutation of silicon. Phosphorous is a major transmutation product in neutron irradiated SiC and is formed when the $^{30}$Si isotope captures a thermal neutron. After neutron capture $^{31}$P forms through negative beta decay ($^{30}$Si + n $\rightarrow$ $^{31}$Si $\rightarrow$ ($\beta$ decay) $^{31}$P) [Baranov (2007)]. Although the $^{30}$Si has an abundance of only 3.1% [Beiser (2003)] it may affect the integrity of the SiC at the high neutron doses generated in nuclear reactors. The effect of high phosphorus concentrations in SiC may be simulated in out-of-reactor experiments by implanting SiC with phosphorus ions. Although the concentration of P that will be produced in the SiC layer of coated particle in a PBMR during the average lifetime of the fuel has been calculated as 8 ppm [Heinisch et al. (2004)], the high P ion doses used in this investigation resulted in P atom concentrations of a 1000 and 50 000 ppm at the projected ion range. These high P concentrations represent the extreme upper limit case and also allow the easy detection of the defects by transmission electron microscopy.

Single crystalline 6H-SiC and polycrystalline 3C-SiC were implanted with 200 keV P$^+$ ions to doses of $5 \times 10^{16}$ and $1 \times 10^{15}$ ions/cm$^2$ respectively. These samples were subsequently annealed at 800 and 1200°C for 20 min under an argon atmosphere. Polycrystalline 3C-SiC that has been irradiated with fast neutrons to doses in the range of $9.6 \times 10^{17}$ to $9.6 \times 10^{21}$ n/cm$^2$ has been obtained from Oak Ridge National Laboratory in the USA. The sample with the lowest dose was annealed at 800 and 1200°C for 20 min in an argon atmosphere. The samples with the higher dose were annealed at 1600°C for 20 min since irradiation temperatures for these samples were a 1000°C.

The effect of the implantation and irradiation, and also annealing, on the microstructure and hardness of these materials was investigated using transmission electron microscopy and nano-indentation hardness testing respectively. The outline of this dissertation is as follows.
Chapters 2, 3 and 4 are summaries of the theoretical aspects of this investigation. In Chapter 2 the basic theory of crystals and the mechanisms through which lattice disorder arises to form point defects and extended defects are discussed. Chapter 3 summarises the interaction between energetic particles and solids in terms of the factors involved in their interaction. Chapter 4 presents a concise summary of the theory related to the equipment used in this investigation, specifically the Transmission Electron Microscope (TEM) and the Scanning Electron Microscope (SEM) and also the Nano-Indentation Hardness Tester. This is followed by a literature review on ion implantation and radiation damage in GaAs and SiC presented in Chapter 5.

Chapter 6 is a discussion of the relevant experimental methods used to prepare the specimens for analysis by the various techniques as described in Chapter 5. The preparation of the SiC and GaAs samples used in this investigation as well as the ion implantation and neutron irradiation is discussed first. The furnaces used in the annealing of these specimens are described, including the specimen holders used during annealing. The preparation of TEM specimens is discussed in detail due to the complex nature of these methods. Finally the techniques used in the preparation of specimens for nano-indentation hardness measurements are discussed.

The results of these investigations are presented in Chapter 7 and are discussed with reference to findings by other workers. The conclusions derived from these findings are discussed in Chapter 8.
A crystalline material is defined as a regular array of atoms, molecules or ions, with long range three dimensional order. In order to understand the properties of crystals, knowledge of their structure is required. The sections to follow, briefly summarise the basic concepts and definitions commonly used in the study of crystals i.e. crystallography. Real crystals usually contain many defects, which range from single atoms to groups of atoms that destroy the perfect order of the crystal. In this chapter the basic theory of crystals and the mechanisms through which disorder arises to form point defects and extended defects are discussed following the texts by Reimer and Kohl (2008), Hull (1984), Weertman and Weertman (1965), Was (2007), Casey and Pearson (1975) and Holt (1962).

2.1 Fundamentals of Crystallography

2.1.1 The Bravais Lattice and Lattice Planes

The smallest constituents of a crystal lattice are called unit cells. A crystal lattice consists of a regular array of these unit cells. Each unit cell is a parallelepiped, consisting of three non-coplanar, fundamental translation vectors \(a_1, a_2, a_3\) or equivalently \(a, b, c\). The crystal lattice may be constructed through the translation of the unit cell by multiples of the vectors \(a_i\) (Fig. 2.2). The origin of each unit cell within the lattice is described by the translation vector given by [Reimer and Kohl (2008)]

\[
r_g = h a_1 + k a_2 + l a_3 \quad (h, k, l \text{ are integers})
\]

(2.1)

The Bravais lattice is formed by the end points of these vectors. A primitive unit cell is defined as primitive if one single atom in the unit cell is sufficient to describe the positions of the other atoms by the translation vector \(r_g\).
The unit cell may contain more than one atom at the positions given by

\[ \mathbf{r}_n = u_n \mathbf{a}_1 + v_n \mathbf{a}_2 + w_n \mathbf{a}_3 \quad (n = 1, 2, 3, \ldots, N) \]  

where \( N \) is the number of atoms contained in the unit cell. The Bravais lattice is characterised by the values of \( |\mathbf{a}_1|, |\mathbf{a}_2|, |\mathbf{a}_3| = a, b, c \) and the angles between these axes \( \alpha, \beta, \gamma \).

**Figure 2.1.** The basic parameters used to define the unit cell of the Bravais lattice

[Reimer and Kohl (2008)].

Directions in a lattice are expressed as a vector connecting the origin O to the origin Q of another unit cell. The components of direction vectors are scaled so that all are integers. Lattice planes are parallel, equidistant planes, through the lattice with the same periodicity as the unit cells.

**Figure 2.2.** Construction of a lattice by translation of the unit cell as described in the text.

Examples of directions [100], [010], [001] and [312] and lattice planes with Miller indices (312) are shown [Reimer & Kohl (2008)].
Examples of three equidistant lattice planes are shown in Fig. 2.2, such a set of planes may be characterised by the use of Miller indices. A few examples of some unit cells used in the construction of the Bravais lattices are shown in Fig. 2.3.

![Figure 2.3. Examples of some unit cells used in the construction of the Bravais lattices.](image)

From the left: Simple Cubic \((a = b = c\text{ and }\alpha = \beta = \gamma = 90^\circ)\),

Simple Tetragonal \((a = b \neq c\text{ and }\alpha = \beta = \gamma = 90^\circ)\),

Simple Orthorhombic \((a \neq b \neq c\text{ and }\alpha = \beta = \gamma = 90^\circ)\),

Rhombohedral \((a = b = c\text{ and }\alpha = \beta = \gamma \neq 90^\circ)\) and

Hexagonal \((a = b \neq c\text{ and }\alpha = \beta = 90^\circ, \gamma = 120^\circ)\) unit cells among others [Hull (1984)].

### 2.1.2 The Reciprocal Lattice

Each point in the reciprocal lattice may be plotted as a vector \(g_{hkli}\) parallel to the normal of a specific plane with indices \((hkl)\) and length \(1/d_{hkli}\) from the origin O of the reciprocal lattice, where \(d_{hkli}\) is the interplanar spacing in the real lattice (Fig. 2.3). The points in the reciprocal lattice is also defined in a similar way to those in a real lattice such that the reciprocal lattice vector \(g_{hkli}\) can be written as [Reimer and Kohl (2008)]

\[
g_{hkli} = h\mathbf{a_1}^* + k\mathbf{a_2}^* + l\mathbf{a_3}^* \quad (h, k, l \text{ are integers})
\] (2.3)

\(\mathbf{a_1}^*\), \(\mathbf{a_2}^*\) and \(\mathbf{a_3}^*\) are the fundamental vectors of the reciprocal lattice.
2.1.3 Laue Zones

The product of a translation vector \( \mathbf{r}_g \) (equation 2.1) of the real crystal lattice and a reciprocal lattice vector \( \mathbf{g}_{hkl} \) gives

\[
\mathbf{g}_{hkl} \cdot \mathbf{r}_g = M \quad (M \text{ is an integer})
\] (2.4)

In the case where the product \( M = 0 \), all the \( \mathbf{g}_{hkl} \) vectors for a given value of \( \mathbf{r}_g \) lie in a plane through the origin of the reciprocal lattice and are normal to the zone axis \( \mathbf{r}_g \). The system of planes that belong to these values of \( \mathbf{g}_{hkl} \) form a group of planes that have the zone axis as a common line of intersection. The reciprocal lattice plane which contains the corresponding \( \mathbf{g}_{hkl} \) is termed the zero order Laue zone (ZOLZ). In the case where \( M = 1, 2, ... \) the first- (FOLZ), second- and higher order (HOLZ) Laue zones, are obtained. These Laue zones are parallel to zero order Laue zone. Therefore Laue zones are parallel sections through the reciprocal lattice. The construction of Laue zones is useful for use in the indexing and computation of electron diffraction patterns.
2.2 Point Defects
A point defect is a defect generated when the periodicity of the lattice is destroyed at an atom site (lattice point). In the following sections, the types, concentrations and diffusion of point defects in a real crystal are discussed. The behaviour of these point defects is governed by statistics and thermodynamics and the laws of diffusion.

The main types of point defects are: vacancies (vacant lattice sites), interstitials (atoms in the voids between normal lattice sites) and impurities (lattice or interstitial sites occupied by foreign atoms). When the defect is a result of atoms comprising of the parent lattice it is termed an intrinsic defect and when the atom is an impurity it is termed extrinsic.

When an atom moves to the surface or to some other surface within the crystal, the resulting vacancy is termed a Schottky defect. If the atom is displaced to an interstitial site; the resulting vacancy is termed a Frenkel defect. Point defects may arise due to non ideal conditions during crystal growth, through irradiation with highly energetic particles or highly energetic photons (e.g. gamma rays) and also through plastic deformation of the lattice and quenching from high temperatures [Was (2007)].
At any finite temperature, $T > 0$, there exists a finite probability for the existence of a point defect in a crystal. The crystal cannot exist in a state of absolute perfection at any finite temperature and will contain a thermodynamically stable concentration of vacancies and interstitials [Hull (1984)].

2.2.2 Effect of Point Defects on Crystal Properties

Point defects can have the following effects on crystal properties [Billington (1961)]:

**Mechanical Properties**

Point defects such as vacancies, interstitials or impurities introduce a change in the periodic density of solids. The change in lattice spacing and interatomic bonding, due to point defects, cause a change in the elastic behaviour of solids.

**Thermal Properties**

Point defects scatter phonons within solids and therefore cause a change in thermal conductivity, specifically a decrease in thermal conductivity of solids. The specific heat of a solid is also altered by the presence of point defects.

**Electromagnetic Properties**

Point defects also scatter electrons due to the change in crystal potential in the vicinity of defect site resulting in an increase in electrical resistivity.
Localized Electronic States

Localized electronic states are introduced in solids due to the change in crystal potential at the defect site. Optical absorption bands, luminescence, photoconductivity and acceptor or donor states are all a result of the presence of point defects in solids.

2.2.3 Thermodynamics of Point Defects

The equilibrium state of a crystal, at some finite temperature $T > 0$, is determined by minimizing the Gibbs free energy $F = E - TS$; $E$ being the internal energy of the crystal and $S$ the entropy. When a defect is introduced the change in the Gibbs free energy is determined by the associated change in internal energy $\Delta E$ and entropy $\Delta S$ [Was (2007) and Henderson (1972)]

$$\Delta F = \Delta E - T \Delta S$$  \hspace{1cm} (2.5)

The change in internal energy is the sum of the energy required to produce the defect and the change in vibration energy of the neighbouring atoms. The change in entropy is the sum of the change in thermal entropy, due to the change in frequency of the atomic oscillators, and configuration entropy associated with the number of ways of selecting appropriate defect locations. In a crystal with $n$ defects and $N$ available sites; the increase in free energy is given by

$$\Delta F = nE_f - T \Delta S$$  \hspace{1cm} (2.6)

where $E_f$ is the energy required to produce a single defect, including both contributions as described above. The quantity $nE_f$ is relatively large but is offset by the increase in entropy. It follows from the above equation that the equilibrium fraction of defects is given by [Hull (1984)]

$$n_{eq} = N \exp \left( - \frac{E_f}{kT} \right)$$  \hspace{1cm} (2.7)

The formation energy of vacancies is the energy required to remove an atom from the lattice and place it on the surface, whereas the formation energy of an interstitial is the energy required to take an atom from the surface and place at an interstitial site. The formation energy for vacancies is less than that required for interstitials, with the result that vacancies are more prevalent than interstitials at some finite temperature.
2.2.4 Diffusion of Point Defects:
The atoms in a crystal are always in motion due to thermal vibrations, which includes point defects. This random vibrational motion may result in atoms moving due to defects present in the crystal. The driving forces of diffusion are stress, strain, concentration gradients, electric fields and temperature. Consider first the motion of atoms associated with temperature i.e. due to thermal vibration. In order for an atom to jump into a different lattice position it must acquire enough energy, the minimum amount of energy required is termed the activation energy. The vibration of an atom may be viewed as an attempt to jump to a different lattice position, leading to the description of the atomic jump frequency $\Gamma$ as the product of vibrational frequency $v$ and the probability $P$ of the associated atom acquiring energy greater than the activation energy $E_A$ [Was (2007)]

$$\Gamma = P v$$  \hspace{1cm} (2.8)

The probability $P$ that the atom will acquire enough energy to overcome the energy barrier opposing the jump is obtained from the Maxwell-Boltzmann relationship

$$P = A \exp \left( -\frac{E_A}{kT} \right)$$  \hspace{1cm} (2.9)

Consequently the jump frequency becomes:

$$\Gamma = A v \exp \left( -\frac{E_A}{kT} \right)$$  \hspace{1cm} (2.10)

where $A$ is a constant related to the entropy difference of the atom prior to the jump and mid-way between its initial and final positions. The total number of random jumps $N_f$ an atom completes in a time $t$ is given by

$$N_f = \Gamma t$$  \hspace{1cm} (2.11)

The jump direction of the atom due to thermal vibrations is completely random in nature and after a time $t$ the atom will complete a random walk, illustrated in Fig. 2.2 through the lattice over a distance $\lambda$. 
As discussed before, a crystal will contain a finite amount of defects at some finite temperature. These defects will all complete random walks through the lattice. Defects will eventually disperse throughout the entire crystal in such a way as to minimise the free energy. Therefore a net transport of matter i.e. diffusion will take place due to concentration gradients within the crystal. The first law which describes diffusion, also known as Fick’s first law, is given by [Was (2007)]

\[ J = -D \frac{\partial C}{\partial x} \] (2.12)

The flux \( J \) is proportional to the concentration gradient \( \frac{\partial C}{\partial x} \) through the diffusion coefficient \( D \), with the negative sign indicating that diffusion takes place in the direction of decreasing concentration of the diffusing species. The diffusion coefficient is dependent on the mechanism of diffusion. Fick’s second law describes the relationship between concentration gradient and the rate of change of concentration \( \frac{\partial C}{\partial t} \) due to diffusion at a point in the material, i.e.

\[ \frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} \] (2.13)

Furthermore the diffusion coefficient is given by the relation

\[ D = D_0 \exp\left(-\frac{E}{kT}\right) \] (2.14)

where \( E \) is the activation energy, which is dependent on the mechanism of diffusion. \( D_0 \) is termed the pre-exponential factor and is temperature independent.
The average distance that a diffusing species will travel, whether it be a native interstitial, vacancy or an impurity is given by [Casey and Pearson (1975)]

\[
\langle x \rangle \approx \sqrt{Dt}
\]  

(2.15)

where \( D \) is the appropriate diffusion coefficient and \( t \) the time of diffusion and \( \langle x \rangle \) the average distance.

### 2.2.5 Mechanisms of Diffusion

**Interstitial Diffusion**

Interstitial atoms are expected to exhibit the greatest mobility for most lattices. They may move either by the interstitialcy mechanism, in which they exchange places with an atom in a normal lattice site with the replaced atom continuing the process, or by the motion of the same interstitial to a neighbouring interstitial site.

An alternative mechanism is one where the interstitial is displaced to a distant position in the lattice through strain propagation along a close-packed direction, with the interstitial itself not in an interstitial position. In this case the interstitial is no longer localised at a single lattice site, but rather the strain is shared by a number of atoms lying along a close-packed direction. Each of the effected atoms is displaced slightly from its equilibrium position. This is actually a distinct imperfection termed a “crowdion”. The number of atoms that are appreciably displaced depend on the magnitude of the repulsive forces and therefore on the nature of the interstitial.

**Vacancy Diffusion**

Vacancies propagate through the movement of neighbouring atoms into the vacant site resulting in a vacancy at a previously occupied site. Vacancies therefore move through a much simpler mechanism than interstitials.
2.3 Dislocations
Extended Defects

Extended defects or dislocations are permanent deviations from the perfect structure of crystals i.e. deviations from the correct placement of atoms in a real crystal. The types, nature and movement of extended defects are discussed in the sections to follow. Extended defects are a result of the growth and processing of real crystals and are therefore dependent on the history of the crystal.

2.3.1 Dislocation Line and Burgers Vector:

All dislocations are described by two vectors; the first is the vector along $l$ the dislocation line and $b$ the Burgers vector. Consider a dislocation formed by first making a cut in a perfect crystal, let the two sides of the cut shift away from each other by a single translation vector of the specific lattice. The shifted surfaces on either side of the cut are then rejoined by adding in an additional half plane (Fig. 2.9.). The lattice itself remains almost perfect except near the lines...
labelled $AA'$ which indicate the dislocation lines for the three possible types of dislocation (Fig. 2.10). If the atoms over the cut surface are shifted perpendicular to the line $AA'$, an edge dislocation is created; if instead the atoms are shifted parallel to the line $AA'$ a screw dislocation is created and if the shift is neither purely perpendicular nor parallel but a combination of both then a mixed dislocation with characteristics of both screw and edge dislocations is created.

Figure 2.9. Creation of Edge, Screw and Mixed Dislocations [Hull (1984)].
The alignment and length of a Burgers vector, but not its sense (direction), are given by the sign convention FS/RH (finish to start/right-handed) according to following steps [Holt (1962)]:

(i) Select an arbitrary positive direction along the dislocation line \( l \) (Fig. 2.10 a).

(ii) Execute a closed path from atom to atom in the crystal around the dislocation line in a clockwise direction when viewed along \( l \), i.e. in a right-handed screw sense, this is the Burgers circuit in the real crystal (Fig. 2.10 b).

(iii) Execute the corresponding atom to atom path from a Burgers circuit in a perfect reference crystal. The Burgers circuit in the perfect crystal will fail to close and this closure-failure taken in the FS sense is then the Burgers vector \( \mathbf{b} \).

The sense of the dislocation line \( l \) for any single dislocation is arbitrary. Parallel dislocations should have the same sense for \( l \) and if a dislocation should curve around from one direction to the opposite the sense of \( l \) must also be oppositely directed on the opposite side of the dislocation loop. The Burgers vector of an edge dislocation is perpendicular to the dislocation line and that of a screw dislocation is parallel to the dislocation line (Fig. 2.9). Dislocations may exhibit both screw and edge characteristics and the resulting Burgers vector \( \mathbf{b} \) will have edge \( \mathbf{b}_{\text{edge}} \) and screw \( \mathbf{b}_{\text{screw}} \) components given by

\[
\mathbf{b}_{\text{edge}} = b \sin(\phi) \tag{2.16}
\]

\[
\mathbf{b}_{\text{screw}} = b \cos(\phi) \tag{2.17}
\]

\( \phi \) being the angle between the dislocation line \( l \) and burgers vector \( \mathbf{b} \).

Figure 2.10. Burgers circuit in a crystal around an edge (left) and also a screw (right) dislocation, illustrating the Burgers vector in both cases [edited from Hull (1984)].
The dislocation itself is confined to a small area within the crystal known as the dislocation core and may be imagined as an area within a cylinder with a radius of the order of the lattice period (Fig. 2.11). The crystal outside the core may be considered as perfect subject only to elastic strain.

![Figure 2.11. Illustration of the dislocation core (shaded area) [Hull (1984)].](image)

2.3.2 Stacking Faults

A stacking fault is defined as a planar defect, where the stacking sequence of the crystallographic planes of a localised region within a crystal has suffered a disruption. These defects result mainly from plastic deformation through thermal or mechanical strain and may also be introduced due to production conditions. An example of a stacking fault is where an extra plane is inserted or removed in the stacking sequence denoted by ABCABC... (FCC packing), which becomes ABCACBCABC... and ABCACABC... respectively. The two types of stacking faults mentioned are termed extrinsic where an extra plane is inserted (Fig. 2.12 a) and intrinsic where a plane is removed (Fig. 2.12 b).

![Figure 4.12 Illustration of (a) an intrinsic stacking fault and (b) an extrinsic stacking fault [Hull (1984)].](image)
2.3.3 Dislocation Loops

The perfect loop
Clearly a dislocation line can also form a closed loop in the crystal rather than terminating at the surface of the crystal. The loop may present itself in the shape of a square (Fig. 2.12). This square loop is generated by making a cut in the plane bounded by ABCD; atoms on either side of the cut are shifted parallel to the plane of the cut. The sides of the cut are then rejoined by adding extra material in order to fill the shifted cut. The nature of this dislocation is both edge and screw, with specific segments exhibiting one of these properties. Both segments AB and DC have edge character and segments BC and AD have screw character. The segments on opposite sides of the loop have opposite sign.

Figure 2.12. The perfect dislocation loop [Hull (1984)].

The Prismatic Dislocation Loop / Frank Loop
Consider a dislocation loop formed by making a cut in the crystal as in the preceding section but instead shifting the cut planes by an atom distance i.e. perpendicular to the plane of the cut. A cross section through such a loop will reveal that every segment of the loop is of pure edge character (Fig. 2.13 a). A dislocation loop may also form when no extra atoms are placed in the cut and the cut planes are shifted towards each other (Fig. 2.13 b). These loops are also called Frank loops and the Burgers vector of such a loop is perpendicular to plane of the loop.
Frank dislocation loops are in effect stacking faults within the crystal (Fig. 2.13). The hard sphere model of crystals predicts that for a close-packed layer such as the \{111\} plane in the zinc blende structure, with stacking sequence ABCABC..., a close-packed layer such as A may be supported equally well by either the B or the C layer. The regular stacking sequence in this structure may therefore be locally distorted, say for instance ABCACBABC..., this is observed for dislocation loops as discussed above. A dislocation loop consisting of interstitials is termed an extrinsic stacking fault and a vacancy loop is termed an intrinsic stacking fault.

Prismatic dislocation loops form through the agglomeration of either vacancies or interstitials at localized areas within the crystal, through the process of diffusion. In the presence of a gas (e.g. He) the void formed by a vacancy loop may be filled and therefore not collapse, creating a gas filled void or two-dimensional platelet.

![Figure 2.13. Prismatic dislocation loops of (a) vacancy and (b) interstitial nature](Hull (1984))

### 2.3.4 Twinning

Twinning is defined as a process whereby a region within a crystal lattice is deformed through a homogenous shear process, which reproduces the original crystal structure but in a different orientation. The simplest case of twinning is where the twinned area is a mirror image of the original crystal (Fig. 2.14). This defect may be formed due to plastic deformation or as a consequence of the production process. Twinning is observed on the \{111\}<112> system of the FCC and zinc blende structures, due to shear effecting a displacement of 1/6<112> on each consecutive plane and may also be seen as the motion of partial dislocations with \(b = 1/6<112>\) on consecutive \{111\} planes lying parallel to the line (x-y) shown in Fig. 2.14.
2.3.5 Dislocation Energy

Elasticity theory is applied to dislocations in crystals with the exception of the dislocation core where atomic displacements are large and Hooke’s law does not apply. As explained before, the atoms outside the dislocation core, which is assumed to be confined to a cylinder of radius $r_0$, are subject only to elastic strain. It can be shown that the elastic energy of a dislocation is given by [Holt (1984)]

$$E_{total} = E_{core} + \frac{CGb^2}{4\pi} \ln \left( \frac{r_1}{r_0} \right)$$  \hspace{1cm} (2.18)

The constant $C$ is dependent on the type of dislocation and $C \approx 1$ for screw dislocations and $C \approx 3/2$ for edge dislocations, with intermediate types of dislocations having intermediate values for this constant. $G$ is the shear modulus, $b$ is the length of the Burgers vector and $r_1$ is the distance over which the dislocation causes elastic strain. The elastic fields of crystals extend over macroscopic distances that lead to the long-range interactions of dislocations with dislocations and other defects.

2.3.6 Dislocation Motion

The concept of extended defects or dislocations in real crystals were proposed to account for the unexpectedly low critical resolved shear stresses above which single crystals of metals do not recover from plastic deformation.
There exist two types of motion of dislocations termed slip (glide) where the dislocations move in the surface containing both Burgers vector and dislocation line (Fig. 2.15 a) termed the glide plane and climb in which dislocations move out of the glide plane perpendicular to the Burgers vector (Fig. 2.15 b). Dislocation slip is the main process of movement at lower temperatures, where diffusion is difficult, and at higher temperatures the process of climb also becomes possible.

The plastic deformation of crystals occurs due to the glide of specific crystallographic planes over neighbouring planes in specific crystallographic directions. Glide takes place on the close-packed \{111\} planes in the fcc and zinc blende crystal structures.

2.3.7 Dislocation Reactions

The total energy of a dislocation is approximately proportional to \( b^2 \) (equation 2.18). The reaction of dislocations is governed by Frank’s rule which states that any crystallographically possible dislocation reaction will tend to occur if the sum of the squares of the Burgers vectors of the resultant dislocation is less than the sum of the squares of those of the reacting dislocations. These types of reactions are both elastically and energetically favourable.
RADIATION DAMAGE

In this chapter the interaction between energetic particles and solids is discussed. A concise summary of the factors involved in the interaction of energetic particles and solids is presented, but the onus is on the reader to consult other relevant texts on this subject if a more detailed understanding is required [Nastasi and Mayer (2006), Carter and Grant (1976)]. The factors that govern this interaction is discussed in detail, starting with the forces involved then continuing to momentum and energy dynamics, which in turn leads to the definition of various interaction cross-sections. Particle energy loss mechanisms and range calculations along with a discussion on the overall damage caused by energetic particles conclude this chapter.

3.1 The Interaction between Particles

3.1.1 Inter-particle Forces

In general the force between two particles is related to the inter-particle potential involved in their interaction. The main assumption made for this potential is that it depends only on the inter-particle separation $r$, neglecting its dependence on other coordinates. This is called the central force approximation. The expression relating the force $F(r)$ and potential $V(r)$ is given by [Nastasi and Mayer (2006)]

$$F(r) = -\frac{d}{dr}[V(r)]$$  \hspace{1cm} (3.1)

The forces between particles may be divided into two classes, short-range and long-range forces. The nature of the long range force depends on the nature of the interacting particles i.e. charged or neutral. The Coulomb force $V_c(r)$ is most significant at larger separations when the interacting particles are charged and is defined as

$$V_c(r) = -\left[\frac{Z_1Z_2e^2}{r}\right]$$  \hspace{1cm} (3.2)

where $Z_1e$ and $Z_2e$ are the charges of the particles and as before $r$ is the separation distance.
Obviously if both particles are neutral then there is no Coulomb interaction. As the particles approach each other there is an overlap in their wave functions and in the case of atoms the electron orbits begin to overlap. The interaction of the particles now depends on quantum mechanical short-range forces and the Pauli Exclusion Principle. The inter-particle potential at these ranges is usually complex, but it is not necessary to know the exact form thereof. Empirical particle interactions are based on a simple analytical model, which gives a simple expression for this interaction. An example of such an expression which models the condensed states of solids or liquids is the Lennard-Jones potential \[ V(r) = \frac{pq}{p-q} \Delta E \left[ \frac{1}{p} \left( \frac{r_0}{r} \right)^p - \frac{1}{q} \left( \frac{r_0}{r} \right)^q \right] \]

where \( r_0 \) is the equilibrium interatomic separation, \( \Delta E = V(r_0) \) and \( p \) and \( q \) are fitting parameters.

The universal potential energy curve for solid materials is shown in Figure 3.1 (a). The minimum in this curve corresponds to the most stable configuration for atom spacing (equilibrium distance \( r_0 \) for atom neighbours) and gives the energy required to free an atom from its position in the solid. The minimum in the potential energy suggests that at this point there is net no force on the atoms. Any deviation from this equilibrium position results in an increase in the energy of the material, resulting in instability. Figure 3.1 (b) shows a plot of the relationship \( F = \frac{dV}{dr} \), which predicts that an increase in the atom spacing will result in an attractive restoring force and a decrease in the spacing results in an attractive restoring force and no force at the position \( r_0 \). The distance \( r_0 \) can be estimated for crystalline materials from the knowledge of the crystal structure.

Figure 3.1 (a). Interatomic potential function, \( V(r) \), plotted against interatomic distance, \( r \). (b) Interatomic force plotted as a function of \( r \) \([\text{Nastasi and Mayer (2006)}]\).
3.1.2 Energetic Collisions

In the case of interactions where the particle energies exceed thermal energies; the interaction distance \( r \), which depends on the energy of the collision, is less than \( r_0 \) \( (r < r_0) \). The interpenetration of the closed electron energy shells at this distance will cause alterations in the wave functions at the moment of impact. In order to understand particle-solid interactions, the inter-particle potential must be determined. This potential can also be used to calculate the rate of energy loss of an energetic particle during penetration.

Consider the interaction of two atoms with masses \( M_1 \) and \( M_2 \) and atomic numbers \( Z_1 \) and \( Z_2 \) respectively with a separation distance \( r \). The force between the atoms is best described by a potential which arises from the many bodied interaction of the electrons and nuclei.

In the case where the interaction distance is an order of magnitude smaller than the Bohr radius \( a_0 \) of a hydrogen atom \( (r < a_0) \), the most significant interaction is the Coulomb repulsion of the two nuclei and the Coulomb potential will be dominant.

If instead the interaction distance is much greater than the spacing between neighbouring atoms in the solid \( (r \gg r_0) \) then the Lennard-Jones potential will best describe the interaction of the atoms. At intermediate distances \( (a_0 < r < r_0) \) a positive interaction potential results in a repulsive force between the atoms, which has two contributions; firstly the electrostatic repulsion between the two nuclei and also the extra energy required to maintain the electrons of the atoms in the same region of space, without violating the Pauli Exclusion Principle. There is also a reduction in the Coulomb potential due to the screening of the nuclei by the inner shell electrons and the screened Coulomb potential will be in effect [Nastasi and Mayer (2006)]

\[
V(r) = \left[ \frac{Z_1 Z_2 e^2}{r} \right] \chi(r) \tag{3.4}
\]

where \( \chi(r) \) is the screening function and is defined as the ratio of the actual atomic potential, at some radius \( r \), to the Coulomb potential. Under ideal circumstances the function \( \chi(r) \) moderates the Coulomb potential so that it describes interaction at all distances.

In the low velocity regime the ion-atom approach distance falls within the range \( a_0 < r < r_0 \) so that the nuclear charge is screened by the electrons. A model describing the atom is necessitated in order to develop a screening potential. Most of these atomic models are usually simple statistical models in which the shell structure of the atom is neglected and depend only on atomic
number. The charge distributions obtained from the classical models developed by Thomas-Fermi (TF), Bohr, Lenz-Jensen and Moliere are used in these functions. The screening functions developed by various researchers are listed in Table 3.1 below.

**Table 3.1. The screening functions developed by various researchers as listed. The functions developed by Sommerfeld and Lennard et al. make use of the Thomas-Fermi charge distribution and the others make use of the charge distributions developed by the researchers as listed [Nastasi and Mayer (2006)].**

<table>
<thead>
<tr>
<th>Screening Function</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sommerfeld (TF)</td>
<td>( \chi(r) = \left[ 1 + \left( \frac{r}{12^{2/3}} \right)^{0.772} \right]^{-3.886} ) (3.5)</td>
</tr>
<tr>
<td>Lennard et al. (TF)</td>
<td>( \chi(r) = 1 - \frac{r}{(3 + r^2)} ) (3.6)</td>
</tr>
<tr>
<td></td>
<td>( \chi(r) = 1 - \frac{1}{2r} ) (3.7)</td>
</tr>
<tr>
<td>Moliere atom</td>
<td>( \chi(r) = 7p \exp(-qr) + 11p \exp(-4qr) + 2p \exp(-20qr) ) (3.8)</td>
</tr>
<tr>
<td>Bohr atom</td>
<td>( \chi_{Bohr}(x) = \exp(-x) \text{ where } x = r/a_{TF} ) (3.9)</td>
</tr>
<tr>
<td>Lenz-Jensen atom</td>
<td>( \chi_{LJ}(r) = [0.7466 \exp(-1.038r)] + [0.2433 \exp(-0.3876r)] + [0.01018 \exp(-0.206r)] ) (3.10)</td>
</tr>
</tbody>
</table>

An analytical model developed by Ziegler, Biersack, and Littmark (ZBL 1985) gives a universal screening function

\[
\chi_{U}(x) = 0.1818 \exp(-3.2x) + 0.5099 \exp(-0.9423x) + 0.2802 \exp(-0.4028x) + 0.02817 \exp(-0.2016) \]

(3.11)

The reduced distance \( x = r/a_U \) and \( a_U \), the universal screening length is given by

\[
a_U = \frac{0.8854a_0}{(Z_1^{0.23} + Z_2^{0.23})} \]

(3.12)
3.2 Collision Dynamics

3.2.1 Scattering Theory

The description of the interaction between energetic particles usually involves the following assumptions: (1) only the interaction between two particles is considered, (2) classical dynamics are applicable, (3) electron excitation or ionization only has an effect as an energy loss and does not alter collision dynamics, and (4) one of the two particles is initially assumed to be at rest. Although these assumptions may not be applicable under all conditions they are valid in most cases and solutions have been developed for situations where these assumptions fail.

The interaction potentials discussed in the preceding section forms a basis for expressions which govern the interaction between particles. During the passage of a particle travelling through a solid it may collide with atoms and electrons and the interaction will depend to some degree on the nature of the particle itself. The greatest changes in the flight direction are usually caused by collisions with individual atoms within the solid.

3.2.2 Kinematics of Elastic Collisions

This section only focuses on collisions in which the kinetic energy of the system is conserved, termed elastic collisions. The energy transfer in elastic collisions between two particles can be solved by applying the principles of conservation of kinetic energy and momentum. Consider an incident energetic particle with mass $M_1$ with velocity $v_0$ and consequently energy $E_0$ given by [Nastasi and Mayer (2006)]

$$E_0 = \frac{1}{2} M_1 v_0^2 \quad (3.13)$$

As stated before the atom of mass $M_2$ with which the particle will collide is assumed initially at rest. After the collision the velocities $v_1$ and $v_2$ as well as the energies $E_1$ and $E_2$ of the projectile and target, respectively, are determined by the scattering angle $\theta$ and the recoil angle $\phi$. The meaning of these quantities is illustrated in Fig. 3.2 (a) and (b).
After solving the equations for conservation of energy and momentum the energy transferred to the atom within the solid may be shown to be

$$ T = E_2 = E_0 \frac{4M_1M_2}{(M_1 + M_2)^2} \sin^2 \left( \frac{\theta}{2} \right) $$

Equation (3.14) may be used to calculate the maximum energy $T_{\text{max}}$ transferred to the atom, which is, when the scattering angle $\theta = 0^\circ$, given by

$$ T_{\text{max}} = \frac{4M_1M_2}{(M_1 + M_2)^2} E_0 = \gamma E_0 $$

These relationships give the energy loss of a particle through elastic collisions. They will be used again later in this chapter when energy-loss, cross-section and nuclear stopping is discussed.

### 3.2.3 Motion Under a Central Force

In order to simplify calculations the central force approximation is applied which implies that in particle-solid interactions the potential $V(r)$ is a function of $r$ only. As before the atom within the solid is assumed to be at rest and the force on the incident particle is given by the central force $F(r)$, which also depends only on the separation distance $r$. The problem then has spherical symmetry.
For conservative central forces with an interaction potential \( V(r) \) the mechanical energy \( E \) of the particle of mass \( M_1 \), a distance \( r \) away from the central force \( F(r) \), is given by

\[
E = \frac{M_1}{2}[v_r^2 + v_\theta^2] + V(r) \tag{3.16}
\]

where \( v_r \) and \( v_\theta \) are the radial and transverse velocities respectively. The first term on the right hand side represents the kinetic energy of the particle in polar coordinates. The conservation of total angular momentum also holds i.e.

\[
\ell = M_1 r v_\theta \tag{3.17}
\]

Therefore equation (3.16) can be written as

\[
E = E(r) = \frac{M_1 v_r^2}{2} + \frac{\ell^2}{2M_1 r^2} + V(r) \tag{3.18}
\]

All the terms depend on \( r \) only, the first is termed the kinetic energy for the radial component, the second is the centrifugal energy and the last is the inter-particle potential energy.

### 3.2.4 Angular Orbital Momentum and Impact Parameter

The situation where a potential \( V(r) \) which tends to zero as \( r \) tends to infinity is considered next, this corresponds to the condition that a particle in motion has positive kinetic energy at infinity. This potential will have no limit in the maximum value of \( r \) but it will have a minimum value, the distance of closest approach \( r_{\text{min}} \), dependent on the particle’s total energy and the nature of the interaction potential. The effective potential energy \( V'(r) \) is given by [Nastasi and Mayer (2006)]

\[
V'(r) = V(r) + \frac{\ell^2}{2M_1 r^2} \tag{3.19}
\]

The distance of closest approach is determined by the situation where \( E = V'(r) \). At large distances the magnitudes of centrifugal energy and the interaction potential will be negligible; under these conditions a particle of energy \( E \) travels with the velocity \( v_0 = (2E/M_1)^{1/2} \).
The particle’s direction of motion is offset from a parallel line through the centre of force (target atom) by a distance $b$ directly related to the centrifugal energy and orbital angular momentum. From the conservation of angular momentum in the limit as $r$ tends to infinity

$$\ell = M_r r_{\text{min}} v_0 \rightarrow \ell = M_r v_0 b$$

(3.20)

Since angular momentum is conserved in central force scattering, $\ell$ is defined by either form (3.20) or (3.21) and the distance $b$ is called the impact parameter.

Applying the condition $E = V'(r)$ in order to determine the distance of closest approach $r_{\text{min}}$ to (3.19) and also the definition of angular momentum from (3.20)

$$0 = 1 - \frac{V(r_{\text{min}})}{E} - \frac{b^2}{r_{\text{min}}^2}$$

(3.21)

This shows that $r_{\text{min}}$ depends on the energy of the particle and the interaction potential.

![Figure 3.3. Illustration of the distance of closest approach $r_{\text{min}}$ and the impact parameter $b$ for a particle with velocity $v_0$ [Nastasi and Mayer (2006)].](image)

### 3.2.5 Distance of Closest Approach

The distance of closest approach is defined in (3.22) and may also be written as [Nastasi and Mayer (2006)]

$$\frac{V(r_{\text{min}})}{1-b^2/r_{\text{min}}^2} = E = \frac{M_2}{M_1+M_2} E_0$$

(3.22)
For a Coulomb potential energy and a head on collision where $b = 0$ it is found that

$$d_c \equiv (r_{\text{min}})_{b=0} = \frac{M_1 + M_2}{M_2 E_0} Z_1 Z_2 e^2 = \frac{Z_1 Z_2 e^2}{E}$$  \hspace{1cm} (3.23)

where $d_c$ is called the impact diameter, which is the lower limit of $r_{\text{min}}$ for a given energy and interaction potential.

### 3.3 Cross-Section

#### 3.3.1 Scattering Cross-Section

The large number of collisions in particle solid interactions forces the use of statistics in order to determine the energy transferred as well as the scattering angle. The differential scattering cross-section, which is the first step in developing the concept of cross-sections, is a measure of either the probability that an energy $T$ in the range between $T + dT$ will be transferred to an atom or of the probability of a particle being scattering by some angle $\theta$ in the range between $\theta + d\theta$.

Consider the experiment depicted in Fig. 5.4 where a beam of particles is incident on a thin solid and is scattered into a detector of area $\Delta a$ at a polar angle $\theta$ between $\theta + d\theta$. Each particle in the beam possesses a unique impact parameter $b$ and is scattered through a different angle. Thus the differential scattering cross-section $d\sigma(\theta)$ per unit angle is given by \[Nastasi \text{ and Mayer (2006)}\]

$$\frac{d\sigma(\theta)}{d\Omega} = \frac{1}{I_0} \frac{dn_\theta}{d\Omega}$$  \hspace{1cm} (3.24)

Where $I_0$ is the number of particles incident on the solid per unit time, $dn_\theta$ is the number of particles scattered into the detector of area $\Delta a$ between angles $\theta$ and $\theta + d\theta$, per unit time and $\Delta \Omega$ is the solid angle of the detector. Note that where $\Delta a \to 0$ we have $\Delta \Omega \to d\Omega$. 
All particles with impact parameter $b$ will strike the edge of a circle of radius $b$ around the target atom and will be deflected by an angle $\theta$. All particles with impact parameter less than $b$ will be scattered by an angle greater than $\theta$. This target area defined by the impact parameter is called the total cross-section [Nastasi and Mayer (2006)]

\[
\sigma(\theta) = \pi b^2
\]  \hspace{1cm} (3.25)

For projectiles with a small impact parameter $b$ the cross-section defined by equation (3.25) will be small but, due to interaction forces, the scattering angle will be large. Therefore $b \propto \sigma(\theta)$, whilst $b$ and $\sigma(\theta)$ are inversely related to $\theta$, that is $b = b(\theta)$. It may be shown that this relationship is given by [Nastasi and Mayer (2006)]

\[
b^2 = 2 \int_0^\pi d\sigma(\theta) \sin \theta d\theta
\]  \hspace{1cm} (3.26)

All the symbols have the same meaning as above.
3.3.2 Energy-Transfer Cross-Section

The expression for the energy transfer cross-section is developed by using probability functions for particle scattering. Consider the situation depicted in Fig. 3.5; a flux of energetic particles traverses a solid of thickness $\Delta x$ of unit area with density of $N$ atoms per unit volume. Each target atom presents an effective scattering area $\sigma$ to the incident particles. Thus this solid contains a total of $N\Delta x$ atoms per unit area. The total fraction of target surface area is represented by the product of the scattering area $\sigma$ and the total number of atoms per unit area $N\Delta x$ i.e. $\sigma N\Delta x$.

![Figure 3.5. Illustration of a section of a scattering solid with each target atom presenting an effective scattering area, $\sigma$ [Nastasi and Mayer (2006)].](image)

The probability $P(E)$ of a particle with energy $E$ experiencing a scattering event whilst traversing a solid of thickness $\Delta x$ is given by [Nastasi and Mayer (2006)]

$$P(E) = \sigma(E) N\Delta x$$

(3.27)

where $\sigma(E)$ is the total collision cross-section which gives a measure of the probability for any type of collision to occur, where energy transfer is possible. The probability $P(E,T)$ that a particle of energy $E$ will transfer an amount of energy between $T$ and $T + dT$ to a target atom whilst traversing a distance $\Delta x$ is obtained by differentiating (3.27)

$$P(E,T)dT \equiv \frac{dP(E)}{dT}dT = N\Delta x \frac{d\sigma(E)}{dT}dT = \frac{1}{\sigma(E)} \frac{d\sigma(E)}{dT}dT$$

(3.28)

where $d\sigma(E)/dT$ is the differential energy transfer cross-section.
The total energy transfer cross-section is given by [Nastasi and Mayer (2006)]

\[ \sigma(E) = \frac{\tau_{\text{max}}}{\tau_{\text{min}}} \frac{d\sigma(E)}{dT} dT \]  

(3.29)

The total energy transfer in terms of scattering angle \( \theta \) may be found by considering the probability of scattering a particle into the angular range between \( \theta \) and \( \theta + d\theta \) while it travels a distance \( dx \) [Nastasi and Mayer (2006)]

\[ \sigma(\theta) = \frac{\sigma(\theta)}{b_{\text{max}}} db = \int \frac{db}{b_{\text{max}}} \int 2\pi db \]  

(3.30)

where \( T_{\text{max}} \) is the maximum energy that may be transferred and \( T_{\text{min}} \) is a lower limit to the energy transfer process, \( b_{\text{max}} \) is the maximum impact parameter. The total cross-section given by equations (3.29) and (3.31) is the same i.e. \( \sigma(E) = \sigma(\theta) \).

3.4 Energy Loss/Ion Stopping

3.4.1 The Energy-Loss Process

An energetic particle traversing a solid will undergo a series of collisions with atoms and electrons within the solid. The energy loss rate \( dE/dx \) of the particle is dependent on initial energy \( E_0 \) of the particle and the nature of incident particle (the atomic number \( Z_1 \) in the case of an ion) and the atomic number of the target atom \( Z_2 \), and is therefore also dependent on the screened Coulomb interaction with the atoms and electrons. The energy loss rate has two distinct contributions, firstly nuclear collisions (elastic) in which energy is transmitted to the lattice atoms and secondly electronic collisions (inelastic) in which the moving particle excites or ejects atomic electrons. The energy loss rate can therefore be expressed as [Nastasi and Mayer (2006)]

\[ \frac{dE}{dx} = \frac{dE}{dx}_{n} + \frac{dE}{dx}_{e} \]  

(3.31)

The subscripts \( n \) and \( e \) denote nuclear and electronic losses respectively. Nuclear energy loss is the mechanism responsible for lattice disorder through the displacement of atoms, whereas electronic collisions involve smaller energy losses and negligible deflection of the incident particle with almost no atomic displacement.
Nuclear energy loss predominates for low energies and high mass of the incident particle and electronic loss is dominant for high energies and low mass (see Fig. 3.6).

The energy loss rate $S(E)$ or the energy loss rate per scattering centre is defined as [Nastasi and Mayer (2006)]

$$S(E) = \frac{1}{N} \frac{dE}{dx}$$

(3.32)

where $N$ is the atomic density.

\[ \text{Figure 3.6. Energy loss from electronic } S_e \text{ and nuclear } S_n \text{ stopping as a function of energy. Nuclear stopping is dominant at lower energies whilst electronic stopping is dominant at higher energies as discussed [Nastasi and Mayer (2006)].} \]

3.4.2 Nuclear Stopping

Nuclear energy loss is the loss of energy due to elastic collisions of the incident particle with lattice atoms. The nuclear stopping cross-section for a particle with energy $E$ is given by [Nastasi and Mayer (2006)]

$$S_n(E) = \frac{1}{N} \left| \frac{dE}{dx} \right|_{n} = \frac{T_{\text{max}}}{T_{\text{min}}} \int_{T_{\text{min}}}^{T_{\text{max}}} \frac{d\sigma(E)}{dT} TdT$$

(3.33)

where $d\sigma(E)/dT$ is the energy transfer differential cross-section.
3.4.3 Electronic Stopping

Electronic stopping involves the interaction of charged particles. The best example is an energetic ion incident on a solid. At high velocities (energies) the charge state of the ion increases up to a point where it is completely devoid of all its electrons at \( v \geq v_0 Z_1^{2/3} \). At this point the ion may be viewed as a positive point charge \( Z_1 \), moving with a velocity greater than the orbital velocity of the atomic electrons of the target atom. In this high velocity regime the influence of the ion on the target atom may be viewed as a small and sudden external perturbation, producing a transfer from the ion to the target electron. The energy loss from a fast particle to a stationary nucleus or electron may be calculated by means of scattering theory in a central field. The stopping cross-section decreases with increasing velocity, because the ion spends less time in proximity with the atom.

High-Energy Electronic Energy Loss

In the situation where the ions velocity is greater than \( v_0 Z_1^{2/3} \), at this point the ion may be viewed as a positive point charge \( Z_1 \). The energy loss in this case is given by [Nastasi and Mayer (2006)]

\[
\frac{dE}{dx} \bigg|_e = \frac{2 \pi Z_1 e^4}{E} N Z_2^2 \left[ \frac{M_1}{m_e} \right] \ln \frac{2 m_e v^2}{I}
\]

(3.34)

where \( m_e \) is the mass of an electron, \( N \) is the atomic density, \( M_1 \) the mass of the incident charged particle, \( v \) the velocity of the particle, and the other symbols have their usual meaning.

The average excitation energy \( I \), in electron volts for most elements is given by

\[
I \cong 10 Z_2
\]

(3.35)

where \( Z_2 \) is the atomic number of the target atoms. The description of stopping power thus far ignores the shell structure of the atoms and variation in electronic binding.
Low-Energy Electronic Energy Loss
In the situation where $v < v_0$ equation (3.34) is no longer valid. For energetic charged particles moving with a velocity $v < v_0 Z_i^{2/3}$ the majority of the atomic electrons are moving with velocities greater than that of the incident particle. In this situation the electrons cannot gain energy from the ions through direct collision. The model developed by Firsov involves the transfer of momentum when the target electrons are picked up or captured by the particle. The electron needs to be accelerated to the ion velocity $v$ and through this process the ion loses a small amount of momentum proportional to $m_e v$. The other model developed by Lindhard and Scharff which may be obtained through the procedure followed by Firsov. The primary difference between the models lies in the choice of interaction potential. The Lindhard-Scharff stopping cross-section is given by [Nastasi and Mayer (2006)]

$$S_s(E) = 3.83 \frac{Z_1^{7/6} Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{3/2}} \left[ \frac{E}{M_1} \right]^{1/2} = K_l E^{3/2}$$

(3.36)

Where all the symbols have their usual meaning.

3.5 Particle Range
3.5.1 Range Concepts
As discussed in the preceding sections an implanted particle loses energy by means of nuclear and electronic interactions with the target atoms. Nuclear interactions are individual elastic collisions between the particle and the target atom. Electronic interactions may be viewed as a continuous viscous drag phenomenon between the incident particles and the sea of electrons surrounding the target atoms. Fig. 3.7 illustrates the path of a particle as it comes to rest within the target material. The ion does not travel in a straight line due to collisions with the target atoms.

The total distance covered by the particle is called the range $R$. The ion’s net penetration within the solid, which is the distance measured perpendicular to the surface of the sample to the point where the particle comes to rest is called the penetration depth $R_p$. 
3.5.2 Range Distributions

The stopping of particles by a solid is a random process, because the collision sequence, the particle deflection and the total path length vary randomly from particle to particle. As a result particles with the same energy incident at the same angle onto the same material would be straggled across range of different depths with the most probable projected range referred to as the average or mean projected range. The depth distribution $N(x)$, normalised for a dose of $\phi_i$, is given by [Nastasi and Mayer (2006)]

$$N(x) = \frac{\phi_i}{(2\pi)^{1/2}\Delta R_p} \exp\left[-\frac{1}{2}\left(\frac{x - R_p}{\Delta R_p}\right)^2\right]$$  \hspace{1cm} (3.38)

where $R_p$ is the projected range (mean depth of the distribution) and $\Delta R_p$ is the projected range straggling (standard deviation of the distribution).

Figure 3.7. A particle incident on a solid penetrated with a total path length $R$, resulting in a projected range $R_p$, along the direction parallel to the incident ion [Nastasi and Mayer (2006)].

The range of the ion is determined by the rate of energy loss along the path of the ion and is given by [Nastasi and Mayer (2006)]

$$R = \int_{E_0}^{0} \frac{1}{dE/dx} dE$$  \hspace{1cm} (3.37)

where $E_0$ is the incident energy of the particle.
Assuming all implanted particles are retained, the total dose related to the depth distribution is given by [Nastasi and Mayer (2006)]

$$
\phi_i = \int_{-\infty}^{\infty} N(x)dx
$$

(3.39)

The expression for peak atomic density for the implanted particle distribution is found by setting $x = R_p$ in equation (3.39) [Nastasi and Mayer (2006)]

$$
N(R_p) = N_p = \frac{\phi_i}{(2\pi)^{1/2} \Delta R_p} \equiv \frac{0.4\phi_i}{\Delta R_p}
$$

(3.40)

The analytical approach used to obtained range quantities was pioneered by Lindhard, Scharff and Schiott (1963), referred to as LSS theory. Although it is not perfect it allows for the calculation of range values with an accuracy of approximately 20%.
3.5.3 LSS Theory

The LSS theory makes use of the Thomas-Fermi (TF) statistical model of the interaction between heavy ions in order to derive a universal nuclear stopping power $S_n(E)$ and an electronic stopping power $S_e(E)$ proportional to the velocity, $v$, of the projectile. The potential has the form [Carter and Grant (1976)]

$$V(r) = \frac{Z_1 Z_2 e^2}{4 \pi \varepsilon_0 r} \phi \left( \frac{r}{a} \right)$$

(3.41)

$$a = a_0 \left( Z_1^{2/3} + Z_2^{2/3} \right)^{\frac{1}{2}}$$

and $\phi$ is the TF screening function approximated by the function

$$\phi \left( \frac{r}{a} \right) = \left[ \frac{r/a}{(r^2/a + c^2)^{1/2}} \right]$$

(3.42)

with $c = \sqrt{3}$ resulting in the best average fit to the TF potential.

Using approximation methods in finding the solution the LSS theory predicts a nuclear stopping power $S_n(E)$ of the form shown in Fig. 3.9.

Figure 3.9. Nuclear and electronic stopping powers in reduced units. The electronic stopping power variable $k$ is dependent on the mass and atomic number of the incident particle and the atoms of the target [Nastasi and Mayer (2006)]
Energies and distances are expressed in terms of the dimensionless parameters $\varepsilon$ and $\rho$ with

$$\varepsilon = E \frac{aM^2_1}{Z_1 Z_2 e^2 (M_1 + M_2)} \quad \& \quad \rho = RN 4\pi a^2 \frac{M_1 M_2}{(M_1 + M_2)^2} \quad (3.43) \& (3.44)$$

Using these parameters the nuclear stopping power $S_n$, i.e. $\frac{d\varepsilon}{d\rho}$, is a function of $\varepsilon$ only and is independent of the incoming particle or the stopping substance so that the curve in Fig. 3.8 is for a universal stopping power. Using the same units the electronic stopping $S_e$ is given by

$$\left\{ \frac{d\varepsilon}{d\rho} \right\}_n = ke^{\frac{1}{2}} \quad (3.45)$$

$$k = \xi e^{0.0793Z_1^{1/2}Z_2^{1/2}(M_1 + M_2)^{3/2}} \quad (Z_1^{2/3} + Z_2^{2/3})^{3/4} M_1^{3/2} M_2^{1/2} \quad (3.46)$$

$$\xi \approx Z_1^{1/6}$$

A universal curve for electronic stopping is not attainable since $k$ depends on the colliding atom. In the situation $Z_1 > Z_2$, $k$ is of the order of 0.1 - 0.2 and only when $Z_1 << Z_2$ does $k$ become greater than 1. In Fig. 3.9 $S_e$ is plotted for two particular values of $k$, indicating that $S_e$ is proportional to $v$ (velocity).

The average total path length may now be calculated from

$$\rho = \frac{\varepsilon}{\int_0^\infty \frac{d\varepsilon}{S_n(\varepsilon) + S_e(\varepsilon)}} \quad (3.47)$$

Different curves for $\rho$ vs. $\varepsilon$ may be plotted through the use of numerical integration for different values of $k$ (Fig. 3.10).
3.6 Displacements and Radiation Damage

3.6.1 Displacement Energy

Lattice atoms displaced by incident particles are called primary knock on atoms or PKAs, and may displace other atoms, possibly causing a cascade of displacement events. This leads to the creation of vacancies, interstitials and other types of lattice disorder, within a crystalline material, in the region of the particle track. As the number of particles incident on the solid increases the individual disordered regions begin to overlap. At some point a heavily damaged layer forms, with the total amount of disorder and depth distribution dependent on the nature of the particle, temperature, energy, dose and channelling effects.

In order for a lattice atom to be displaced a minimum amount of energy must be transferred to the target atom. This threshold energy is called the displacement energy $E_d$. In the case that the energy transmitted to the lattice atom $T$ is less than the displacement energy the target atom will undergo large amplitude vibrations without leaving its lattice site. The vibration energy of the struck atom is transferred to its neighbours and appears as a localised source of heat.
3.6.2 Displacements Produced by a Primary Knock-on (PKA)

In the case that the energy $T$ transferred to the PKA is large enough the PKA may continue the knock-on process ($E \gg E_d$), producing secondary recoil atom displacements which in turn may displace additional atoms, referred to as a collision cascade. The average number of displaced atoms in such a cascade is denoted by $\langle N_d(E) \rangle$, also known as the displacement damage function. The simplest calculation of the damage function is based on the hard-sphere model developed by Kinchin and Pease (KP) (1955). The KP model is based on the following assumptions:

(1) Collisions are between like atoms ($M_1 = M_2$)

(2) The probability of transferring energy during the collision process is determined by the hard sphere cross-section:

$$P(E,T)dT \equiv \frac{dT}{\gamma E} = \frac{dT}{E} \quad (\gamma = 1, \text{ for } M_1 = M_2)$$

(3) The cascade is created by a series of two bodied collisions

(4) All collisions are elastic (nuclear processes only, electronic stopping ignored)

(5) The energy $E_d$ used in the displacement of an atom, is neglected in the energy balance of the binary collision that transfers energy to the struck atom

(6) Effects due to crystal structure is neglected

(7) If a lattice atom receives energy less than the displacement energy $E_d$ it is not displaced with the same conditions applying to knock-on atoms. Atoms receiving energy between $E_d$ and $2E_d$ are displaced but do not contribute further to the cascade.

The following conditions hold

$$\langle N_d(E) \rangle = 0 \quad \text{for } E < E_d \quad \text{and} \quad \langle N_d(E) \rangle = 1 \quad \text{for } E_d \leq E \leq 2E_d$$

For the situation where $E > E_d$, the average recoil energy due to a PKA with energy $E$ is given by

$$\langle T \rangle = \int_0^{T_{\text{max}}} P(E,T)TdT = \frac{1}{T_{\text{max}}} \int_0^{T_{\text{max}}} TdT = \frac{E}{2}$$
Since the minimum energy needed to cause a displacement is $E_d$, the average number of displacements produced by recoil energy $\langle T \rangle$ is simply $\langle T \rangle / E_d$ or equivalently $E / 2E_d$. PKA with energy greater than $E_c$ the number of subsequent displacements is given by

$$\langle N_d(E) \rangle = \frac{E_c}{2E_d} \text{ for } E > E_c$$

(3.50)

Thus the total PKA function from the KP model is therefore given by

$$\langle N_d(E) \rangle = \begin{cases} 
0 & \text{if } E < E_d \\
1 & \text{if } E_d < E < 2E_d \\
E / 2E_d & \text{if } 2E_d < E < E_c \\
E_c / 2E_d & \text{if } E > E_c 
\end{cases}$$

(3.51)

![Figure 3.11. Illustration of the number of displaced atoms in the cascade as a function of the PKA energy according to the KP model [Nastasi and Mayer (2006)].](image)
The second and forth KP assumptions, result in an overestimate of $\langle N_d(E) \rangle$. Accounting for the electronic stopping and employing a realistic interaction potential the KP model is modified to

$$\langle N_d(E) \rangle = \frac{\xi \nu(E)}{2E_d}$$

(3.52)

where $\xi < 1$, dependent on the interaction potential, and $\nu(E)$ is the energy retained despite electronic excitation, termed the damage energy. The best estimate for the constant $\xi = 0.8$. The modified KP model is therefore given by

$$\langle N_d(E) \rangle = \begin{cases} 
0 & \text{for } E < E_d \\
1 & \text{for } E_d < E < 2E_d / \xi \\
\xi \nu(E) / 2E_d & \text{for } 2E_d / \xi \leq E < \infty
\end{cases}$$

(3.53)

### 3.6.3 Electronic Energy Transfer

In the high energy regime the fraction of the total energy loss that is due to electron excitation and ionization increases until it goes above the crossover energy $E_c$ ($S_e > S_n$) as explained in the preceding section. This is due to the ion now having enough energy to penetrate the electronic cloud of the lattice atom. The KP model is used to approximate the transition from nuclear scattering to electronic scattering. The assumption of this theory is that the presence of the electronic cloud inhibits Coulomb interaction between the nuclei of the moving and stationary atoms at a distance [Nastasi and Mayer (2006)]

$$r_0 = \frac{a_0}{(Z_1^{2/3} + Z_2^{2/3})^{1/2}}$$

(3.54)

If the kinetic energy of the incident ion is less than the Coulomb potential between the moving and stationary nuclei the collisions are assumed to be nuclear. In the case where the kinetic energy of the incident ion is more than this potential the interaction will be electronic in nature.
The kinetic energy $E_A$ at which this transition occurs is defined by [Nastasi and Mayer (2006)]

$$E_A = \frac{2E_R Z_1 Z_2 (Z_1^{2/3} + Z_2^{2/3})^{1/2} (M_1 + M_2)}{M_1}$$  (3.55)

where $E_R$ is the Rydberg energy and $M_1$ the mass of the stationary atom. It can also be shown that the assumption of electronic scattering is only valid for scattering angles of the order $r_{\text{min}}/a$, where $r_{\text{min}}$ is the distance of closest approach and $a$ was defined in equation (3.41). At lower angles the screening electrons still affect the interaction. Thus collisions only occur for impact parameters less than $r_0$, at which point the amount of energy that may be transferred is given by

$$T^* = \frac{4E_R^2 Z_1^2 Z_2^2 (Z_1^{2/3} + Z_2^{2/3})}{E} \left( \frac{M_2}{M_1} \right)$$  (3.56)

Therefore if $T^* > E_d$ all electronic collisions displace atoms, but there exists an energy $E_B$ above which only some electronic collisions cause displacement. This energy is given by [Nastasi and Mayer (2006)]

$$E_B = 4 \frac{E_R^2}{E_d} Z_1^2 Z_2^2 (Z_1^{2/3} + Z_2^{2/3}) \left( \frac{M_2}{M_1} \right)$$  (3.57)

The energy transferred to a lattice atom may be dissipated through lattice vibrations termed thermal spikes.

This is the why only some electronic collisions displace lattice atoms. The transition energy $E_c$ mentioned before is approximated by

$$E_c \approx \frac{1}{4} \left( \frac{M_2}{m_e} \right) \Delta E_G$$  (3.58)

where $\Delta E_G$ is the band gap between the valence and conduction band and $m_e$ electron mass.
In the case of metals the expression becomes

\[ E_c \approx \frac{1}{4} \left( \frac{M_2}{m_e} \right) \varepsilon_f \]  \hspace{1cm} (3.59)

where \( \varepsilon_f \) is the Fermi level but in general \( E_c \) can be approximated by the atomic weight \( M_2 \) in keV.

### 3.6.4 Damage Production Rate and DPA

Displacements per atom (dpa) is a widely used unit in the subject of radiation damage. An approximation for the dpa\((x)\) per unit dose may be found through the assumption that \( N_d(x) \), the number of displacements per unit volume at a depth \( x \) can be expressed by a modified KP expression of the form [Nastasi and Mayer (2006)]

\[ N_d(x) = \frac{0.8 F_D(x)}{2E_d} \phi \]  \hspace{1cm} (3.60)

where \( F_D(x) \) has the units of energy per unit length.

The dependence of dpa vs. depth for a given dose \( \phi \) may be approximated by [Nastasi and Mayer (2006)]

\[ dpa(x) = \frac{N_d(x)}{N} \approx \frac{0.4 F_D(x)}{NE_d} \phi \]  \hspace{1cm} (3.61)

In order to calculate the dpa produced over the range of the ion equation (3.61) must be integrated over the ion energy as the ion comes to rest. Instead an estimate may be made in the case where \( \varepsilon < 1 \) and \( Z_i > 5 \) and calculating \( N_d(v_p(\varepsilon)) \), assuming \( v_p(\varepsilon) \approx 0.8 \varepsilon \). For an ion dose \( \phi \) (ions/cm\(^2\)) and range \( R \) the approximate dpa in the implanted region is given by

\[ dpa \approx \frac{N_d(v_p(\varepsilon))}{NR} \phi \approx \frac{0.4 v_p(0.8 \varepsilon)}{NRE_d} \phi \]  \hspace{1cm} (3.62)

where \( N_d(v_p(\varepsilon)) \) is the modified KP damage function given by equation (3.52) and calculated for a damage energy given by 0.8\( \varepsilon \).
3.6.5 Spikes

A spike is defined as a high density cascade that possesses a limited volume in which the majority of atoms are temporarily in motion. Consider the spatial distribution of point defects as a particle or PKA slows to rest. The mean free path or average distance $\lambda_d$ of a particle with energy $E$, between displacement collisions with target atoms is given by [Nastasi and Mayer (2006)]

$$\lambda_d = \frac{1}{N\sigma(E)}$$  \hspace{1cm} (3.63)

where $N$ is the atomic density of the target and $\sigma(E)$ is the total collision cross-section. This equation may be used to calculate the average distance between defects for a particle of energy $E$. Analysis of the mean free path [Brinkman (1956)] suggests that as it approaches the lattice spacing of the target atoms a highly damaged region forms where every PKA is forces away from the path of the particle. This produces an area composed of a core of vacancies surrounded by a shell of interstitial atoms, referred to as a displacement spike.

![Fig 3.12 Illustration of a displacement spike within a crystal lattice](Nastasi & Mayer (2006)).
The time required for the displacement spike to form is equivalent to the time it takes for a PKA to come to rest and is given by [Nastasi & Mayer (2006)]

\[ t = \int_0^E \frac{dE}{S_n(E)N\nu} \approx \frac{R(E)}{1/2\nu} \]  

(3.64)

where \( \nu = (2E/M)^{1/2} \) is the ion velocity, \( S_n(E) \) is the nuclear stopping cross-section and \( R(E) \) the total range of the particle. At a certain point in the formation of the displacement spike, all the mobile displaced atoms reach a point where they have insufficient energy to cause further displacements. At this point the energy will be dissipated through thermal vibrations or heat. After a time a state of dynamic equilibrium is reached, where the vibration energy distribution approximates a Maxwell-Boltzmann (MB) function; known as the thermal spike phase of the cascade. This thermal spike may exist for several picoseconds before being quenched to ambient temperatures. For a MB energy distribution the temperature is related to the mean deposited energy density in the spike by

\[ \bar{\theta}_D = \frac{3}{2} k_B T \]  

(3.65)

where \( k_B \) is the Boltzmann constant.

The time it takes to quench the thermal spike may be approximated by

\[ t_q = \frac{r^2}{4D_T} \]  

(3.66)

where \( D_T \) is the thermal diffusivity and \( r \) is the radius of the thermal spike.
3.7 Defects Produced by Specific Particles
Radiation damage is largely dependent on the nature of the incident particle. The main differences due to specific types of radiation are listed below [Neethling (1985)].

**Neutron Irradiation**
Due to their neutral nature, neutrons only interact through elastic collisions with the nuclei of the target solid. This type of interaction is not very efficient (low stopping cross-section) due to the lack of Coulomb interactions and the damage per unit dose for neutrons is significantly less than that of other particles.

**Low Mass Ion Irradiation**
Ions of lower mass interact mainly through electronic excitation of the atomic electrons and have a small stopping cross-section. These ions may penetrate much deeper into the target material than the individual collision cascades. A limited number of atomic displacements occur in cascades due to light ions with the majority as isolated defects along the ion track.

**Proton Irradiation**
Proton irradiation is the extreme case of light ion irradiation. The interaction mechanism involved is long ranged unscreened Coulomb interactions, with a limited amount of large energy transfer occurring. This type of radiation is unlikely to cause amorphization of the target material and leads only to the creation of single defects.

**Heavy Ion Irradiation**
Ions of large mass interact with crystals through both elastic and inelastic collisions, these interactions involve the transfer of energy through kinetic and electronic mechanisms respectively (Fig. 3.13) The stopping cross-sections for heavy ions are large with the result that the total range of the ion is comparable with collision cascades produced by PKAs.
**Electron Irradiation**

In the case of electron irradiation the PKAs have energies just above the minimum displacement energy with the result being well spread out collisions of single atoms. *Kimberling at al. (1975)* found that 1MeV electron irradiation damage is similar to 400keV proton damage.

*Figure 3.13. An ion incident on a crystal lattice is deflected in nuclear collisions with the lattice atoms and also loses energy in collisions with electrons [Nastasi & Mayer (2006)].*
CHAPTER 4

EXPERIMENTAL TECHNIQUES – THEORY AND PRACTICE

This chapter presents a concise summary of the theory related to the equipment used in this investigation, specifically the Transmission Electron Microscope (TEM) and the Scanning Electron Microscope (SEM) and the Nano-Indentation Hardness Tester. The theory of electron microscopy is discussed in great detail in the literature used in compiling this summary (see for example Hirsch (1965), De Graef (2003), Edington (1975), Goldstein (1992) and Reimer and Kohl (2007). This chapter only highlights the key details of electron microscopy relevant to this study. The theory on the Nano-Indentation Hardness Tester is also briefly discussed based on the work of Oliver and Pharr (1991).

4.1 Interaction of Electrons with Matter
4.1.1 The Advantages of Electrons
The wave nature of electrons and the fact that they possess shorter wavelengths than visible light may be used to resolve smaller objects than is possible with visible light. Energetic electrons are capable of removing the tightly bound inner-shell electrons from the attractive field of the atomic nucleus, through transmission of energy to individual atoms within a specimen. The nature of interaction of electrons with solids allows the production of a wide range of secondary signals, summarised in Fig 4.1. Both the secondary and primary signals will be discussed in the sections to follow.

![Diagram of electron interactions](image)

**Figure 4.1.** Signals generated through the interaction of a high energy electron beam with a thin specimen [Reimer and Kohl (2007)].
The electrons accelerated down the column of the electron microscope travel at velocities comparable with the speed of light and it is therefore necessary to consider special relativity when calculating the wavelength. The wavelength $\lambda$ (in Angstrom) of the electron, considering relativistic effects is given by [Williams and Carter (1996)]

\[
\lambda = \frac{h}{2m_0eV \left( 1 + \frac{eV}{2m_0c^2} \right)^{1/2}}
\]  

(4.1)

where $h$ is Planck’s constant, $m_0$ the electron rest mass, $c$ the speed of light and $V$ the accelerating voltage.

<table>
<thead>
<tr>
<th>Accelerating Voltage (keV)</th>
<th>Non-relativistic wavelength (nm)</th>
<th>Relativistic wavelength (nm)</th>
<th>Mass ($\times m_0$)</th>
<th>Velocity ($\times 10^8$ m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.00386</td>
<td>0.00370</td>
<td>1.196</td>
<td>1.644</td>
</tr>
<tr>
<td>120</td>
<td>0.00352</td>
<td>0.00335</td>
<td>1.235</td>
<td>1.759</td>
</tr>
<tr>
<td>200</td>
<td>0.00273</td>
<td>0.00251</td>
<td>1.391</td>
<td>2.086</td>
</tr>
<tr>
<td>300</td>
<td>0.00223</td>
<td>0.00197</td>
<td>1.587</td>
<td>2.330</td>
</tr>
<tr>
<td>400</td>
<td>0.00193</td>
<td>0.00164</td>
<td>1.783</td>
<td>2.484</td>
</tr>
</tbody>
</table>

4.1.2 Electron Scattering

Electrons interacting with a solid may undergo elastic and inelastic scattering. No energy is lost by the incident electron during the elastic scattering event, whereas the electron loses a finite amount of energy during inelastic scattering. The nature of the scattering event may result in different angular distributions. The electrons may be forward scattered or back scattered, where the terms refer to the scattering angle with respect to the incident beam and a specimen normal to the beam.

Electron diffraction is a special case of elastic scattering. Diffraction of light is a well understood subject and much of the concepts used are also applicable to electron diffraction. Diffraction may be divided into two types, namely Fraunhofer and Fresnel diffraction. Fraunhofer diffraction occurs when a flat wave front interacts with an object and since a wave emitted by a point source becomes planar at large distances this is also called far-field diffraction. Fresnel diffraction occurs in the opposite case to Fraunhofer and is also called near-field diffraction. Electron diffraction patterns correspond closely to the Fraunhofer case, whereas the effect of Fresnel
diffraction is observed during imaging. The inelastic scattering of electrons may lead to the generation of many useful signals from which different images or spectroscopic data about the chemistry and electronic structure of the specimen may be extracted.

4.2 Electron Diffraction

4.2.1 Ewald Sphere and Bragg Condition

The Ewald sphere is a theoretical tool used to determine whether electron diffraction will occur within a crystal lattice. In order to construct the Ewald sphere, consider an electron of wavelength $\lambda$ and with wave vector $\mathbf{k}_0$, with $|\mathbf{k}_0| = k_0 = 2\pi/\lambda$. The vector $\mathbf{k}_0$ is drawn, parallel to the incident electron beam, so that it terminates on a reciprocal lattice point with this point now selected as the origin of the reciprocal lattice (Chapter 2). The Ewald sphere is the sphere with its centre as the origin of the vector $\mathbf{k}_0$ and radius $|\mathbf{k}_0|$. Diffraction will occur if this sphere intersects any other point in the reciprocal lattice. The wave vector $\mathbf{k}_0$ is connected via a reciprocal lattice vector $\mathbf{g}_{hkl}$ to the point intersected by the Ewald sphere, i.e. the direction in which the beam is scattered given by [Reimer and Kohl (2007)]

$$\mathbf{k} = \mathbf{k}_0 + \mathbf{g}_{hkl} \quad (4.2)$$

The Bragg law of diffraction may be exploited in the case of electrons, the difference is that for electrons only a fixed Bragg angle $\theta_B$ is allowed. The incident beam experiences scattering through an angle $2\theta_B$ when the Bragg condition is satisfied and it follows that

$$|\mathbf{k} - \mathbf{k}_0| = |\mathbf{g}_{hkl}| = 2\sin \theta / \lambda \quad \text{where} \quad |\mathbf{g}_{hkl}| = 1/d_{hkl}$$

$$2d_{hkl} \sin \theta_B = \lambda \quad (4.3)$$

It is possible that more than one reciprocal lattice point may be intersected by the Ewald sphere, which means that multiple beam diffraction may occur. This occurs due to the relaxation of the Bragg condition due to sample geometry, causing the reciprocal lattice points to extend into rods [Hirsch (1965)]. Note that the Bragg equation only describes geometric aspects of diffraction and does not predict the intensity of the diffracted wave.
Figure 4.2. Projection of the Ewald sphere in two dimensions. A Bragg reflection occurs when the sphere intersects a reciprocal lattice point, such as N [Reimer and Kohl (2007)].

4.2.2 Structure and Lattice Amplitude

The amplitude of the scattered wave in the direction of the vector $k$ may be obtained from the Fourier transform of the crystal lattice in question. Consider the $k$th ($k = 1, \ldots, n$) atom within a single unit cell. The crystal is assumed to be a parallelepiped with edge lengths $L_i = M_i a_i$ ($i = 1, 2, 3$) parallel to the fundamental vectors $a_i$. The Fourier sum is given by [Reimer and Kohl (2007)]

$$F = \sum_{m=1}^{M_1} \sum_{n=1}^{M_2} \sum_{\alpha=1}^{M_3} \sum_{k=1}^{n} f_k \exp[-2\pi i(k - k_0) \cdot (r_g + r_k)]$$

(4.4)

The summation over $k$, corresponding to the different atoms of the unit cell, can be extracted i.e.

$$F = \sum_{k=1}^{n} f_k \exp[-2\pi i(k - k_0) \cdot r_k] \cdot \sum_{m=1}^{M_1} \sum_{n=1}^{M_2} \sum_{\alpha=1}^{M_3} \exp[-2\pi i(k - k_0) \cdot r_g]$$

(4.5)

$$\frac{F_{cell}}{G}$$

The first term $F_{cell}$ is termed the structure amplitude or structure factor and is dependent on the atomic positions and nature. The second term $G$ is termed the lattice amplitude and is dependent only on the external shape of the crystal.
The structure factor describes how the atom arrangement, given by \( uvw \) for each atom, affects the scattered beam. If a unit cell contains 1, 2, 3, ..., \( k \) atoms with fractional coordinates \( u_k v_k w_k \) and atomic scattering factors \( f_k \) then the structure factor \( F_{cell} \) for the \( hkl \) reflection is given by

\[
F_{cell} = \sum_{k=1}^{n} f_k \exp(-2\pi i\mathbf{g} \cdot \mathbf{r}_k) = \sum_{k=1}^{n} f_k \exp[-2\pi i(u_k h + v_k k + w_l l)]
\]  

(4.6)

It should be noted that the intensity of the diffracted beam is proportional to the structure factor i.e. \( I_g \propto |F_{cell}|^2 \). The value of \( F_{cell} \) may be calculated for various unit cells.

### 4.2.3 Kinematical Theory of Image Contrast

In order to predict the contrast produced due to defects in crystalline solids it is useful to consider the intensity at a point \( P \) just below the specimen. The incident wave of amplitude \( \psi_0 \) is assumed to be planar. The amplitude of a scattered electron wave exiting the bottom surface of a perfect crystal of thickness \( t \) is given by [Hirsch (1965)]

\[
\psi_g = \frac{i\pi}{\xi_g} \int_0^t \exp(-2\pi i s z) dz = \frac{i\pi \sin(\pi ts)}{\xi_g \pi s} e^{-i\xi ts}
\]  

(4.7)

\( \xi_g \) is the extinction distance, which increases with increasing \( g \) and decreases with increasing \( |s| \). The extinction distance is often used in conjunction with \( s \) to describe the deviation from the Bragg condition as \( w = \xi g s \) (see section 4.3.5). A real crystal contains imperfections such as dislocations. The amplitude of the scattered electron wave exiting the bottom surface of an imperfect crystal is given by

\[
\psi_g = \frac{i\pi}{\xi_g} \int_0^t \exp(-2\pi i g \cdot \mathbf{R}) \exp(-2\pi i s z) dz
\]  

(4.8)

\( \mathbf{R} \) is the vector giving the displacement of the unit cell from its proper position. It may be shown that the diffraction intensity at the point \( P \) \((I_0 = 1)\) is given by

\[
I_g = \psi_g \psi_g^* = \frac{\pi^2 \sin^2(\pi ts)}{\xi_g^2 (\pi s)^2}
\]  

(4.9)
It is evident from the above equations that a defect is invisible when \( g \cdot R = M \) \((M = \text{an integer})\), which leads to the \( g \cdot b = 0 \) invisibility criterion for determining the Burgers vector of a dislocation [Edington (1975)]. This criterion only holds for a screw dislocation since it does not experience elastic displacement perpendicular to its slip plane. Edge dislocations have displacement components parallel and perpendicular to the slip plane and contrast may still exist even when \( g \cdot b = 0 \). To ensure complete invisibility the condition \( g \cdot b \times l = 0 \) must hold, where \( l \) is a unit vector along the positive direction of the dislocation line. The Burgers vector may then be determined by finding the reflections for which the dislocation is invisible.

4.2.4 Dynamical Theory of Image Contrast

The kinematic theory is restricted to thin films where the reflection intensity \( I_g \) is small and the decrease of primary-beam intensity \( I_0 \) may be neglected. An incident wave with amplitude \( \psi_0 \) and a diffracted wave of amplitude \( \psi_g \) fall on a layer of thickness \( dz \) within a thin crystal. After traversing this layer, the amplitude \( \psi_0 \) experiences a change \( d\psi_0 \) and \( \psi_g \) by \( d\psi_g \). These changes may be calculated by employing Fresnel diffraction theory. The result is a linear system of coupled differential equations, given by [Hirsch (1965)]

\[
\begin{align*}
\frac{d\psi_0}{dz} &= i\frac{\pi}{\xi_0} \psi_0 + i\frac{\pi}{\xi_g} \psi_g \exp(2\pi i sz); \\
\frac{d\psi_g}{dz} &= i\frac{\pi}{\xi_g} \psi_0 \exp(-2\pi i sz) + i\frac{\pi}{\xi_0} \psi_g
\end{align*}
\]

(4.10)

The second term of the first equation results from the scattering of the diffracted wave back into the primary beam; the sign of the excitation error \( s \) is the reverse of that for scattering in the opposite direction (first term in the second equation). These equations are also called the Darwin-Howie-Whelan (DHW) equations. The DHW equations may be generalized to include the case of imperfect crystals with variation in atomic positions.
The same method is followed as for kinematic theory resulting in the equations describing the wave amplitude in the imperfect crystal given by

\[
\frac{d\psi_0}{dz} = \frac{i\pi}{\xi_0} \psi_0 + \frac{i\pi}{\xi_g} \psi_g \exp(2\pi i s z + 2\pi i g \cdot R)
\]

\[
\frac{d\psi_g}{dz} = \frac{i\pi}{\xi_g} \psi_0 \exp(-2\pi i s z - 2\pi i g \cdot R) + \frac{i\pi}{\xi_0} \psi_g
\]

(4.11)

It may be shown that the intensity \( I_g \) of the diffracted wave at the bottom of the sample of thickness \( t \) is given by

\[
I_g = \left( \frac{\pi}{\xi_g} \right)^2 \frac{\sin^2(\pi t s_{\text{eff}})}{\left(\pi s_{\text{eff}}\right)^2}
\]

(4.12)

where \( s_{\text{eff}} = \sqrt{s^2 + 1/\xi_g^2} \) is the modified deviation parameter which becomes approximately equal to \( s \) when \( s \gg 1/\xi_g \) and \( \xi_g \) is the extinction distance. It is clear from equation (4.12) that the expression for the diffracted intensity reduces to that from kinematical theory for large deviations from the reflecting position or for thin samples.
4.3 The Transmission Electron Microscope (TEM)

4.3.1 Image Formation in the TEM

An electron microscope typically consists of an electron gun, a complex arrangement of electromagnetic lenses, apertures, a specimen stage, a fluorescent viewing screen and CCD (charged coupled device) camera and various other analytical attachments.

![Schematic ray path of a TEM](Reimer and Kohl (2007)).

The electron gun emits and accelerates electrons into the vacuum down the column producing a beam of high brightness and good temporal and spatial coherence. The condenser lens system, including apertures, control specimen illumination. This may range from uniform illumination of a large area at low magnification to stronger focusing for higher magnifications and also the production of an electron probe, of the order of a few nanometres, for scanning transmission electron microscopy (STEM) or analytical techniques. The specimen stage is used to control the specimen orientation with respect to the incident beam. The viewing screen and CCD are used for viewing and recording the image formed by electron-specimen interaction i.e. diffraction.
patterns or magnified image of the sample itself. The other analytical devices will be discussed in sections to follow.

The objective lens disperses electrons emerging from the bottom of the specimen in order to from a diffraction pattern in the back focal plane and subsequently recombines them to form an image in the image plane.

In order to view the diffraction pattern on the viewing screen the strength of the intermediate lens is adjusted, allowing the back focal plane of the objective lens to act as the object plane for the intermediate lens. The diffraction pattern is then projected onto the viewing screen (Fig. 4.4 a).

In order to view an image of the specimen, the strength of the intermediate lens is adjusted, allowing the object plane to coincide with the image plane of the objective lens. The image is then projected onto the viewing screen (Fig. 4.4 b).

**Bright Field Imaging**

In bright field (BF) imaging an aperture is inserted in the back focal plane objective lens (Fig. 4.5 a), which allows only the transmitted beam to pass through to the final image. The image is then formed only by the transmitted beam and any low angle inelastic scattering. The contrast in the image is produced by differences in intensities of electrons scattered into Bragg reflections from various parts of the specimen and is therefore termed diffraction contrast.

**Dark Field Imaging**

Images may also be formed by any single diffracted beam by either displacing the aperture (Fig. 4.5 b) or tilting the beam (Fig. 4.5 c) to allow the required beam to pass through this aperture.
Figure 4.4. Ray paths in the electron microscope (a) under diffraction conditions and (b) imaging conditions [modified image from Williams and Carter (1996)].

Figure 4.5. Mechanisms of diffraction contrast (a) bright field, (b) dark field and (c) dark field by tilting the beam [from Williams and Carter (2008)]
4.3.2 Image Effects of Perfect Crystals

There are certain types of image effects (or contrast) which are unrelated to crystal defects and may be observed in almost all electron microscopy specimens. These effects are predicted by theory and details concerning this may be found in the literature [Edington (1975)]. This section aims only to highlight the appearance of these effects.

**Thickness Fringes**

The variation of transmitted electron intensity in a perfect crystal is observed as dark fringes (zero intensity) which connect regions of the same thickness. The thickness of the sample at the location of these dark lines may be calculated for a known crystal orientation using the relationship given by [Edington (1975)]

\[
t = (n + \frac{1}{2})\xi_g \quad n \text{ is an integer}
\]  

(4.13)

\(\xi_g\) is the extinction distance for a specific reflection and may be calculated or obtained from literature.

**Bend Extinction Contours**

This occurs when the specimen is elastically bent about a large radius.

**Bend Contours**

In very thin regions of the sample, bending often occurs over very short distances leading to the formation of diffuse dark lines in the BF image. These fringes are wide and move rapidly across the field of view as the specimen is tilted through a small angle.

**Bend Centres**

Characteristic bend extinction contours occur in thin regions of bent samples when the beam is parallel to a simple crystallographic direction.
4.3.3 Image Effects of Imperfect Crystals

A large number of image effects due to scattering by defects of crystalline materials exist, therefore this section only aims to summarise some of the most well known effects and for a more detailed discussion the relevant literature should be consulted [Edington (1975) and Reimer and Kohl (2007)].

Stacking Faults

This is the simplest type of planar imperfection in the crystal lattice (see Chapter 2). The crystal below the fault is identical to that above the fault in spacing and orientation. The intensity distribution produced by this defect is a form of cosine fringes with depth periodicity $s^{-1}$, parallel to the intersection of the fault and the surface of the sample. These fringes are similar to thickness fringes superimposed on a uniform background. Theory predicts that stacking faults are invisible under specific orientation conditions; this property allows the determination of the nature of the fault.

Moiré Fringes

Moiré fringes are observed when two crystals, with differing lattice parameters or orientation overlap. Characteristic light and dark interference bands, usually parallel are observed for this kind of defect. The pattern arises from interference between the transmitted and doubly diffracted beams. The fringe spacing is related to interplanar spacing and therefore allows for the determination of the lattice parameter, if the lattice parameter of the other crystal is known.

Perfect Dislocations

When a dislocation is parallel to the specimen surface it is visible as a dark line on a bright background in BF mode; inclined dislocations are seen with a dotted-line or zigzag contrast if the condition $\tau >> \tilde{\xi}_g$ holds.
**Dislocation Loops**

Dislocation loops are separated into three classes, with respect to size, on account of the different size related image behaviour. The three classes are defined as [Edington (1975)]

(a) Large loops; diameter \( \geq 500 \text{ Å} \)

(b) Medium loops; diameter \( \sim 100 – 400 \text{ Å} \)

(c) Small loops; diameter \( < 100 \text{ Å} \)

Loops usually lie on inclined planes, causing the formation of elliptical images. Images of large loops (a) have similar characteristics described for straight perfect dislocations. Medium loops (b) may appear as a single dot or as two arcs depending on the size. The contrast behaviour of small loops (c) depends on the position relative to the top or bottom of the sample. If it lies within \( \sim 1.25 \xi_g \) of the top/bottom they will appear as lobes of black/white contrast under certain orientation conditions. Loops within the foil appear as black dots due to anomalous absorption effects. The image characteristics of many other types of dislocations may be found in literature such as *Edington (1975).*

**4.3.4 Diffraction Patterns in the TEM**

The structure of the diffraction pattern depends on the nature of the material under investigation. The Ewald reflection sphere gives the direction of the diffracted beams after interaction with the sample. Electron diffraction theory gives the relationship between the wavelength \( \lambda \), interplanar spacing \( d_{hkl} \) and the distance from the transmitted to the diffracted spot \( R \) (Fig. 4.6) where

\[
R = \frac{\lambda L}{d_{hkl}}
\]  

(4.14)

and \( L \) is the camera length in question.
Electron diffraction patterns usually result from only a single crystal grain and are therefore single-crystal diffraction patterns. These patterns may be constructed from knowledge of the Ewald sphere construction in the reciprocal lattice. The reciprocal lattice must however be modified to account for the thin sheet shape of the specimen. It may be shown that diffraction spots along the z direction, i.e. perpendicular to the surface of the specimen, are in fact streaks parallel to this direction due to the thin sample. This is equivalent to the relaxation of the Bragg condition in this direction which implies that the diffraction intensity is observed even when this condition is not exactly satisfied. The modified Ewald sphere construction which accounts for this condition is shown in Fig. 4.7. The vector $s$ describes the deviation from the exact Bragg condition. As $s$ increases the diffraction intensity will decrease. In the case where $s \neq 0$ the reciprocal lattice vector $g'$ is given by (see Fig. 4.7)

$$g' = g + s$$

(4.15)
Figure 4.7. Definition of vectors \( g', s, g + s \) in terms of the Ewald sphere construction in reciprocal space [Edington (1975)].

**Single Crystals**

The diffraction pattern generated by a single crystal is a periodic arrangement of discrete spots. Each spot corresponds to a set of crystallographic planes within the crystal. The angles between these spots are the same as the angles between the corresponding directions in the crystal. These patterns may be used to determine:

(a) Sample orientation with respect to the direct beam direction \( B \).

(b) Precipitates, twins and other defects may be identified.

(c) The type crystal lattice may be identified and also the lattice parameter \( a \).

**Bi-Crystals**

The diffraction pattern taken from an area of two discrete structures with specific orientation correlation corresponds to overlapping of the diffraction patterns from the two independent crystal structures. This type of pattern is useful to determine the relationship between the two crystalline parts of the material such as lattice mismatch.

**Twins**

Twins as explained in Chapter 2 lead to a modification of the diffraction pattern, which is seen as a different set of diffraction spots according to crystallographic orientation, superimposed onto the diffraction pattern from the perfect crystal.
Figure 4.8. Modification of the diffraction pattern due to twinning in a FCC crystal with incident beam along <110> [Hirsch 1965].

Polycrystalline Materials
The diffraction pattern generated by a large number of discrete randomly oriented crystalline segments with the same structure consist of diffraction spots arranged in concentric rings around the direct beam direction. The number of spots in each ring depends on the number and size of the crystallites. When the spots are distinct it indicates that the area contains a small number of large crystallites, whereas when the spots are not distinct it indicates that the area contains a large number of small crystallites.

Amorphous Materials
The diffraction pattern generated by an amorphous material is a set diffuse concentric rings arranged around the direct beam direction.

Kikuchi Patterns
In addition to the spots, single crystal diffraction patterns may also contain a complex pattern of pairs of parallel light and dark lines, termed Kikuchi lines. The origin of these lines involves elastic and inelastic scattering. A simplified treatment originally proposed by Kikuchi (1928), considers that these lines arise from electrons which suffer an inelastic scattering, with only a small energy loss and some of these electrons that satisfy the Bragg condition are subsequently diffracted from crystallographic planes (Fig. 4.9). The diffraction process results in the formation
of cones of radiation centred on the specimen (Fig. 4.10). These cones intersect the Ewald sphere in hyperbolae and due to the fact that they have large radii are observed as straight lines, one brighter than the background and one darker. Kikucki lines are parallel to the reflecting planes from which they originate and also behave as if attached to the specimen.

Kikuchi lines may used to determine:
(a) Sample orientation with respect to the direct beam direction $B$.
(b) The sign and magnitude of the deviation $s$ from the exact Bragg condition (see next section).
(c) The crystal symmetry.
(d) Many other useful applications [see e.g. Edington (1975)].

**Figure 4.9. Illustration of the process involved in the formation of Kikuchi lines**  
[Edington 1975].

**Java Electron Microscope Simulator**
The electron diffraction pattern simulation software employed in this study is called Java Electron Microscope Simulator (JEMS). It is a transmission electron microscope image simulation package for electron diffraction analysis and HREM image simulation in materials science. Diffraction patterns are solved by both the multislice method and Bloch wave analysis. The software package is suitable for unit cells with small defects, or large cells with extended defects.
4.3.5 Determination of the Deviation from the Bragg Condition

The orientation of a crystal in the electron microscope may be determined by analysing the Kikuchi lines present in the diffraction pattern. When a crystal is oriented at the exact Bragg condition for reflection from the $hkl$ plane and the crystal is of sufficient thickness for the appearance of Kikuchi lines, the $hkl$ Kikuchi line will pass through the $hkl$ spot whilst the $hkl$ Kikuchi line passes through the origin.

The deviation from the Bragg condition $s$ can be calculated by measuring the distance of the $hkl$ (bright) Kikuchi line from its associated diffraction spot. The value of $s$ is given by [Edington (1975)]

$$|s| = \left( \frac{\Delta x}{x} \right) \frac{\lambda}{d^2}$$ (4.16)

where $\lambda$ is the wavelength of the electrons and $d$ is the interplanar spacing of the reflecting planes. Conventionally $s$ is taken as positive when $g$ lies inside the Ewald sphere. The Bragg deviation parameter $w$, is defined as $w = \xi_g s$. 

Figure 4.10. Illustration of Kikuchi cones and their intersection with the Ewald sphere [Edington (1975)].
4.3.6 The Method of Inside Outside Contrast

In order to determine the interstitial or vacancy nature of a dislocation loop, one may employ the method of inside-outside contrast as explained in Edington (1975) as long as the loops are large enough to be viewed comfortably in the microscope. Since dislocation loops often lie on inclined planes, they appear elliptical when projected onto the viewing screen. The loops may consist of an extra inserted plane (interstitial loop) or a missing atomic plane (vacancy loop). Four different configurations of loop type and orientation thus arise and are shown in Fig. 4.12, with their respective projections seen on the viewing screen.

Figure 4.11. Geometric arrangement of Kikuchi lines for s negative and positive [Edington (1975)].
Fig. 4.12. The four possible arrangements of dislocation loops in a specimen, with their respective projections on the microscope viewing screen. The size-orientation relationship can be used to identify the nature of the loops [Edington (1975)].

The method of inside-outside contrast depends on whether the loop image falls inside or outside the actual loop and can be determined by the sense of rotation of the reflecting planes around the dislocation. Consider the situation depicted in Fig. 4.13. (a) with \( s \) positive. Fig. 4.13. (b) shows the rotation of the reflecting planes around an edge dislocation. The reflecting plane XX is rotated clockwise towards \( s = 0 \) by the strain field while plane YY is rotated anti-clockwise away from \( s = 0 \). In this way, positions in Fig. 4.12 marked with an A correspond to the situation where the reflecting plane is rotated towards \( s = 0 \) and those labelled B correspond to areas where the plane is rotated away from \( s = 0 \).

Fig. 4.13. (a) The Ewald sphere construction showing the reciprocal lattice point corresponding to the reflecting plane. (b) The reflecting planes are rotated around the dislocation by the strain field [Edington (1975)].
Images thus appear approximately at A relative to the core of the dislocation and the result is the formation of images as depicted in Fig. 4.12. The dashed lines indicate the positions of the dislocation cores and the solid lines indicate the actual images. Contrast is thus inside the core for 1 and 3 while it is outside the core for 2 and 4, this implies that the sign of $g \cdot b$ is the same for 1 and 3 and opposite for 2 and 4. Fig. 4.14 shows the Burgers vectors of the dislocations as well as the sign of $g \cdot b$ if the positive direction around the loop is chosen as clockwise when looking down onto the specimen from the electron gun, and using the FS/RH criterion as explained by Holt (1962) to define $b$ (see Chapter 3).

The inclination of the loop with respect to the electron beam is first determined by tilting the sample through a large angle whilst noting the change in the shape of the projected image. Knowing the sense of the tilt direction the inclination of the loop can be determined. In the case of smaller loops (diameters ≤ 200Å) the habit plane and therefore also its inclination with respect to the electron beam can be determined by tilting the loop into an edge-on configuration. Secondly the change in loop size is noted on reversing the $g$ whilst keeping $s$ positive and constant. Finally direction of the Burgers vector of the loop can be determined by using the $g \cdot b = 0$ condition.

This definition of $b$ allows the following conclusions to be drawn:
If $g \cdot b > 0$ for positive $s$, then the image lies outside the real position of the loop. If $n \cdot b < 0$, then the loop is a vacancy loop. Otherwise if $n \cdot b > 0$, then the loop is an interstitial loop. Here $n$ is defined as the upward drawn normal to the habit plane of the loop.
It is thus evident that vacancy/interstitial nature of a loop can be determined if both the sense of inclination of the loop as well as the sign of $g \cdot b$ is known.
4.4 The Scanning Electron Microscope (SEM)

4.4.1 Image Formation in the SEM

The principles employed in image formation in the SEM are different to those used in TEM. Signal detection in the SEM begins when the primary electron beam penetrates a specimen. An electron from the incident beam may travel some distance before interacting with the atoms comprising the specimen. The beam will experience scattering as explained in sections 4.1.3. The interaction volume is usually limited to a volume shaped like a teardrop (Fig. 4.15).
The image in a SEM is formed electronically by passing the electron beam in a raster pattern across the specimen surface and measuring the intensity of the emitted electrons (SE, BSE) at each position of the beam (see sections 4.4.2–3). The beam is focussed by a series of electromagnetic lenses like in the TEM and the position is controlled by deflection coils (Fig.4.16).

\[\text{Figure 4.16. Simplified schematic representation of a SEM [Reimer and Kohl (2008)]}\]

### 4.4.2 Energy and Wavelength Dispersive X-ray Spectroscopy (EDS & WDS)

**EDS**

During the interaction of high energy electrons with a material it is possible for the electron to penetrate the outer valence/conduction bands of the atoms, comprising the material, and interact with the inner (tightly bound) electrons. In the event that an amount of energy more than the bonding energy holding the electron to the nucleus is transferred to a core electron it may be ejected, escaping the attractive field of the nucleus. The atom is therefore left in an excited state and may return to a more stable configuration by filling the vacant electron site with an electron from an outer shell. This transition leads to the emission of an X-ray or Auger electron (Fig. 4.17). In both cases the energy of the emitted photon or electron is characteristic of the difference in energy between the two electron shells and the energy difference is also unique to the specific atom. The X-rays emitted during this process are called a characteristic X-rays.
The X-ray energy depends on the difference in the inner-shell energies and these differences increase with increasing atomic number $Z$; therefore these X-rays may be used to identify the presence of an element in an electron microscopy specimen. The wavelength $\lambda_x$ of a characteristic X-ray is given by Moseley’s law \cite{Goldstein1992}.

$$\lambda_x = B(Z - C)^2$$  \hspace{1cm} (4.17)

*where* $Z$ is atomic number of the element involved and $B$ and $C$ are constants dependent on the family of electronic transitions ($K\alpha$, $L\beta$, …) The analysis of elements using these X-rays in the electron microscope is called energy dispersive X-ray spectrometry (EDS).

*Figure 4.17. Illustration of an inner shell ionization and de-excitation with X-ray emission* \cite{Goldstein1992}.

**WDS**

WDS is similar to EDS in that both techniques involve the analysis of X-rays produced through the interaction of energetic electrons with a material. EDS analysis involves the measurement X-ray energies whereas WDS involves the measurement of X-ray wavelengths. Only some of the X-rays incident on the sample satisfy the Bragg condition and will be diffracted by the sample which allows for the measurement of X-rays from only a single element for a specific detector orientation. In order to detect X-rays from a different elements the position of the analytical crystal inside the spectrometer must be adjusted. The WD spectrometer can achieve a high X-ray count rate at high beam current, due to the fact that only one wavelength is measured at a time.
The spectral resolution of the WDS system is approximately 2eV, with detection rates of up to 100ppm.

### 4.4.3 Secondary Electrons (SEs)

Secondary electrons (SEs) are electrons within the material that are ejected from conduction or valence bands of the material due to inelastic interaction of the incident electrons with the atoms of the material. SEs are considered as free electrons, i.e. they are not associated with a specific atom nor do they contain specific elemental information. These electrons have low energies and can only escape from areas near the surface of the material under investigation. Secondary electrons that are unable to escape from the sample are reabsorbed. SEs are the standard signals used in scanning electron microscopes. The reasons for utilising secondary electrons for imaging are to obtain topographical information and high resolution. The secondary electron coefficient $\eta_{SE}$ is defined by [Goldstein (1992)]

$$\eta_{SE} = \frac{N_{SE}}{N_0} = \frac{I_{SE}}{I_0}$$  \hspace{1cm} (4.18)

where $N_{SE}$ is the number of backscattered electrons, $N_0$ is the number of incident electrons, $I_{SE}$ is the backscattered electron current and $I_0$ the incident current.

### 4.4.4 Backscattered Electrons (BSEs)

In the interaction of high energy electrons with a material there exists a possibility that electrons of normal incidence may be scattered in such a way that they exit the sample where they entered. These electrons are termed backscattered electrons and may arise due to a single or multiple scattering events with a total deflection $> 90^\circ$. The energy of the backscattered electrons is close to the original energy. The fraction of electrons that are backscattered is quantified by the backscatter coefficient $\eta_{BSE}$ defined by [Goldstein (1992)]

$$\eta_{BSE} = \frac{N_{BSE}}{N_0} = \frac{I_{BSE}}{I_0}$$  \hspace{1cm} (4.19)

where $N_{BSE}$ is the number of backscattered electrons, $N_0$ is the number of incident electrons, $I_{BSE}$ is the backscattered electron current and $I_0$ the incident current. The intensity of backscattered
electrons is dependent on the atomic number of the target atoms, local inclination of the specimen surface, crystallography and internal magnetic field. These characteristics may be used to generate contrast in the scanning electron microscope. In general the backscatter coefficient $\eta_{BSE}$ increases with increasing atomic number. Operating in the backscattered imaging mode enables the display of information related to relative atomic density information in conjunction with topographical information.

4.4.5 Electron Backscattered Diffraction (EBSD)

During the interaction of energetic electrons with a material a fraction of the electrons may undergo inelastic scattering with a small loss in energy forming a divergent source of electrons at the point of scattering. Some of these inelastically scattered electrons are incident on atomic planes in such a way that they satisfy the Bragg condition (equation 4.3). The electrons scattered and diffracted in this way form a set of paired, large angle cones corresponding to each diffracting plane. This is the same as in the situation described in section 4.3.4, except that the Kikucki lines in the TEM are formed by forward scattered electrons and in the SEM by backscattered electrons. When the electrons are used to form an image on a fluorescent screen the regions of enhanced electron intensity between the cones lead to the formation of Kikuchi lines. These lines are characteristic of crystal structure and orientation.

4.5 Nano-Indentation Hardness (NIH)

The Hardness of a solid material is defined as the amount of resistance thereof to permanent deformation under strain. Hardness is usually characterised as:

(a) Scratch hardness – commonly used in mineralogy and defined as the ability of a material to penetrate a softer material, i.e. a harder material will scratch a softer material.

(b) Rebound/Dynamic hardness – this technique measures the height of backwards deflection of a diamond tipped hammer dropped from fixed height onto a material.

(c) Indentation Hardness – This technique is based on the premise of measuring the critical dimensions of an indentation with specific dimensions and specific load and is employed in the current investigation.
Instrumented hardness testing relies on the indentation of a material surface with an indenter of specified geometry, whilst monitoring the applied load and penetration depth throughout the insertion and removal of the indenter. The resulting data enables one to estimate properties such as material hardness, elastic modulus and fracture toughness [Doerner et al. (1986) and Oliver and Pharr (1992)]

![Figure 4.18. Illustration of the Nano-indenteter Head Assembly [CSM Instrument Presentation].](image)

Figure 4.18 shows a schematic representation of the indenter head. The diamond Berkovich indenter is pushed into the material by means of magnetic repulsion due to the configuration of the magnetic fields of the coil and the permanent magnet. The displacement of the indenter through the reference ring and displacement sensor assembly is measured with respect to the surface, which limits the compliance of the system to the few millimetres of material between the indenter tip and sensor arrangement. Nano-indentation is a well established technique for measuring mechanical properties of thin layers and bulk materials. In order to accurately measure the mechanical properties by nano-indentation, knowledge of shape and nature the contact area is required. The maximum load $F_{\text{max}}$ and maximum penetration depth $h_{\text{max}}$, indicated on the graph (Fig. 4.19), allows the calculation of the hardness of the material given by [Oliver and Pharr (1992)]

$$H_{IT} = \frac{F_{\text{max}}}{A_p}$$

(4.20)

where $A_p$ is the projected contact area, corresponding to the depth $h_p$. 
The reduced modulus $E_{rr}^*$, which accounts for the effects of non-rigid indenters on load-displacement data, is given by [Oliver and Pharr (1992)]

\[
\frac{1}{E_{rr}^*} = \frac{(1-v^2)}{E_{rr}} + \frac{(1-v_i^2)}{E_i} \quad \text{and} \quad (4.21)
\]

\[
E_{rr}^* = S \left[ \frac{\pi}{A_p} \right]^{1/2} \quad \text{(4.22)}
\]

$S = dF/dh$ is the experimentally measured stiffness of the upper portion of the unloading data, $v$ is Poisson’s ratio of the material in question, $v_i$ Poisson’s ratio for the indenter material and $E_i$ the elastic modulus of the indenter material. The elastic modulus of the material is consequently given by

\[
E_{rr} = \frac{1-v^2}{\frac{1}{E_{rr}^*} - \frac{1-v_i^2}{E_i}} \quad \text{(4.23)}
\]

Figure 4.19. Illustration of a depth displacement curve for nano-indentation hardness testing [Oliver and Pharr 1992].
Figure 4.20 shows a cross section of an indentation and identifies the various parameters. At any time during the loading the total displacement $h$ is given by

$$h = h_c + h_s$$  \hspace{1cm} (4.24)

$h_c$ is the vertical distance along which the contact is made (contact depth), $h_s$ is the displacement of the surface at the perimeter of the contact and $h_p$ is the final depth, i.e. the depth of the residual imprint, when the indenter is fully withdrawn.

![Figure 4.20. Schematic representation of a section through an indentation, showing the various quantities used in the analysis [Oliver and Pharr 1992].](image)

The projected contact area for a tip with pyramidal geometry (Berkovich) is given by [Oliver and Pharr (1992)]

$$A_p = C_0 h^3$$  \hspace{1cm} (4.25)

$C_0$ is a constant which depends on tip geometry and $h$ the height of the tip. Due to the fact that the tip tends to deform, i.e. become rounded, the projected contact area is instead approximated by

$$A_p = C_0 h^3 + C_1 h + C_2 h^{1/2} + C_3 h^{1/4} + \ldots$$  \hspace{1cm} (4.26)

The constants $C_n$ are determined from the indentation data of a standard sample of fused silica.
Due to permanent deformation of the sample surface the projected contact area is calculated from the reduced depth $h_c$ and not the maximum penetration depth. The reduced depth is given by

\[ h_c = h_{\text{max}} - \varepsilon \left( \frac{F_{\text{max}}}{S} \right) \]  

(4.27)

where $\varepsilon$ is a constant dependent on the indenter geometry. The projected contact area is a good approximation to the residual imprint area for most materials.
CHAPTER 5

A LITERATURE REVIEW ON SILICON CARBIDE AND GALLIUM ARSENIDE

5.1 Silicon Carbide (SiC)
SiC is an important material with applications as a semiconductor (opto-electronic devices) and a structural material in fission and fusion reactors [Snead et al. (2007), Katoh et al. (2007)]. Various irradiation studies of SiC have been carried out, including ion implantation and irradiation with electrons and neutrons [Aihara (2000)]. The physical properties that make SiC a suitable material for these applications include high hardness, excellent radiation resistance, low thermal conductivity, a wide bandgap and chemical inertness [Helary (2006), Snead et al. (2007)]. The use of SiC as a structural material in fission and fusion reactors necessitates the investigation of its structural response to ion and neutron irradiation.

5.1.1 Production of SiC
The mechanical properties of SiC are dependent on the method of production making this an important factor for the quality of the SiC. Many different production techniques exist such as sintering, direct conversion, gas phase reaction and polymer pyrolysis. Sintering techniques are classified through sintering agents, consolidation mechanisms and the method of pressurisation. SiC produced through sintering is limited to simple shape components due to the requirement of uniform pressure during sintering. SiC produced through sintering techniques usually have degraded mechanical properties due to the addition of additives such as Al$_2$O$_3$ and Y$_2$O$_3$ [Snead et al. (2007)]. The direct conversion process is represented by reaction bonding, where compacts consisting of mixtures of SiC and C are infiltrated with liquid or vapour metallic Si. The Si and C react forming SiC, which in turn bonds with the original SiC. Low density and degraded bulk performance of SiC due to residual Si are drawbacks of the reaction bonding technique. The most familiar technique of gas phase reaction is chemical vapour depositioning (CVD). A fluidized bed CVD process is employed in the production of fuel particles for the high temperature gas reactors (HTRs) such as the pebble bed modular reactor (PBMR), since the SiC produced is pure, highly crystalline, and stoichiometric [Snead et al. (2007)].
5.1.2 Crystal Structure

The bonds in SiC are mostly covalent in nature with sp$^3$ hybridised orbitals connecting the two different atoms of the lattice. The bonds between the two atoms of the crystal are tetrahedral in shape, with four equidistant atoms of the opposite kind arranged around each atom in the structure at the corners of the tetrahedron (Fig. 5.1). The tetrahedral formation of Si and C atoms is found in all polytypes of SiC [Snead et al. (2007)].

![Figure 5.1 Tetrahedral shape of bonds in SiC.](image1)

The SiC crystal structure can be considered as a network of strong <111> directional bonds between Si and C atoms. The difference in electron negativity of the Si and C atoms gives rise to a slight ionic nature of the bonds between the two atoms [Kittel (1976)]. SiC exists in many different crystal polytypes, defined by the ordering of the Si-C close packed atomic planes [Jepps (1983)]. The most common of more than 200 polytypes are 3C, 4H, 6H and 15R [Fisher (1990)]. The number indicating the repetition of the Si-C pair, in the cubic (C), hexagonal (H) or rhombohedral (R) crystals. 3C-SiC is also known as β-SiC and is the only polytype which displays cubic symmetry, whereas all other polytypes are classified as α-SiC. Cubic SiC crystallises in the zinc blende crystal structure (Fig. 5.2), with silicon at 000 position and carbon at the ¼ ¼ ¼ position. This structure may also be viewed as two FCC structures, one consisting of Si atoms and the other of C atoms displaced by one quarter of the conventional unit cell diagonal from each other. There are 8 atoms within the conventional FCC unit cell of the zinc blende structure with 9.64x10$^{22}$ atoms/cm$^3$ for 3C-SiC. The {111} plane is the most densely packed plane in the zinc blende structure.

![Figure 5.2. The zinc blende structure.](image2)
The 6H polytype is the most common of the α-SiC modification. The stability of different SiC polytypes is largely dependent on temperature and also affected by small amounts of impurities and deviation from 1:1 stoichiometry. The 3C polytype is found to be more stable than the 6H below 2373K, although not all studies agree on this. The 2H polytype is usually observed at lower temperatures. Transformation of the 2H to 3C polytype may be achieved by annealing in argon at temperatures above 1673K [Snead et al. (2007)].

![Figure 5.3](image)

Figure 5.3. (a) Three-dimensional perspective views of the primitive hexagonal unit cells of the most common SiC polytypes. The cubic (C) or hexagonal (H) character of a bilayer is defined by the nonparallel bond in this plane [modified from Wen et al. (2008)]. (b) Ramsdell zigzag sequences for 2H, 3C, 4H and 6H SiC polytypes [Snead et al. (2007), Iwami (2001)].
All SiC polytypes have hexagonal unit cell dimensions

\[
\text{where } n \text{ is the period of the stacking sequence in the structure [Verma and Krishna (1976)].}
\]

A phase diagram illustrating the prevalence of the various SiC polytypes at different temperatures is shown in Figure 5.4 below.

![Figure 5.4. Phase diagram of SiC polytypes [Jepps et al. (1983)]](image)

### 5.1.3 Lattice Parameter

The lattice parameter of SiC is dependent on the polytype (Table 5.1) and to a small degree temperature. The lattice parameter is seen to increase slightly with increasing temperature for all polytypes and may be described by a third order polynomial [Snead et al. (2007)]

\[
a = 0.43577 + 1.3887 \times 10^{-6}T + 7.8494 \times 10^{-10}T^2 - 2.4434 \times 10^{-13}T^3 \pm 2.6 \times 10^{-5} \text{nm}
\]

where \(T\) is the temperature in degrees Celsius.

<table>
<thead>
<tr>
<th>Polytype</th>
<th>Density (g/cm(^3))</th>
<th>Lattice Parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>3.219</td>
<td>(a = 0.3081, c = 0.5031)</td>
</tr>
<tr>
<td>3C</td>
<td>3.215</td>
<td>(a = 0.43589)</td>
</tr>
<tr>
<td>4H</td>
<td>3.215</td>
<td>(a = 0.3081, c = 1.0061)</td>
</tr>
<tr>
<td>6H</td>
<td>3.215</td>
<td>(a = 0.3081, c = 1.5092)</td>
</tr>
</tbody>
</table>
5.1.4 Hardness

The hardness of a material is largely dependent on the manufacturing process and may be defined in terms of bonding energy, covalence level, atomic spacing and by the fracture toughness and deformation under stress. SiC is one of the hardest materials known and is rated as 9.2 to 9.3 on the Mohs hardness scale. The hardness varies slightly with polytype, though it is minor in the case of the polycrystalline material such as CVD SiC. The relationship between porosity and hardness is given by [Snead et al. (2007)]

\[ H_V = 27.7 \exp(-5.4V_p) \]  \hspace{1cm} (5.3)

where \( V_p \) is the porosity and \( H_V \) is the Vicker’s hardness of SiC in GPa. The uncertainty of room temperature hardness as a function of porosity is ±7%. The hardness of SiC remains nearly constant at lower temperatures but decreases rapidly with increasing temperature.

*Table 5.2. Vickers, Knoop and nano-indentation hardness of SiC at room temperature [Snead et al. (2007)].*

<table>
<thead>
<tr>
<th>Material</th>
<th>Sintering Additives</th>
<th>Vickers hardness (GPa)</th>
<th>Knoop hardness (GPa)</th>
<th>Nano Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered α-SiC</td>
<td>B, C</td>
<td>24.9-26.7</td>
<td>22.4-27.4</td>
<td>n/a</td>
</tr>
<tr>
<td>Hot-pressed α-SiC</td>
<td>Al₂O₃, WC, Co</td>
<td>19.3</td>
<td>22.3</td>
<td>n/a</td>
</tr>
<tr>
<td>Hot isostatic pressed α-SiC</td>
<td>AlN</td>
<td>25.0-27.3</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>CVD β-SiC</td>
<td>---</td>
<td>20.7-24.5</td>
<td>24.5</td>
<td>32.5-40.6</td>
</tr>
<tr>
<td>Sintered β-SiC</td>
<td>B, C</td>
<td>21.1-23.9</td>
<td>20.9</td>
<td>n/a</td>
</tr>
<tr>
<td>Hot-pressed β-SiC</td>
<td>Al</td>
<td>26.7-29.7</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Hot-pressed β-SiC</td>
<td>Al₂O₃, RE₂O₃ (RE = La, Nd, Y, Yb)</td>
<td>3.4-21.2</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>
5.1.5. Elastic Modulus
The elastic modulus of SiC has been studied through various techniques which include sonic resonance, tensile, flexural, nano-indentation, Vickers indentation and ring compression. The elastic modulus is a function of various factors such as porosity and impurity concentration, but is minimally affected by grain size and polytype. The elastic modulus $E$ at room temperature is given by [Snead et al. (2007)]

$$E = E_0 \exp(-CV_p)$$  (5.4)

where $V_p$ is the porosity, $E_0$ is the elastic modulus of pore free SiC and $C$ a constant.

The elastic modulus of SiC decreases slightly at elevated temperatures, with some materials showing a large decrease due to the effects of residual silicon and grain boundary relaxation. The elastic modulus at elevated temperatures is given by [Snead et al. (2007)]

$$E = E_0 - BT \exp(-T_0/T)$$  (5.5)

where $B$ and $T_0$ are constants characteristic of the material (unit of GPa/K and K respectively) and $T$ is the temperature in K. $E_0$ is assumed to be the elastic modulus at room temperature i.e. 460 GPa.

5.1.6 Poisson’s Ratio
The Poisson’s ratio of SiC is dependent on stoichiometry, crystallinity, impurities and the porosity, with the highest ratio for pure CVD SiC of 0.21. Sintered SiC and reaction bonded forms of SiC typically have lower values for Poisson’s ratio of between 0.14 - 0.20.

5.1.7 Fracture Toughness
The fracture toughness of SiC is largely dependent on grain size with the maximum at a grain size of approximately 1-5 μm. At elevated temperatures the reaction bonded and sintered forms of SiC show no significant deviation in fracture toughness, whilst CVD SiC shows an increase due to a small plastic deformation at the crack tip and possible temperature-related stress relaxation effects. The fracture toughness of SiC produced through various techniques can be found in the work by Snead et al. (2007) with values ranging between 2.0 and 4.7 MPa.m$^{1/2}$. 
5.1.8 Chemical Properties

SiC is a non-oxide compound and may suffer oxidation at higher temperatures affecting its physical properties. The oxidation of SiC is divided into passive and active oxidation regions with a broad transition region. Under high oxygen partial pressure and high temperature, a SiO$_2$ surface layer will form due to the reaction of SiC with O$_2$. This oxidation is accompanied by significant mass gain and is termed passive oxidation. The reaction may be written as [Snead et al. (2007)]

$$SiC + \frac{3}{2}O_2 \rightarrow SiO_2 + CO$$  \hspace{2cm} (5.4)

The SiO$_2$ layer is amorphous in nature at temperatures below 1673 K. The overall oxidation rate of SiC is dependent on atmosphere, temperature, oxygen partial pressure, impurities, polytype and microstructure among other factors. The primary rate-limiting factor for passive oxidation is the diffusion of oxygen through the SiO$_2$ layer. Under low oxygen partial pressure and very high temperatures, SiC will decompose into SiO and CO gases. This decomposition excludes the formation of a protective SiO$_2$ layer and is termed active oxidation. The decomposition reaction may be written as [Snead et al. (2007)]

$$SiC + O_2 \rightarrow SiO + CO$$  \hspace{2cm} (5.6)

The active-to-passive oxidation transition depends largely on impurity concentration in SiC.

5.1.9 Specific Heat

The specific heat of SiC is found to be higher than that of other refractory carbides and nitrides. A rapid increase is observed at lower temperatures with a more gradual increase at higher temperatures, with similar behaviour for different polytypes. The specific heat of SiC at room temperature is $671 \pm 47$ J/kg.K [Snead et al. (2007)].
5.1.10 Thermal Creep
Creep deformation in SiC occurs through primary and steady-state creep mechanisms. Steady-state creep depends largely on crystallographic orientation and therefore the temperature at which it operates depends on crystallographic characteristics and loading direction. Primary creep deformation depends largely on material quality [Snead et al. (2007)].

5.1.11 Threshold Displacement Energy ($E_d$)
The threshold displacement energies (TDE or $E_d$) of Si and C are dependent on the nature of the atom, the bonding structure and the direction of the incident particle with respect to the crystal. Various studies have been attempted in order to determine the displacement energies of the Si and C atoms of SiC crystals. By using molecular dynamics (MD) simulations, Perlado et al. (2000) predicted TDE values, at 300K, ranging from 42 – 112 eV for Si and 26 – 61 eV for C depending on the angle of incidence. MD simulations carried out by Devanathan and Weber (2000) on 3C-SiC and 6H-SiC of both single displacements and cascades suggest that minimum values, averaged over all directions in SiC, of 35 eV for Si and 20 eV for C atoms be used. Average TDE values of 93 eV for Si and 16.3 eV for C in 3C-SiC are suggested by El-Azab and Ghoniem (1992) from MD simulations.
Currently no standard set of realistic threshold displacement energy values exists and consequently MD simulations are used to predict the mechanisms involved in damage formation within SiC.

5.1.12 Ion Implantation
The effects of ion irradiation on SiC may include defect formation and amorphization and also the response of the implanted SiC to annealing and the resulting recrystallisation. An overview on the effects of irradiation on SiC by Benyagoub (2008) places the effects of ion implantation into two main classes, low energy ions and swift heavy ions (SHI).

Low Energy Ions
Ions with energies of a few hundred keV will suffer energy loss by means of nuclear collisions. SiC is easily damaged by low energy ion implantation at or below room temperature, irrespective of the ion species. The ion distribution observed at low ion doses is similar to that of atoms
slowed through nuclear collisions, with a maximum depth $R_d$ where atomic displacement is most prevalent. As the dose increases the damage profile grows monotonically up to a point where total disorder is reached at $R_d$; beyond this dose further implantation results in total disorder throughout the entire implantation depth.

The resulting damage, which depends on ion dose, corresponds to partial or total amorphization; consequently the density is seen to decrease from 3.21 to 2.85 g/cm$^3$ due to this phase transformation. The decrease in density results in a significant amount of swelling of the implanted region, especially in the case of total amorphization.

In the case of heavy ions implanted at room temperature, total amorphization occurs at a critical (threshold) energy of 20 – 30 eV/atom, which corresponds to 0.2 - 0.3 dpa. Sigmodal dependence in the relative disorder at $R_d$ is observed for heavy ions. The proposed mechanism is that within the displacement cascade of each incoming ion an amorphous region surrounded by a defective crystalline region is created. This defective crystalline region eventually becomes amorphous after subsequent ion impacts as a result of either defect accumulation or the agglomeration of existing amorphous regions.

The amorphization threshold dose is seen to increase for lighter ions, indicating a high degree of dynamic annealing during irradiation for small displacement cascades. The rate of the disorder decreases with increasing irradiation temperature and above a critical temperature of approximately 250°C no amorphization occurs.

The amorphous region which forms as a result of ion implantation is seen to recrystallise at annealing temperatures exceeding 950°C, resulting in recovery of the density of this layer to that of crystalline SiC. The amorphous layer can also recrystallise through ion-beam-induced epitaxial crystallisation (IBIEC) at temperatures below 1000°C. The mechanism involved is the growth of 6H-SiC columns, very close to the underlying undamaged (crystalline) region. The columnar growth proceeds from the amorphous-to-crystalline transition region and is eventually terminated due to competition of random nucleation and spherical 3C-SiC grains within the amorphous region, resulting in a polycrystalline structure.
Swift Heavy Ions (SHI)
High energy ions will suffer energy loss by the electronic excitation and ionization of atoms within the target material. Ionization of atoms within the target lead to various types of atomic rearrangements which may include giant anisotropic deformation in amorphous materials and damage creation in a crystalline material when the electronic excitations exceed a certain threshold energy, dependent on the nature of the material. Research by Benyagoub et al. 2006 has shown that, even for high doses, swift heavy ions are less efficient than low energy ions in causing a crystalline-to-amorphous phase transformation in SiC (given that $S_{\text{e}}/\text{ion} \leq 33$ keV/nm). In the same study it was revealed that the damage induced by low energy irradiation could be removed through epitaxial recrystallisation induced by irradiation with swift heavy ions. The fact that SiC does not suffer amorphization due to SHI irradiation is explained by means of the thermal spike model (see Chapter 5); the same principles can also be employed to explain the recrystallisation of amorphous SiC through SHI irradiation. It should be noted that the thermal conductivity of amorphous SiC is less than its crystalline counterpart due to an increase in the number of phonon scattering centres and the melting temperature is also lower and lies in the region of 2445 K. These features lead to a significant change in the reaction of SiC to SHI irradiation. Thus amorphous SiC may be melted by irradiation with SHI irradiation. As a SHI traverses an amorphous region in SiC it creates a molten region around its trajectory and where this region is in contact with a crystalline region, epitaxial recrystallisation may occur as the region cools. The repetition of this process ultimately leads to epitaxial recrystallisation of the entire amorphous region. This phenomenon occurs at room temperature and cannot be explained by a macroscopic beam heating mechanism. The reasons why the last mentioned mechanism is precluded is due to the fact that target heating is not expected to exceed a few tens of °C and also that crystallisation of SiC only occurs at temperatures close to 1000°C, as observed by Wendler et al. (1998).

Defect Production, Ion-Solid Interactions and Amorphization
In a study by Gao et al. (2002) the defect production process due to PKAs, employing a optimized form of the Tersoff inter-atomic potential, was investigated (see Chapter 5). As was mentioned earlier, the threshold displacement energy (TDE) surface is highly anisotropic for both Si and C sublattices within SiC and furthermore C atoms are more easily displaced than
Si atoms along most directions in the crystal. The TDE used in the simulations is 20 eV for C and 35 eV for Si, which is the lower bound suggested by Devanathan and Weber (2000). The calculated damage state of SiC due to a typical 10keV cascade is depicted in Fig. 2.5, showing only atoms which have suffered displacement. The Si PKA travelled along the [001] creating multiple branches along its path before coming to rest.

![Figure 2.5. Illustration of a typical 10keV cascade at the final damage state in 3C-SiC. The defect type is distinguished by size and are coloured grey [Gao et al. (2002)].](image)

Interstitial and vacancies dominate the final damage state, with C defects more prevalent than Si defects, since C atoms have a smaller TDE (the ratio of C:Si interstitials is approximately 3:1). The number of C atoms on Si lattice sites C$_{Si}$ (antisite defect) is slightly larger than the number of Si atoms on C lattice sites Si$_{C}$, due to the lower formation energy of Si antisite defects. In studies by Gao et al. (2000) and Devanathan et al. (2001), simulating higher energy cascades (up to 50 keV), cascades are found to be more linear than spherical in form since localized melting of cascades in SiC does not occur. Single interstitials and defect clusters in SiC are the most prevalent form of interstitial type defect. Single vacancy defects make up approximately 90% of vacancy type defects with defects clusters of more than three vacancies rarely occurring, which is in agreement with results of Perlado et al. (2000). The probability of forming large clusters are reduced by the short lifetime of thermal spikes in SiC, preventing short range diffusion during the first few ps. after the collision stage.
Examples of damage states due to defect accumulation as a result of 10 keV cascade events are shown in Fig. 5.6. The dose is shown as displacements per atom (dpa) for the specific region shown. Single interstitials and mono-vacancies are most prevalent at low dose, although some small clusters have also formed (circled in Fig. 5.6 a). The concentration of these clusters increase with increasing dose and are randomly distributed. Small clusters start to agglomerate during cascade overlap, forming larger clusters and eventually amorphous domains (Fig. 5.6 b). The amorphous domains consist of both interstitials and antisite defects which indicate that these defects may be important in energy storage leading to amorphization in irradiated SiC.

Figure 5.6. Computer simulations showing the process of cascade overlap and defect agglomeration as a function of dose, the nucleation of small clusters and the coalescence of clusters, where only interstitials and antisite defects are present [Gao et al. (2002)].

Small defect clusters are sometimes destroyed by direct impact with highly energetic atoms during the collision phase of the cascade process. The process of cluster formation is dynamic since the nucleation and recovery processes of small clusters are in competition, but since the number of clusters increase with dose the nucleation process occurs at a greater speed.
Large amorphous regions are formed through the coalescence of amorphous domains, with both small and large defect clusters, with complete amorphization reached at a dose of 0.28 dpa (Fig. 5.6 d) which is in agreement with experimental observations by Jiang et al. (1998) and Zinkle and Snead (1996). In the study by Gao et al. (2002) the implantation of Xe\(^+\) ions into 3C-SiC confirmed the results predicted by MD simulations as discussed above.

Wendler et al. (1998) found that the ion dose necessary for amorphization of SiC increases with implantation temperature, due thermal annealing of the primary collision cascades. Amorphization is prevented if the implantation temperature exceeds a critical temperature, which varies between 400 – 650 K and is dependent on the energy transferred to recoils. The recrystallisation of SiC is observed at post irradiation annealing temperatures exceeding 900 °C. Implantation at elevated temperatures leads to the formation of complex defects which require annealing at high temperatures to be removed.

The epitaxial regrowth from the amorphous to crystalline interface competes with the nucleation and growth of crystallites, resulting in a complex defect structure with 3C inclusions within a 6H structure.

5.1.13 Neutron Irradiation

The main cause of unstable behaviour of neutron irradiated SiC is due to the effects of impurities with significant concentrations, whereas stoichiometric SiC has a high radiation tolerance [Snead et al. (2007)].

dpa Cross-Sections

The dpa cross-sections for SiC were calculated by Heinisch et al. (2004) using the Norgett et al. (1975) (NRT) formulation of the model developed by Kinchin and Pease (1955) (see Chapter 5). Fig. 5.8 shows the contributions from both the Si and C PKAs.
Irradiation Induced Swelling

In a study by Newsome et al. (2007) on the irradiation of SiC and SiC composites with neutrons volumetric swelling was observed. The relative amount of swelling is dependent on temperature but not on dose. The swelling was saturated at approximately 1.9%, 1.1% and 0.7% at irradiation temperatures of 300 °C, 500 °C and 800 °C, respectively.

Effects on Mechanical Properties

Newsome et al. (2007) also reported on the effects of neutron irradiation on mechanical properties. A slight increase in the mechanical strength of CVD-SiC is observed with a slight decrease in the elastic modulus after irradiation.

A study by Nogami et al. (2002) focused on the mechanical properties of neutron irradiated CVD-SiC irradiated to doses of \(10^{20} - 10^{21} \text{n/cm}^2 (E_n > 0.1 \text{MeV})\), with irradiation temperatures in the range 80 – 1150 °C. This study included the measurement of hardness, elastic modulus and fracture toughness measured by micro and nano-indentation techniques. Both the micro and nano-indentation hardness rapidly increase below an irradiation temperature of 100 °C, with almost no change beyond this temperature. The elastic modulus decreases rapidly with irradiation temperature below 100 °C, recovering almost fully beyond 1000 °C.

*Figure 5.8. Total dpa cross sections (barns) for SiC as a function of neutron energy (MeV) [Heinisch et al. (2004)].*
The fracture toughness decreases slightly below 400 °C, with a significant increase with temperature up to 1000°C. The results of this study indicate a significant dependence of the mechanical properties on irradiation temperature and a minimal dependence on dose.

**Defects and Amorphization**

*Katoh et al. (2006)* investigated the effects of neutron irradiation on the microstructure of 3C-SiC at elevated temperatures. At relatively low temperatures < 800°C, small dislocations loops and black spot features are observed. The size of these defects increase with increasing radiation temperature. The swelling of irradiated SiC is attributed to small interstitial clusters. Frank faulted and perfect loops are observed for intermediate doses and these develop into dislocation networks at high doses. It was suggested that these loops are Frank faulted loops of the (a/3)<111> interstitial type or perfect loops of the (a/2)<110> interstitial type.

A study by *Yano et al. (2009)* on the high temperature (725°C) neutron irradiation (dose = 8.1×10^{24} n/m^2, E_n > 0.1MeV) of polycrystalline 6H-SiC revealed no change in the crystal structure. The presence of point defects is indicated by a change in the lattice parameter. After annealing the lattice parameter is seen to recover due to dislocation pair recombination, with full recovery at 1400°C. *Snead and Hay (1999)* investigated the effects of neutron irradiation on single crystalline 6H-SiC and polycrystalline 3C-SiC up to a dose of 2.6×10^{25} n/m^2 (~ 2.6dpa, E_n > 0.1MeV) at 60°C. Amorphization is observed for both materials with a reduction in density of 10.8%. Nano-indentation revealed that the harness decreased to 54% and 65% of un-irradiated 6H and 3C SiC, respectively. The elastic moduli decreased to 55% and 58% of the un-irradiated material. The results of this study indicate that the threshold temperature for amorphization is ~125°C at 2.6dpa.

**Transmutation**

In the study of the transmutation of SiC irradiated with neutrons for 10 full power years by *Heinisch et al. (2004)* the presence of five transmutation elements with significant concentrations are predicted, i.e. P, He, H, Mg and Be (see Table 5.4).
Table 5.4. Concentrations of elements in SiC produced by neutron irradiation-induced transmutations after irradiation in the PBMR for 10 full power years, compared to that in the HFIR-PTP [Heinisch et al. (2004)].

<table>
<thead>
<tr>
<th>Element</th>
<th>MPBR (PBMR)</th>
<th>HFIR-PTP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>appm</td>
<td>appm/dpa</td>
</tr>
<tr>
<td>P</td>
<td>36</td>
<td>8.2</td>
</tr>
<tr>
<td>H</td>
<td>8.0</td>
<td>1.8</td>
</tr>
<tr>
<td>He</td>
<td>5.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Mg</td>
<td>3.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Be</td>
<td>1.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The concentrations of these elements increase linearly with dose over the 10 full power years and are extremely low when compared to the usual concentration of intrinsic impurities in unirradiated SiC. Even though He and H may be present in small concentrations they may concentrate at undesirable locations in SiC due to their high mobilities.

5.2 Gallium Arsenide (GaAs)

GaAs is a semiconductor used in the manufacture of integrated circuits, field effect transistors, low-loss optical waveguides, semiconductor lasers and isolated p-n junction diodes [Zanoti (1983), McLevige (1977), Deutch (2002)]. Some of the above mentioned uses involve ion, proton and certain impurity atom implantations in order to alter certain properties of the material. The study of the interaction of radiation with GaAs (zinc blende, Fig. 5.2) is important since materials such as β-SiC, which has the same crystal structure, is used in the nuclear industry. The atoms in the GaAs crystal have smaller displacement energies than that of SiC which makes it an ideal material to study in order to gain an understanding of the effects of radiation on this type of crystal structure.
5.2.1 Production of GaAs
Polycrystalline GaAs may be produced from the direct reaction of gallium and arsenic, though this process is complicated by the different vapour pressures of the reagents and the exothermic nature of the reaction. Single crystalline GaAs is produced mainly through two techniques: the Bridgman technique and the Czochralski (LEC) technique; both of which involve the use of seed crystals. The Bridgman technique is largely favoured, but larger crystals may be obtained through the Czochralski technique [Barron (2010)].

Alternatively GaAs may be grown through the vapour phase epitaxial (VPE) reaction of gaseous gallium metal and arsenic trichloride (\(2\text{Ga} + 2\text{AsCl}_3 \rightarrow 2\text{GaAs} + 3\text{Cl}_2\)) and also metalorganic chemical vapor deposition (MOCVD) involving the reaction of trimethylgallium and arsine (\(\text{Ga(CH}_3)_3 + \text{AsH}_3 \rightarrow \text{GaAs} + 3\text{CH}_3\)) [Moss and Ledwith (1987), Smart and Moore (2005)]. GaAs has also been produced by means of molecular beam epitaxy (MBE) [Hjort et al. (1994)].

5.2.2 Crystal Structure of GaAs
The crystal structure of GaAs is zinc blende, the same as that of cubic SiC. As in SiC, the bonds in GaAs are mostly covalent in nature [Stirland and Straughan (1976)] with \(sp^3\) hybridised orbitals connecting the two different atoms of the lattice. The bonds between the two atoms of the crystal are tetrahedral in shape (see Fig. 5.1), with four equidistant atoms of the opposite kind arranged around each atom in the structure at the corners of the tetrahedron [Kittel (1976)]. GaAs has an atomic density of \(4.428 \times 10^{22} \text{ atoms/cm}^3\). The \{111\} plane of GaAs is the most densely packed plane in the zinc blende structure. The GaAs crystal structure can be considered as a network of strong \(<111>\) directional bonds between Ga and As atoms. The difference in electron negativity of the Ga and As atoms gives rise to a slight ionic nature of the bonds between the two atoms. This increases cleavage surface energy of the \{111\} planes so that the cleavage plane in GaAs is the \{110\}. Dislocation glide (or slip) in GaAs takes place on the \{111\} planes. In each pair of the eight \{111\} surfaces one surface consists of Ga atoms and the opposite of As atoms, which has an effect on properties that depend on surface orientation and conditions such as epitaxial growth rates and etch rates [Henderson (1972)]. Hardness anisotropy and varying dislocation velocities in GaAs is a consequence of the difference in critical resolved shear stress for \{111\}As and \{111\}Ga slip planes [Hjort et al. (1994)].
5.2.3 Physical Properties

Table 5.5 lists some of the most important physical properties of GaAs compared to other semiconductors.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Si</th>
<th>GaAs</th>
<th>AlAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure</td>
<td>diamond</td>
<td>zinc blende</td>
<td>zinc blende</td>
</tr>
<tr>
<td>Lattice Constant $a$ (Å)</td>
<td>5.4311</td>
<td>5.6533</td>
<td>5.6611</td>
</tr>
<tr>
<td>Density $\rho$ ($10^3$ kg.m$^{-3}$)</td>
<td>2.329</td>
<td>5.360</td>
<td>3.760</td>
</tr>
<tr>
<td>Melting Point $T_M$ (°C)</td>
<td>1413</td>
<td>1238</td>
<td>1740</td>
</tr>
<tr>
<td>Fracture Toughness $K$ (MPa.m$^{1/2}$)</td>
<td>0.9</td>
<td>0.44</td>
<td>1.7</td>
</tr>
<tr>
<td>Hardness $H_v$ (GPa)</td>
<td>10</td>
<td>7</td>
<td>5</td>
</tr>
</tbody>
</table>

Single crystal GaAs exhibits elastic anisotropy. Both Poisson’s ratio and the elastic (Young’s) modulus are dependent on the crystallographic orientation (see Fig 5.9).

As an example, the values for Poisson’s ratio for the [110]<hkl> system is illustrated (see Fig. 5.9), i.e. tension along the [110] axis and contraction along a perpendicular <hkl> direction. The outer circular contour in Fig. 5.9. (b) illustrates the cross-section of the unstrained rod and the inner contour that of the strained state. The ratio of the difference between the two cross-sections and the unstrained cross-section is the Poisson ratio for the respective direction [Hjort et al. (1994)].
5.2.4 Electron Irradiation and Ion Implantation

Ion implantation into GaAs is used to modify the electrical properties for the production of various electronic devices. Many different ions have been implanted into GaAs in order to achieve specific effects. Some of the results from other researchers are summarised in this section. In general the theoretically calculated critical amorphization ion dose for GaAs is $3.6 \times 10^{17}$ ions/cm$^2$ as given by Pearton (1990) and the displacement energy for Ga and As atoms are given as $7 – 11$ eV by Lanoo and Bourgoin (1981).

Protons and Electrons

Some lattice defects produced during ion implantation of GaAs may have detrimental effects on device performance. One such defect is prismatic dislocations loops which have been observed by Neethling and Snyman (1986) in GaAs implanted with protons to doses ranging from $10^{15}$ - $10^{16}$ protons/cm$^2$ and also in GaAs irradiated with electrons to a dose of $2.4 \times 10^{22}$ electrons/cm$^2$ [Neethling (1994)]. In both cases the samples were annealed after irradiation at temperatures exceeding $500$ °C.

Hydrogen ion implantation of (001) GaAs at temperatures ranging between 45 to 160 °C to doses ranging from $4 \times 10^{16}$ to $4 \times 10^{17}$ ions/cm$^2$ with an energy of 50 keV was investigated by Gawlik et al. (2001). The room temperature implantations only resulted in some displacements and small amorphous clusters as measured by RBS analysis techniques. Hydrogen defect complexes containing many hydrogen atoms were also observed and are thought to be a likely precursor to the formation of hydrogen bubbles.

Udhayasankar et al. (1999) implanted (001) GaAs wafers with 100 keV H$^+$ ions to doses in the range from $1 \times 10^{16}$ to $1 \times 10^{18}$ ions/cm$^2$. TEM investigations revealed two heavily damaged regions; a 140 nm thick layer at the surface and a 250 nm thick buried layer at a depth of 700 nm in the sample implanted to a dose of $1 \times 10^{18}$ ions/cm$^2$. The latter result was attributed to the high implantation current.

Low Energy Ions

Jenčič et al. (2001) reported on the implantation of GaAs with 50 keV Xe$^+$ ions to a dose of $1 \times 10^{11}$ ions/cm$^2$ at 90 and 300 K and subsequently irradiated with electrons with energies in the range from 25 to 300 keV.
The Xe implantation resulted in the formation of small (~8 nm diameter) amorphous regions within the crystal. Recrystallisation of these amorphous zones was observed by TEM upon irradiation of these samples with electrons. It was found that the recrystallisation rate is dependent on electron energy.

*Kulik et al. (2001)* investigated the implantation of (111) GaAs with 270 keV In\(^+\) ions to a dose of \(3 \times 10^{16}\) ions/cm\(^2\) at room temperature and subsequent annealing at 600 and 950°C. In the as-implanted samples, indium atoms were observed by means of RBS analysis in the form interstitial atoms. Migration of the indium atoms to the surface was observed for the sample annealed at 600°C and migration into the bulk was observed for the 950°C anneal, which resulted in the substitution of Ga atoms by In atoms leading to the formation of localised layers of Ga\(_{(1-x)}\)In\(_x\)As.

*Chen et al. (2007)* reported on the effects of (001) GaAs implanted with 80 keV Mn\(^+\) ions to a dose of \(7.5 \times 10^{15}\) ions/cm\(^2\) at room temperature. RBS analysis revealed an almost amorphous layer at the implanted surface, with the most prominent defects Mn ions in substitutional Ga sites. Ion beam-induced epitaxial crystallization was also achieved by means of the implantation of 2.5 MeV He\(^+\) ions.

Ion beam synthesis of GaN precipitates in GaAs has been achieved by *Amine et al. (2002)* by means of the implantation of 50 keV nitrogen ions into GaAs wafers to a dose of \(7.5 \times 10^{15}\) ions/cm\(^2\). Two types of nano-scale objects were observed at the projected range by TEM analysis techniques; voids and GaN nano-particles (nps). Voids were only observed at annealing temperatures greater than 700°C. The size of both the voids and nps increased with annealing temperature.

*Wang et al. (2006)* investigated the recrystallisation of (001) GaAs wafers implanted with 60 keV N\(^+\) ions to a doses ranging from \(1.6 \times 10^{15}\) to \(1.1 \times 10^{17}\) ions/cm\(^2\). A 100 nm thick amorphous layer was produced due to this high dose implantation. Raman spectroscopy revealed the recrystallisation of this layer after thermal annealing at 800°C. The recrystallised layer was seen to consist of 30 to 60 nm sized crystallites, depending on the initial implantation dose.

Defect generation in 140 keV Si\(^+\) ion implanted (211) GaAs was investigated by *Bublik et al. (1999)* for doses ranging from \(1 \times 10^{13}\) to \(1 \times 10^{14}\) ions/cm\(^2\).
Less defective implanted layers were formed in (211) GaAs wafers compared to the (001) wafers implanted under the same conditions, resulting in a deeper ion penetration depth of Si⁺ ions in GaAs wafers. Rapid photon annealing at 1000°C for 10 s and 30 s respectively resulted in recrystallisation of the implantation damage.

**Swift Ions**

*Ghose et al. (1999)* investigated <001> GaAs single crystals implanted with 1.0 MeV C⁺ ions to a dose of 5×10¹⁴ ions/cm² and 2.0 MeV C₂⁺ ions to a dose of 2.5×10¹⁴ ions/cm². In both cases the samples were co-implanted with 2.58 MeV Ga²⁺ to a dose of 5.6×10¹⁴ ions/cm². Using RBS and TEM techniques, it was determined that the GaAs samples were rendered amorphous by C₂⁺ and Ga²⁺ co-implantation at depths between 600 - 1200 nm and recrystallised after annealing at 800°C for 30 min with little damage observed in the C⁺ case.

**5.2.5 Dislocation Loops in GaAs**

The presence of a high concentration of vacancies a GaAs sample, may lead to the precipitation of a disc of vacancies on a close packed {111} plane. If this disc is of sufficient size it may collapse to produce a stacking fault bounded by a partial dislocation. The burgers vector of this prismatic dislocation loop is normal to the plane of the loop and of the (a/3)<111> type (see Fig. 2.13 a). A prismatic dislocation loop may also form as a result of the precipitation of interstitial atoms into a platelet on a close packed plane. These interstitial atoms may be present as a result of ion implantation. In both cases i.e. collapse or expansion a Frank dislocation loop with Burgers vector $\mathbf{b} = -(a/3)[111]$ or $\mathbf{b} = + (a/3)[111]$ normal to the (111) plane of the fault is formed. These loops on {111} planes are also called Frank partial dislocation loops and since Frank loops are edge dislocations with the Burgers vector not contained in a close packed plane it cannot glide and will move through the process of climb. Prismatic dislocation loops may also form on the {110} plane of GaAs through the same mechanisms described above. The existence of pure edge vacancy loops on the {110} planes of GaAs has been observed by *Narayahan and Kachare (1974)* by means of TEM techniques. In the presence of a gas, such as implanted H or He ions, in a solid containing mobile vacancies, gas-filled voids or platelets may form.
The equilibrium size of the void is determined by a balance between the surface energy and the gas pressure in the void. Gas filled voids are visible in the TEM as dark lobes with a line of zero contrast perpendicular to the operating vector $g$ [Thompson (1969)].

Figure 5.10. is an excerpt from a TEM bright field micrograph showing the image contrast of a dislocation loop viewed edge-on. A line of zero contrast passes through the centre of the image with contrast in the form of lobes on either side.

![Figure 5.10. An excerpt from a bright field TEM micrograph illustrating the image contrast of a dislocation loop. The dashed line indicates the line of zero contrast with the operating vector perpendicular to it as shown.](image)

Figure 5.11 is a schematic representation of an interstitial edge dislocation on the [101] plane of GaAs. The extra half plane, which consists of GaAs atoms, is indicated by the dotted lines.

![Figure 5.11. Schematic representation of an interstitial edge dislocation on the [101] plane in GaAs, showing the Burgers vector $b = (a/2)[101]$ projected onto the $[\bar{1}01]$ plane. The full and open circles represent atoms on adjacent $(101)$ planes which are a distance $(a/4) [\bar{1}01]$ apart [Hutchinson and Dobson (1980)].](image)
5.2.6 Effect of Irradiation on Hardness

Udhayasankar et al. (1999) and (1996) investigated the effects of 100 keV H$^+$ implantation into GaAs to doses in the range from $1\times10^{14}$ to $1\times10^{18}$ ions/cm$^2$. The micro-hardness was found to increase with increasing dose up to $1\times10^{17}$ ions/cm$^2$ and then suddenly decreases for a dose of $1\times10^{18}$ ions/cm$^2$. The increased hardness of GaAs at lower doses up to $1\times10^{16}$ ions/cm$^2$ is attributed to point defect hardening. The elastic strain within the low dose region is due to point defects only since their probability of interaction is low. The concentration of point defects was found to increase linearly with irradiation dose.

The micro-hardness still increased for doses between $1\times10^{16}$ and $1\times10^{17}$ ions/cm$^2$ but by a much smaller amount, which is attributed to the saturation of point defect formation. Dislocation loops may also form by point defect agglomeration in this dose region since the density of point defects is just below that required for the crystalline to amorphous phase transformation. Annealing of the implanted samples resulted in a reduction of micro-hardness for all doses except at the highest dose. The reduction in hardness for lower doses is attributed to the annihilation of point defects through recombination of vacancies and interstitials during annealing resulting in a decrease in lattice strain.
CHAPTER 6

EXPERIMENTAL PROCEDURE

In this chapter the methods used to prepare the specimens for analysis by the various techniques described in the previous chapter are discussed. The fabrication of the SiC and GaAs samples employed in this investigation and the ion implantation as well as neutron irradiation thereof is discussed first. The furnaces used in the annealing of these specimens are described, including the specimen holders used during annealing. The preparation of TEM specimens is discussed in detail due to the complex nature of these methods. Finally the techniques used in the preparation of specimens for nanoindentation hardness measurements are discussed.

6.1 Fabrication of Materials

Single Crystal 6H-SiC wafers
The 6H-SiC (0001) wafers used in this study were grown by NovaSiC in France by employing the sublimation method in which SiC powder is sublimated under low pressure and high temperature and allowed to crystallize on a seed crystal at the top of the growth chamber maintained at a slightly lower temperature.

3C-SiC Bulk Material
The 3C-SiC bulk material used in this study was supplied by Rohm and Haas, Advanced Materials Co, USA.

Single Crystal GaAs Wafers
The single crystal GaAs wafers used in this study was supplied by Rohm and Haas, Advanced Materials Co, USA.
6.2 Implantation of Materials

Table 6.1. Irradiation details of SiC and GaAs

<table>
<thead>
<tr>
<th>Species</th>
<th>Polytype</th>
<th>Energy (MeV)</th>
<th>Dose (cm$^2$)</th>
<th>Annealing Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$^+$ into SiC</td>
<td>6H (Single)</td>
<td>0.200</td>
<td>5×10$^{16}$</td>
<td>0, 800, 1200</td>
</tr>
<tr>
<td></td>
<td>3C (Poly)</td>
<td>0.200</td>
<td>1×10$^{15}$</td>
<td>0, 800, 1200</td>
</tr>
<tr>
<td>$n$ into SiC</td>
<td>3C (Poly)</td>
<td>&gt;1.0</td>
<td>9.6×10$^{17}$</td>
<td>0, 800, 1200</td>
</tr>
<tr>
<td></td>
<td>3C (Poly)</td>
<td>&gt;1.0</td>
<td>5.9×10$^{21}$</td>
<td>1000 $^{irradiation temp}$</td>
</tr>
<tr>
<td></td>
<td>3C (Poly)</td>
<td>&gt;1.0</td>
<td>9.6×10$^{21}$</td>
<td>1000 $^{irradiation temp}$</td>
</tr>
<tr>
<td>$n$ into GaAs</td>
<td>Zinc Blende</td>
<td>&gt;1.0</td>
<td>1×10$^{20}$</td>
<td>0, 600, 800, 1000</td>
</tr>
</tbody>
</table>

*Note 0°C indicates the as-irradiated samples

Phosphorous Ion Implantation of SiC

Single crystalline 6H wafers and polycrystalline 3C bulk samples were implanted with 200 keV P$^+$ ions by CORE Systems in the USA.

Neutrons Irradiation of SiC

Polycrystalline 3C-SiC bulk material was irradiation with thermal and fast neutrons by Oak Ridge National Laboratory (ORNL) in the USA.

Neutron Irradiation of GaAs

Single crystalline GaAs wafers were irradiated with thermal and fast neutrons by NECSA in South Africa.
6.3 Specimen Preparation

6.3.1 Cutting
The as-implanted samples were cut using a Well Precision Diamond Wire Saw (Fig. 6.1). Strips of approximately 2mm in width were cut from the central region of the sample to ensure that the samples used in analysis were implanted to the full dose.

![Well Precision Diamond Wire Saw](image)

Figure 6.1. Well Precision Diamond Wire Saw

6.3.2 Annealing
The strips cut by means of the diamond saw were annealed using a resistively heated Heraeus Quartz Tube Furnace (Fig. 6.2 a and b) for temperatures up to 1000 °C and a Webb 89 Vacuum Furnace (Fig. 6.4) for temperatures exceeding 1000 °C.

Heraeus Tube Furnace
Annealing temperatures exceeding 1000 °C will result in bending of the quartz tube of this furnace. Sample annealing in the tube furnace is done under argon flow to limit oxidation and to ensure safety. The furnace is heated to the required temperature before inserting the sample and removed after the required time employing the quartz sample holder. The sample is then allowed to cool down quickly outside the furnace but still within the quartz tube, under an inert argon atmosphere. This allows the freezing in of defects that may result from thermal treatment of the material.
Webb 89 Vacuum Furnace

The design of this furnace does not allow the insertion of samples at the annealing temperature; instead the sample is resistively heated with the furnace heating element at a rate of 25°C per minute. After the required temperature is reached the furnace is allowed to cool down before the sample may be removed and quenching is thus not possible. Annealing within this furnace is also done under argon flow.

Figure 6.3. Webb 89 Vacuum Furnace used for annealing at temperatures above 1000°C.
The samples annealed in the Webb 89 furnace (Fig. 6.3) are enclosed in specially made graphite containers (Fig. 6.4). This container prevents contamination of the furnace and since temperature in the furnace is monitored by means of a thermocouple and pyrometer, which is calibrated for the emission spectrum of graphite, it is not necessary to calibrate it for a different material.

![Graphite specimen holder used to contain specimen during annealing in the Webb 89 furnace.](image)

### Figure 6.4. Graphite specimen holder used to contain specimen during annealing in the Webb 89 furnace.

#### 6.3.3 TEM Specimens

The main challenge of specimen preparation for TEM analysis techniques is the preparation of a very thin specimen with a uniform finish. TEM samples must be thin enough to be electron transparent in order for electrons to pass through the sample and from an image on the viewing screen. There are two types of specimens used in TEM analysis namely planar and cross-sectional (XTEM) samples. The preparation technique is related to the nature of the sample.

#### Plan View Samples

Plan view TEM samples were prepared for the neutron irradiated samples, since neutron irradiation leads to uniform damage throughout the sample depth measured from the surface on which the neutrons are incident. A sample, approximately 3 mm × 3 mm in size, is cut from the as irradiated sample using a diamond wire saw. The one side of the sample is polished using a Buehler Beta Grinding/Polishing system, this side is then glued to a TEM specimen grid (Fig. 6.5) and the exposed side is ground/polished until the sample is approximately 50μm thick. The sample is then ion milled using a Gatan PIPS system.
Cross-sectional Samples

Cross-sectional (XTEM) samples are prepared for the samples implanted with ions in order to allow among other factors the measurement of implantation depth. Each specimen consists of two pieces, approximately 3 mm × 2 mm in size, cut from the as-irradiated sample using a diamond wire saw. The pieces are glued together with the implantated surfaces in contact (Fig. 6.6). The glued samples are placed in an oven at 140 °C for 20 min to allow the glue to harden. The samples are then ground and polished in the same way as the planar samples (Fig. 6.5). Note that the implanted surface is never polished as this would destroy the very thin implanted surface region of the sample. The sample is then milled as in the plan view case.

Figure 6.5 Illustration of a TEM grid along with cross-sectional and plan samples after glueing.

Figure 6.6 Schematic representation of the preparation steps for a cross-sectional sample [Neethling 1980].
Grinding and Polishing
A Buehler Beta Rotating Grinding/Polishing setup is used in sample preparation. Samples are first ground using 30μm and 9μm grinding discs, where after the samples are polished using 9μm, 6μm, 3μm and 1μm polishing suspensions with relevant polishing mats. Each stage of polishing is continued until the damage induced by the previous step is no longer observable under a light microscope at 56x magnification. This procedure is followed for both sides of the sample. First the one side is polished and then glued to a TEM specimen grid after cleaning. The exposed unpolished side is then thinned to approximately 50μm thickness and also polished to a 1μm finish.

Ion Milling
The polished samples (both plan and XTEM) were ion milled using a Gatan Precision Ion Polishing System (PIPS) (Fig. 6.7 a). This system bombards the specimen from both the top and bottom surfaces with 5kV argon ion beams at an incident angle of 3 - 6° (Fig. 6.7 b). The ion milling is terminated when a small hole is observed in the centre of the sample.

Figure 6.7 (a) Gatan Precision Ion Polishing System used for TEM sample preparation, (b) schematic representation of the sample holder. The ion beams are modulated to prevent erosion of the metal specimen holder.
6.3.4 SEM Specimens
All the samples for SEM analysis were prepared by polishing of the surface to a 0.05μm finish using colloidal silica. The SEM analyses included SE and BSE imaging modes, WDS, EDS and EBSD.

6.3.5 Nano-Indentation Hardness Tester Samples
Nano-indentation techniques require specimens with an average surface roughness of less than 5% of the indentation-penetration depth. The samples are prepared using the same polishing techniques as in TEM sample preparation, followed by a final polish to create a very smooth surface finish by polishing up to a 0.05μm finish with colloidal silica. The surface of the ion implanted samples was not polished for the same reasons as stated in the previous section. Neutron irradiated samples may be polished due to the distribution of neutron damage as discussed in the previous section. The hardness measurement of both annealed and irradiated samples are compared with unannealed and unirradiated samples.

6.4 Equipment
6.4.1 Electron Microscopes

TEMs
The TEMs used in this investigation are a Philips CM20 and JEOL JEM 2100 LaB6. Both these transmission electron microscopes are equipped with a LaB₆ filament and were operated at an accelerating voltage of 200 kV.

SEM
The SEM used in this investigation is a JEOL JSM 7100F, with various analytical attachments including an Oxford EDS spectrometer, Oxford WDS spectrometer and a HKL EBSD detector. This SEM is equipped with a Field Emission Gun (FEG) as the source of electrons.
6.4.2 Nano-Indentation Hardness Tester

A CSM Nano-Indentation Hardness Tester with atomic force microscope (AFM) as shown in Fig. 6.8 is employed in the investigation of the mechanical properties of the materials in this investigation.

![Figure 6.8. CSM Nano-Indentation Hardness Tester with AFM and Optical Microscope.](image)
CHAPTER 7

RESULTS AND DISCUSSION

7.1 Introduction

This chapter is a discussion of the results obtained by means of TEM, EDS and Nano-Indentation Hardness measurements for the different irradiation species used. These results are compared with the findings of other researchers who investigated similar topics.

The aim of this study is to investigate the microstructure of SiC and GaAs irradiated or implanted with different energetic particles. The relationship between the radiation induced changes in microstructure and the mechanical properties (specifically hardness) of these materials are also investigated.

Firstly the investigation of radiation damage in SiC is of great importance since it is used as a structural material in TRISO (Tri-Isotropic) coated particles in the PBMR design [Snead et al. (2007)]. The effects of irradiation by energetic particles on the microstructure and mechanical properties of SiC are important in order to predict the stability of SiC under reactor environment conditions. Fission products of varied mass and energy are produced during the nuclear fission process necessitating the study of the effects of different types of ions and the damage they produce in SiC. The effect of neutron irradiation on SiC is particularly important since neutrons with a wide energy range interact with any material within the reactor core. Neutron irradiation of SiC will also create elements such as phosphorous by the transmutation of Si.

Secondly the interaction of energetic particles with GaAs is of importance due to its use in the fabrication of various electronic devices some of which involve doping by means of ion implantation. GaAs has a lower radiation tolerance and is an ideal material for the prediction of radiation damage effects in other related materials with greater radiation resistance.

All 6H-SiC and GaAs samples used in this investigation are single crystal wafers whereas the 3C-SiC is polycrystalline bulk material. The fabrication an irradiation details of these materials are summarised in Chapter 6.
7.2 Ion Range and Radiation Damage
7.2.1 Phosphorous Implanted 6H-SiC and 3C-SiC
The projected ion range and damage depth distribution of 200 keV P\(^+\) ions implanted into 6H-SiC and 3C-SiC was calculated with the aid of TRIM2010 (SRIM). The maximum ion concentration is found at 174.4 nm with a straggle of 46.7 nm (Fig. 7.1). The largest number of point defects (calculated for vacancies) is generated at depths below 200 nm (Fig 7.2).

**Figure 7.1.** The depth distribution of 200 keV P\(^+\) ions implanted into SiC parallel to the (001) direction calculated using TRIM2010.

**Figure 7.2.** The damage profile of 200 keV P\(^+\) ions implanted into 6H-SiC parallel to the (001) direction, calculated using TRIM2010.
7.2.2 Displacements Per Atom (dpa)

It can be seen in Table 7.1 that the displacements per atom (dpa) for carbon atoms in the SiC lattice is greater than that of Si atoms due to its smaller threshold displacement energy. This is in agreement with predictions by Gao et al. (2002) employing MD simulations. The equation for calculating dpa is given by (equation 3.62)

\[
dpa = \frac{0.4v(E)\phi}{NRE_{d}} = \frac{0.4(0.8E)\phi}{NRE_{d}}
\]

\(\phi\) = ion dose, \(E\) = energy of incident ion, \(N\) = density of the target material, \(R\) = ion range and \(E_d\) = minimum displacement energy.

In order to estimate the dpa values for SiC the Si and C sublattices are considered separately each having an atomic density of \(N_{Si} = N_{C} = 2.21 \times 10^{22}\) atoms/cm\(^3\). The displacement threshold values used for Si and C are 35 eV and 20 eV respectively, as stated in Chapter 5. The purpose of this calculation is to estimate the amount of disorder created by irradiation (or implantation) and inaccuracies due the assumptions made should be minimal.

In order to calculate the dpa for neutrons the energy related dpa cross sections calculated by Heinisch et al. (2002) are simply multiplied with the dose of neutrons as discussed in the paper mentioned yielding the dpa for a certain dose. The equation used for ions is not valid for neutrons since neutrons are not subject to electronic interaction and interact almost exclusively through elastic collisions with the atomic nuclei.

The threshold displacement energy (TDE) for Ga and As atoms is assumed to be the same, resulting in an equal number of dpa for both atoms. The upper limit as given by Lanoo and Bourgoin (1981) for the TDE for GaAs of 10eV is used in the calculations. Since Ga and As atoms are very similar in mass and electron negativity it is reasonable to assume that their bonding energies in the GaAs lattice are very similar. These factors are most significant in calculating threshold displacement energy which means that Ga and As should have very similar displacement energies.
Table 7.1. Calculated values for the mean number of displacements \(<N_d(E)>\) and dpa for both SiC and GaAs implantation and irradiation experiments.

<table>
<thead>
<tr>
<th>Species</th>
<th>Dose (cm(^{-2}))</th>
<th>(&lt;N_d(E)&gt;)</th>
<th>dpa</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(^+) (Si)</td>
<td>5\times10(^{16})</td>
<td>2.3\times10(^3)</td>
<td>236</td>
</tr>
<tr>
<td>P(^+) (C)</td>
<td>4.0\times10(^3)</td>
<td>413</td>
<td></td>
</tr>
<tr>
<td>P(^+) (Si)</td>
<td>1\times10(^{15})</td>
<td>2.3\times10(^4)</td>
<td>5</td>
</tr>
<tr>
<td>P(^+) (C)</td>
<td>4.0\times10(^3)</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>n (SiC)</td>
<td>5.9\times10(^{21})</td>
<td>3.06 - 5.43*</td>
<td></td>
</tr>
<tr>
<td>n (GaAs)</td>
<td>1\times10(^{20})</td>
<td>16.0\times10(^3)</td>
<td>116</td>
</tr>
</tbody>
</table>

* dpa for neutrons in the energy range between 1 MeV and 10 MeV.

7.3 Diffusion in GaAs

The average diffusion distances for Ga and As atoms in GaAs versus the annealing temperature are shown in Fig. 7.3 below. The diffusion mechanism is assumed to be purely vacancy diffusion. Since thermodynamic considerations (Chapter 2) require that any crystal contains a certain number of vacant lattice sites with the number dependent on temperature this assumption is validated. The values below are calculated at the hand of considerations by Neethling (1985) and also data from Potts and Pearson (1966) and Casey and Pearson (1975). It is clear from Fig. 7.3 that As (black) is more mobile than Ga (red) at both low and high temperatures. As becomes mobile at temperatures exceeding 600°C with Ga mobile at temperatures exceeding 800°C. The higher mobility of As allows for the desorption of arsenic during annealing, which may affect the mechanical properties of GaAs.

![Figure 7.3. Self-diffusion data for Ga and As in GaAs as a function of temperature calculated for 20 minute annealing runs.](image-url)
Table 7.2 Diffusion Coefficients for Ga and As in GaAs for 20 min [Neethling (1985)].

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(D_{\text{As}})</th>
<th>(D_{\text{Ga}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°C</td>
<td>9.23x10^{-12}</td>
<td>9.13x10^{-25}</td>
</tr>
<tr>
<td>800°C</td>
<td>4.84x10^{-5}</td>
<td>5.25x10^{-13}</td>
</tr>
<tr>
<td>1000°C</td>
<td>5.21x10^{-1}</td>
<td>5.97x10^{-6}</td>
</tr>
</tbody>
</table>

The diffusion of Ga and As in GaAs is seen to increase (Table 7.2) as the temperature increases with an exponential trend in both the diffusion coefficient and the average diffusion distance.

7.4 TEM Results

Cross-sectional and plan view TEM samples were prepared from the as-irradiated and annealed samples of SiC and GaAs using the techniques outlined in Chapter 4.

7.4.1 As-implanted 6H-SiC and 3C-SiC

Fig. 7.4 (a) shows a bright field TEM micrograph of 6H-SiC implanted with 200 keV P\(^+\) ions to a dose of 5x10\(^{16}\) ions/cm\(^2\). The presence of an amorphous region across the implantation depth is observed as indicated by the diffraction rings in Fig 7.4 (b) obtained by selected area diffraction from this region. The region beyond the implantation depth retained its crystalline nature as indicated by the SAD pattern shown in Fig. 7.4 (c). Simulations with the software package JEMS indicate that the diffraction pattern matches the [100] zone axis of 6H-SiC. The amorphous nature of the region at the implanted side of the sample is visible in Fig. 7.5, with lattice fringes present in the region beyond the implantation depth evident of its undisturbed crystalline nature. The middle of the amorphous band should coincide approximately with the peak of the calculated damage profile and the projected ion range. Having lost most of their energy through electronic collisions the slowed ions start losing the remaining energy through elastic collisions as they come to rest resulting in many atomic displacements at the projected ion range. The darker contrast within the transition region is indicative of the presence of a high density of extended lattice defects which should coincide with the tail of the damage profile. This is due to the fact that extended lattice defects can only be observed in crystalline material.

The \(dpa\) in SiC as a result of 200 keV P\(^+\) implants to a dose of 5x10\(^{16}\) ions/cm\(^2\) exceeds the critical amorphization \(dpa\) value of 0.3 \(dpa\) given by Benyagoub (2008). RBS/C analyses of 6H-SiC wafers irradiated with 550 keV Si\(^+\) ions to a dose of 6x10\(^{15}\) ions/cm\(^2\) by Jiang et al. (1998) also revealed the amorphization of the region across the implantation depth. Similar amorphization effects were also observed by Aihara et al. (2000) in 6H-SiC implanted with 20
keV Ne$^+$ ions to a dose of $3.75 \times 10^{15}$ ions/cm$^2$ and 30 keV N$_2^+$ ions to a dose of $3.0 \times 10^{15}$ ions/cm$^2$ also employing TEM techniques.

Figure 7.4. (a) Bright field TEM micrograph of single crystal 6H-SiC implanted with 200 keV P$^+$ ions to a dose of $5 \times 10^{16}$ ions/cm$^2$ before any annealing. The diffraction rings (b) indicate the amorphous nature of the region across the implantation depth and the SAD pattern (c) indicates the crystalline nature of the region beyond the implantation depth.

Figure 7.5. Bright field TEM micrograph of single crystal 6H-SiC implanted with 200 keV P$^+$ ions to a dose of $5 \times 10^{16}$ ions/cm$^2$ before annealing. Lattice fringes are visible in the crystalline region along with the amorphous nature of the region across the implantation depth.
Fig. 7.6 shows EDS composition maps and a STEM bright field image of the region at the implanted side of the sample. It seems that the ion implantation caused some depletion of Si close to the implanted surface as can be seen in the Si K map. This effect may also be due to a thickness variation at the edge of the sample as a result of the preparation process. Most important is that the Phosphorous K map indicates that the highest concentration of phosphorous is found at a depth which is in good agreement with the projected range calculated by TRIM 2010.

![Figure 7.6. EDS mapping of the amorphous layer at the implanted side of the as-implanted single crystal 6H-SiC sample showing the location of the phosphorous ions (200 keV P\(^+\) ions to a dose of 5×10\(^{16}\) ions/cm\(^2\) before annealing). The front surface is indicated by the white dotted line in the X-ray maps.](image-url)
Fig. 7.7 (a) shows a bright field TEM micrograph of polycrystalline 3C-SiC implanted with 200 keV P⁺ ions to a dose of $1 \times 10^{15}$ ions/cm². Part of a single grain of 3C-SiC is visible at the top left of the micrograph with the crystalline nature thereof confirmed by the SAD pattern shown in Fig. 7.7 (b). Simulations show the diffraction pattern to be consistent with that 3C-SiC viewed along the [101] direction. The amorphous nature of the region across the implantation depth is indicated by the diffraction rings in the SAD pattern from this region as shown in Fig. 7.7 (c).

Fig. 7.8 shows a bright field TEM micrograph of the amorphous-to-crystalline transition region, with the presence of lattice fringes evident of the undisturbed crystalline nature of the region beyond the implantation depth. The implanted region appears to be almost completely amorphous. These results are comparable to that of the unannealed 6H-SiC samples.

![Figure 7.7](image)

**Figure 7.7.** (a) Bright field TEM micrograph of polycrystalline 3C-SiC implanted with $P^+$ ions to a dose of $1 \times 10^{15}$ ions/cm² before annealing. The SAD pattern (b) indicates the crystalline nature of the region beyond the implantation depth and the ring pattern (c) the amorphous nature of the region at the implanted side of the sample.
Figure 7.8. High resolution TEM micrograph of polycrystalline 3C-SiC implanted with $P^+$ ions to a dose of $1 \times 10^{15}$ ions/cm$^2$ before annealing. The lattice fringes are indicative of the crystalline nature of the region beyond the implantation depth, with the amorphous nature of the implanted region also evident from the HRTEM image.

7.4.2 Phosphorous implanted 6H-SiC and 3C-SiC annealed at 800°C

Fig. 7.9 (a) indicates that annealing of the implanted samples at 800°C for 20 min has no observable effect on the amorphous nature of the region shown in (b). The diffraction rings shown in Fig.7.9 (a) indicate that no significant recovery of the amorphous structure of the implanted region has taken place at 800°C. Benyagoub (2008) found that an amorphous layer caused by low energy ion implantation of SiC only recrystallises at temperatures exceeding 950°C. This is supported by results of Jiang et al. (1998) revealing recrystallisation of SiC at temperatures above 900°C. The SAD pattern shown in Fig. 7.9 (c) was obtained from the region beyond the implantation depth and it confirms the single crystalline nature of this region with the 6H-SiC structure viewed along the [100] direction as indicated by the simulation (insert).

The amorphous-to-crystalline transition region is shown in Fig. 7.10. Regular lattice fringe contrast confirms the crystalline nature of the region beyond the implantation depth with the amorphous nature of the implanted region evident from the image.
Figure 7.9 (b). Bright field TEM micrograph of 6H-SiC implanted with 200 keV P+ ions to a dose of $5 \times 10^{16}$ ions/cm$^2$ and annealed at 800°C for 20 min. The diffraction rings (a) indicate the amorphous nature of the implanted region with the SAD spot pattern (c) and the corresponding simulation matching the [100] zone axis diffraction pattern of 6H-SiC.

Figure 7.10 (a). Bright field TEM micrograph of 6H-SiC implanted with 200 keV P+ ions to a dose of $5 \times 10^{16}$ ions/cm$^2$ and annealed at 800°C for 20 min. The crystalline nature of the region beyond the implantation depth is evident from the lattice fringes.
Fig. 7.11 (a) is a bright field TEM micrograph of polycrystalline 3C-SiC implanted with 200 keV P$^+$ ions to a dose of $1 \times 10^{15}$ ions/cm$^2$ followed by annealing at 800°C for 20 min. The SAD pattern indicates the crystalline nature of the previously amorphous layer across the implantation depth at the implanted side of the sample (Fig. 7.7 (a)). The SAD pattern from the region beyond the implantation depth (Fig. 7.11 (b)) confirms its undisturbed crystalline nature. The dpa (Table 7.1) resulting from the dose mentioned above is significantly lower than for the higher dose of $5 \times 10^{16}$ ions/cm$^2$. The lower amount of displacements at the lower dose possibly leads to less disorder in the implanted region, with some crystalline regions remaining. Annealing at temperatures below 950°C (threshold temperature for total recrystallisation) of the implanted samples may then possibly result in recrystallisation of the semi-amorphous layer as observed for this sample.

*Figure 7.11 (a). Bright field TEM micrograph of polycrystalline 3C-SiC implanted with 200 keV P$^+$ ions to a dose of $1 \times 10^{15}$ ions/cm$^2$ and annealed at 800 °C for 20 min. The SAD spot pattern (b) indicates the crystalline nature of both the implanted region and the region beyond.*
7.4.3 Phosphorous implanted 6H-SiC and 3C-SiC annealed at 1200°C

Fig. 7.12 (b) shows a bright field TEM micrograph of the P⁺ implanted 6H-SiC sample (dose = 5×10¹⁶ ions/cm²) annealed at 1200°C for 20 min. The previously amorphous implanted region has recrystallised in the form of polycrystalline 3C-SiC as indicated by the SAD pattern in Fig. 7.12 (a) with corresponding simulation (insert) of 3C-SiC viewed along the [101] direction. The crystalline nature and phase of the region beyond the implantation depth is confirmed by the SAD pattern shown in Fig. 7.12 (c) with corresponding matching simulation (insert) of the 6H-SiC phase viewed along the [100] direction. The fact that amorphous layer in hexagonal 6H-SiC crystallised in the cubic 3C-SiC phase upon annealing at 1200 °C is consistent with the fact that the 3C-SiC phase is stable for temperatures below 1900°C as discussed by Snead et al. (2007). The recrystallisation of the amorphous layer caused by ion implantation is also observed in 3C-SiC as is shown in the bright field TEM micrograph in Fig. 7.13 (b). The crystalline nature of this layer and that of the region beyond the implantation depth are confirmed by the SAD patterns in Figs. 7.13 (a) and (c) respectively.

![Figure 7.12. (b) Bright field TEM micrograph of 6H-SiC implanted with 200 keV P⁺ ions to a dose of 5×10¹⁶ ions/cm² and annealed at 1200°C for 20 min. The SAD pattern in (a) indicates the crystalline nature of the implanted region ([100] zone axis). The previously amorphous implanted layer has recrystallised as the cubic 3C polytype indicated by the SAD pattern (a) while the original hexagonal 6H-SiC bulk phase of the sample is confirmed by the SAD pattern in (c).](image-url)
Figure 7.13. (b) Bright field TEM micrograph of polycrystalline 3C-SiC implanted with 200 keV P⁺ ions to a dose of 1×10¹⁵ ions/cm² and annealed at 1200°C for 20 min. The SAD pattern in (a) indicate the crystalline nature of the previously amorphous implanted region with simulated (insert) of the 3C-SiC structure viewed along the [101] direction. The SAD pattern in (c) indicate the crystalline nature of the SiC beyond the implanted region with simulated (insert) of the 3C-SiC structure viewed along the [001] direction.

7.4.4 Neutron Irradiated SiC

Fig. 7.14 (a) shows a bright field TEM micrograph of polycrystalline SiC irradiated with neutrons to a dose of 5.9×10²¹ n/cm² at an irradiation temperature of 1000°C. Fig. 7.14 (b) is a SAD pattern indicating the crystalline nature of the irradiated material, with corresponding simulation of a 3C-SiC [001] zone axis pattern. Fig. 7.17 shows a bright field TEM micrograph of polycrystalline 3C-SiC irradiated with neutrons to a dose of 9.6×10²¹ n/cm² at a temperature of 1000°C. The irradiation damage in both samples consist of small black spots which are most likely small interstitial clusters since interstitial atoms are more mobile than vacancies in SiC. Snead et al. (2007) stated that defects in SiC due to neutron irradiation that are visible as black spots are most likely self interstitial atoms in various undetermined configurations. The parallel dark lines in the TEM image are stacking fault boundaries on {111} planes.
Figs. 7.15 and 7.16 show bright field TEM micrographs of the polycrystalline 3C-SiC (dose = 5.9×10^{21} n/cm^2) sample annealed at 1600°C for 30 minutes under an inert argon flow. A high concentration of dislocation loops is visible in the samples. It is generally assumed that the dislocation loops form through the agglomeration of point defects generated during neutron irradiation. The parallel dark lines in these TEM images are stacking fault boundaries on {111} planes.

Dislocation loops have also been observed in 3C-SiC irradiated with neutrons to doses exceeding 5×10^{22} n/cm^2 at 640°C by Toyohiko Yano and Takayoshi Iseki (1990). They stated that these loops were lying on the {111} planes of SiC and have a burgers vector \( b = \frac{1}{2}<111> \). Dislocation loops lying on the {111} planes of 3C-SiC have also been observed by Y. Katoh et al. (2006) in 3C-SiC irradiated to 4.5–7.7×10^{21} n/cm^2 at temperatures of 300 and 800°C. T. Yano et al. (1998) identified dislocation loops lying on the {111} planes of 3C-SiC irradiated with neutrons to a dose of 1.9×10^{23} n/cm^2 at temperatures in the range from 370 to 650°C. This author also identified the critical dose and irradiation temperature, for the agglomeration of interstitials to form dislocation loops, as 2×10^{22} n/cm^2 and 500°C respectively.

Figure 7.14 Bright field TEM micrograph of polycrystalline 3C-SiC irradiated with neutrons to a dose of 5.9×10^{21} n/cm^2 at a temperature of 1000°C.
Figure 7.15. Bright field TEM micrograph ([001] zone axis) of polycrystalline 3C-SiC irradiated with neutrons to a dose of $5.9 \times 10^{21}$ n/cm$^2$ and annealed at 1600°C for 30 min.

Figure 7.16. Bright field TEM micrograph ([001] zone axis) of polycrystalline 3C-SiC irradiated with neutrons to a dose of $5.9 \times 10^{21}$ n/cm$^2$ annealed at 1600°C for 30 min.
Figure 7.17. Bright field TEM micrograph of polycrystalline 3C-SiC irradiated with neutrons to a dose of $9.6 \times 10^{21} \text{ n/cm}^2$ at a temperature of 1000°C.

### 7.4.5 Neutron Irradiated GaAs

Fig. 7.18 shows a bright field TEM micrograph of GaAs irradiated to a dose of $1 \times 10^{20} \text{ neutrons/cm}^2$. Point defects such as interstitial atoms, resulting from neutron irradiation, agglomerate through thermal diffusion. This gives rise to the formation of interstitial loops. The number and size of the dislocation loops indicate that the sample temperature must have increased during irradiation to allow for an adequate number of point defects to diffuse and coalesce in the form of dislocation loops. This inference is based on the earlier finding that interstitial loops in GaAs only start to form at a temperature of approximately 500 °C [Neethling, (1994)]. Fig. 7.19 (b) is a SAD pattern which indicates the crystalline nature of the material.
Figure 7.18. (a) Bright field TEM micrograph of neutron irradiated GaAs as-implanted. Many small dislocation loops are visible. The SAD pattern (b) shows the crystalline nature of the sample.

The loop diameters increased after post-irradiation annealing in the range 600 to 800 °C as shown in Figures 7.19 and 7.20 respectively. The dislocation loops with {110} habit planes were found to be of interstitial nature. This finding is in agreement with earlier studies by Neethling et al. (1987) and Neethling at al. (1994) on proton bombarded and 1 MeV electron irradiated GaAs where interstitial loops on {110} planes became visible after annealing at temperatures exceeding 500 °C. The small loops on {110} transformed to large dislocation loops after annealing at 1000 °C as shown in Figs. 7.21 and 7.22.
Figure 7.19. Bright field TEM micrograph of neutron irradiated GaAs annealed at 600 °C for 20 min. Many small defects and dislocation loops are again visible.

Figure 7.20. Bright field TEM micrograph of neutron irradiated GaAs annealed at 800 °C for 20 min. A large number of medium and large dislocation loops are visible.
Figure 7.21. Bright field TEM micrograph of neutron irradiated GaAs annealed at 1200 °C for 20 min. Large loops and a dislocation segment are visible.

Figure 7.22. Bright field TEM micrograph of neutron irradiated GaAs annealed at 1200 °C for 20 min. A large number of dislocation segments are visible.
A plot of the loop diameter as a function of annealing temperature shown in Fig. 7.23, illustrates the increase in loop diameter with temperature. The loops increase in size due to the agglomeration of point defects during annealing.

**Loop Character and Habit Plane**
The method of inside/outside contrast was used to determine the interstitial/vacancy nature of the loops. In this method the change in loop size is noted on reversing \( g \) while \( s \) is kept positive and constant. The (001) plan view GaAs sample was placed in the TEM holder with the [010] direction parallel to the tilt axis of the holder. The loop shown in Fig. 7.24 (a) exhibits outside contrast for \( g = 400 \) and the same loop shown in Fig. 7.24 (c) exhibits inside contrast for \( g = 400 \). Tilting experiments indicated that the loop lies on the (101) plane. This is shown in Fig. 7.25 (a) and Fig. 7.26 (a) where the loop is imaged after a clockwise tilt of 6° and 21° respectively, about the [010] direction. The inside/outside experiments of which a typical example is shown in Figs. 7.24 to 7.26, revealed that these loops are of interstitial nature with \( \{110\} \) habit planes.
Figure 7.24. (a) Determination of the interstitial/vacancy nature of dislocation loops in GaAs irradiated with neutrons to a dose of $1 \times 10^{20}$ neutrons/cm$^2$ and annealed at 900°C for 20 min.

The loop indicated by the red circle exhibits outside contrast in (a) for $\mathbf{g} = \bar{4}00$ and inside contrast in (c) for $\mathbf{g} = 400$. The two-beam SAD patterns in (b) and (d) are associated with (a) and (c) respectively.
Figure 7.25 (a) The GaAs sample is tilted by 6° about the [101] at which point the loop in Fig. 7.25 (a) again exhibits outside contrast. The insert (b) is a SAD pattern showing \( a \mathbf{g} = 311 \) type reflection.

Figure 7.26. (a) The GaAs sample is tilted by 21° about the [010] at which point the loop in Fig. 7.25 (a) again exhibits outside contrast. The insert (b) is a SAD pattern showing \( a \mathbf{g} = 311 \) type reflection.
7.5 Nano Indentation Hardness Results

7.5.1 Phosphorous Implanted 6H-SiC

Samples were prepared from the unannealed and annealed single crystal 6H-SiC wafers implanted with P⁺ ions to a dose of $5 \times 10^{16}$ ions/cm² for nano indentation hardness testing using the techniques described in chapter 4.

The maximum indentation load was set to 50 mN in order to collect information only from a depth affected by ion implantation. Table 7.1 lists the results for the indentation hardness testing including reference hardness from Snead et al. (2007). Fig. 7.27 shows plots of hardness as a function of annealing temperature. The data in red represent implanted SiC and the data in black the unimplanted SiC (used as a reference). Initially the hardness of the unannealed implanted sample is significantly lower than the reference, which can be attributed to the amorphization of the region spanning the implantation depth as shown in Fig. 7.3. This finding is in agreement with a nanoindentation hardness value of approximately 30 GPa measured by El Khakani et al. (1994) for amorphous SiC. The hardness is seen to increase for both 800 and 1200°C anneals. This is most likely a result of recrystallisation and point defect hardening of the amorphous layer in the sample as shown in Fig. 7.9 and Fig. 7.12 for annealing temperatures of 800 and 1200°C respectively. The recrystallized region is polycrystalline and has the cubic 3C-SiC phase. However, it has been documented that the bulk hardness of the 6H and 3C-SiC phases are the same. [Goldberg et al. (2001)]

Table 7.1. Nano indentation hardness results for 6H-SiC implanted with 200 keV P⁺ ions to a dose of $5 \times 10^{16}$ ions/cm².

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Reference Hardness (GPa)</th>
<th>Sample Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as implanted</td>
<td>33.0 ± 0.9</td>
<td>27.8 ± 1.5</td>
</tr>
<tr>
<td>800°C</td>
<td>33.9 ± 0.7</td>
<td>39.0 ± 2.6</td>
</tr>
<tr>
<td>1200°C</td>
<td>34.2 ± 0.6</td>
<td>43.9 ± 2.9</td>
</tr>
</tbody>
</table>
Figure 7.2. Nanoindentation hardness vs. temperature values for 6H-SiC implanted with 200 keV $P^+$ ions to a dose of $5 \times 10^{16}$ ions/cm$^2$ (red) and reference hardness values for unimplanted 6H-SiC wafers annealed at the same temperatures (black).

### 7.5.2 Neutron Irradiated 3C-SiC

Samples were prepared from the as-irradiated and annealed polycrystalline 3C-SiC irradiated to a dose of $9.6 \times 10^{17}$ n/cm$^2$, at room temperature, for nano indentation hardness testing using the techniques described in chapter 4. The maximum indentation load was set to 100 mN for all indents.

The hardness of the as-irradiated sample is initially greater than that of the virgin 3C-SiC bulk sample but decreases for the samples annealed at 800 and 1200°C anneals to values well below the hardness of the virgin samples annealed at the same temperature (Fig. 7.28). It is suggested that the increase in hardness of the irradiated unannealed sample is most likely due to point defect hardening. The decrease in hardness upon annealing is most likely due to the formation of voids in the SiC.

Nano Indentation Hardness measurements on the 3C-SiC sample irradiated to a dose of $5.9 \times 10^{21}$ n/cm$^2$ at a temperature of $1000^\circ$C revealed a much greater hardness of $42.2 \pm 1.1$ GPa as compared to samples mentioned above that were irradiated at a much lower dose. A higher dose of neutrons may lead to a greater amount of point defects which could in turn result in sample hardening as in the lower dose sample.
Figure 7.2. Nano indentation hardness vs. temperature for neutron irradiated 3C-SiC (red) and reference hardness values for virgin 3C-SiC annealed at the same temperatures (black).

7.5.3 Neutron Irradiated GaAs

The hardness of the as-irradiated sample was found to be higher than that of un-irradiated GaAs. After annealing at 600 and 800°C, the hardness decreased, reaching values close to that of un-irradiated GaAs (Fig. 7.29). The following correlation between microstructure and hardness is suggested. The hardness of the as-irradiated sample is initially greater than virgin GaAs due to point defect hardening. Upon annealing at 600 and 800°C the hardness decreases and may be associated with the coalescence of point defects and formation of dislocation loops. The dramatic decrease in hardness after an anneal at 1000 °C is most likely due to the loss of As leading to the decomposition of the surface of the GaAs [Neethling (1985)]. Similar effects on the hardness have been observed by Udhayasankar et al. (1999) and (1996) for 100 keV H⁺ irradiated GaAs. It is interesting to observe the increase in hardness of the un-irradiated GaAs up to 800 °C. This is probably due to point defects created by the annealing and cooling procedure. The decrease in hardness at a 1000 °C can also be ascribed to the onset of surface decomposition due to As out diffusion.
Figure 7.29. Nano indentation hardness versus temperature for neutron irradiated GaAs (red) and reference hardness values for virgin GaAs wafers annealed at the same temperatures (black).
CHAPTER 8

CONCLUSIONS

This chapter summarizes the conclusions of the investigations presented in Chapter 7. Each section presents the TEM results and also nano-indentation hardness (NIH) results where applicable. The relationship between the microstructure as observed by TEM and the hardness measured by means of NIH is discussed.

8.1 Ion Range and Radiation Damage

The ions ranges, for 200 keV P\(^+\) ions in SiC, calculated using TRIM2010 are in good agreement with results from EDS and TEM measurements. TRIM calculations predict the highest concentration of implanted phosphorous ions at 174 ± 47 nm and EDS measurements indicated that the highest concentration is just below 200 nm.

Calculation of dpa values for the various implantation and irradiation experiments (see Table 7.1) suggests that a large amount of damage in 6H-SiC samples will result due to the implantation thereof with 200 keV P\(^+\) to a dose of 5\(\times\)10\(^{16}\) ions/cm\(^2\). The calculated dpa values for this implantation far exceed the minimum amorphization dpa value of 0.28 dpa [Gao et al. (2002)], which would indicate that the implanted material should be rendered amorphous. The TEM results confirm the prediction for this implantation dose revealing the presence of an amorphous layer at the implanted side of the material as shown in Fig. 7.4 (a). The dpa for neutrons is typically lower than that for ions due to the much smaller interaction cross-section as a result of the interaction mechanism; this is discussed in greater depth in Chapter 3. The calculated dpa for ions as shown in Table 7.1 are typically two orders of magnitude greater than the dpa for neutrons. The calculated dpa values for the neutron irradiated SiC indicate that a large amount of irradiation damage may be expected in the samples irradiated to a dose of 5.9\(\times\)10\(^{21}\) n/cm\(^2\). In comparison to this the dpa for SiC irradiated to a dose of 9.6\(\times\)10\(^{17}\) n/cm\(^2\) is much lower yet it may still have an effect on the hardness of the samples. The calculated dpa values for GaAs irradiated to a dose of 1\(\times\)10\(^{20}\) n/cm\(^2\) are even greater than that of SiC at a higher neutron dose. A greater amount of radiation damage can therefore be expected in GaAs. This is confirmed by comparison of the TEM results for SiC and GaAs in the preceding chapter.
8.2 Phosphorous Implanted Single Crystalline 6H-SiC

The effects of 200 keV P⁺ implantation to a dose of $5 \times 10^{16}$ ions/cm² and the subsequent thermal annealing on the microstructure and hardness of 6H-SiC were investigated using TEM and nano-indentation hardness testing. The hardness of the implanted SiC is initially much lower than unimplanted SiC due to the formation of an amorphous layer during ion implantation which is confirmed by micro-diffractometry (Fig. 7.4). After annealing the implanted SiC at 800°C and 1200°C, the hardness increases due to re-crystallisation and point defect hardening. TEM analysis, using micro-diffraction, clearly show that the amorphous layer re-crystallised to exhibit the cubic 3C-SiC phase (Fig. 7.12). The fact that the amorphous layer re-crystallised in the cubic 3C-SiC phase is due to the fact that the hexagonal polytypes of SiC only start to form at temperatures greater than the annealing temperature of 1200°C as discussed by Snead et al. (2007).

8.3 Phosphorous Implanted Polycrystalline 3C-SiC

Similar arguments as presented for 6H-SiC above apply to the implantation of 200 keV P⁺ ions to a dose of $1 \times 10^{15}$ ions/cm² into 3C-SiC. The implantation dose is much lower which leads to a lower number of dpa. The calculated dpa value exceeds the minimum value for amorphization of 0.28 dpa as stated by Gao et al. (2002), which is confirmed by SAD showing the formation of an amorphous layer due to implantation. The layer is seen to recrystallise at 800°C, possibly due to the decreased amount of radiation (lower dpa) damage as compared to the 6H-SiC.

Nano-hardness measurements were not done for this material since the implanted surface was not adequate for indentation purposes. The implanted side of the sample could not be polished as this would have removed the thin implantation affected layer.

The high phosphorous ion doses implanted into this sample resulted in phosphorous atom concentrations of 1000 ppm at the projected ion range, for a dose of $1 \times 10^{15}$ ions/cm². The initial effect of the implanted phosphorous ions was the amorphization of the region across the implantation depth. After annealing at 800°C the amorphous layer is seen to recrystallise in the original 3C polytype. Even at the ion range where the concentration of phosphorous ions is the greatest the microstructure recovered after annealing and no defects or significant changes in the microstructure, due to the presence of phosphorous, were observed.
It is therefore reasonable to assume that the much lower phosphorous concentrations of 8 ppm that will be present, at the end of the fuel cycle, in the SiC layer of a coated particle will have a negligible effect on the microstructure and integrity of a TRISO coated particle.

### 8.4 Neutron Irradiated Polycrystalline 3C-SiC

TEM investigations of neutron irradiated 3C-SiC revealed the presence of defect clusters observed as black spots. These defects are seen in both samples irradiated to a dose of 5.9×10^{21} n/cm² and 9.6×10^{21} n/cm² at an irradiation temperature of 1000°C. The critical dose and irradiation temperature for the formation of dislocation loops in 3C-SiC by interstitial agglomeration is identified by Yano et al. (1998) as 2×10^{22} n/cm² and 500°C respectively. Both these samples lie just below the critical dose but were irradiated at temperatures above the critical temperature. Since no evidence of dislocation loops is observed in these unannealed samples it would suggest that dose is more important in their formation. Dislocation loops are observed in the sample irradiated to a dose of 5.9×10^{21} n/cm² after annealing at 1600°C. The presence of dislocation loops after higher temperature annealing suggests that a large concentration of point defects were present in the as irradiated sample as suggested by the presence of black spot defects in the unannealed samples. These loops observed in the neutron irradiated 3C-SiC are assumed to be similar to that previously observed by other authors as discussed in the preceding chapter. These loops usually lie on the {111} planes of SiC with burgers vector $b = a/3<111>$ for Frank faulted loops and $b = a/2<111>$ for perfect loops both of the interstitial type [Toyohiko Yano and Takayoshi Iseki (1990)].

TEM analysis of the 3C-SiC samples irradiated to a dose of 9.6×10^{17} n/cm² did not show any visible signs of irradiation damage. The overall appearance of these samples is similar to that of unirradiated 3C-SiC. The hardness of this sample is initially higher than that of virgin SiC but decreases with increasing annealing temperature. The, initial, greater hardness may be due to the presence of point defects. TEM analysis did not show proof of point defects within the sample irradiated at lower dose, A certain number of point defects will be generated through neutron irradiation. As discussed previously the presence of point defects may have a hardening effect on a material. It is therefore possible that the number of point defects present in this lower dose
sample is sufficient to harden the material but not to be visible under TEM analysis. The effect of neutron irradiation on the hardness of SiC at this dose is therefore inconclusive.

8.5 Neutron Irradiated GaAs

TEM investigation revealed a high density of dislocation loops in GaAs irradiated to a dose of $1 \times 10^{20}$ n/cm$^2$ before annealing (Fig. 7.20). The presence of these small loops indicates that some annealing occurred during the neutron irradiation process. The loop diameters increased after post-irradiation annealing in the temperature range between 600 and 800 °C (Figs 7.21 and 7.22). The dislocation loops were found to lie on the (110) cleavage planes of GaAs. The dislocation loops were found to be of interstitial nature through the method of inside/outside contrast. This finding is in agreement with earlier studies on 300 keV proton bombarded and 1 MeV electron irradiated GaAs where interstitial loops on (110) planes became visible after annealing at temperatures exceeding 500 °C. The small dislocation loops on the (110) planes of the neutron irradiated GaAs transformed to large extended dislocations and large loops after annealing at 1000 °C (Fig. 7.23). It was found that the dislocation density produced by a dose of $1 \times 10^{20}$ neutrons/cm$^2$ in GaAs, is of the same order as that produced by a proton dose of about $1 \times 10^{16}$ protons/cm$^2$ at the projected range and a 1 MeV electron dose of $2.4 \times 10^{22}$ electrons/cm$^2$.

If this finding is applied to silicon carbide, then some of the effects of neutron irradiation damage can be investigated by using proton bombardment at a total dose of about 4 orders of magnitude lower than the neutron dose of interest. The use of protons will not require the long cooling down period required in the case of neutron irradiated SiC. On the other hand, the use of protons will introduce additional defects due the presence of hydrogen in the specimen after bombardment.

The increase in hardness of the as-irradiated sample may be attributed to point defect hardening evidenced by the presence of a high density of small dislocation loops. The subsequent decrease in hardness following anneals at 600 and 800°C may be attributed to point defect coalescence leading to the formation of larger dislocation loops.
REFERENCES


Barron A. R., *Chemistry of Electronic Materials*, (http://cnx.org/content/col10719/1.6/), Rice University, Texas (2010)


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