An in-situ TEM study of the formation and annealing of the damage resulting from single ion impacts in crystalline silicon.

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Submitted in partial fulfilment of the requirements of the degree of Doctor of Philosophy, January 2007.
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ACKNOWLEDGEMENTS

There are many people that I would like to thank and acknowledge for their contribution towards this PhD. Firstly, I must thank my supervisor Prof. Steve Donnelly for his continued help and support throughout this thesis especially during the time I spent writing.

I would also like to express my thanks to all the people that helped me during my extended period spent at Argonne National Laboratory, USA. These include Dr Bob Birtcher, whom I thank for making my visit possible and for the long discussions we had, Ed Ryan for his assistance and teachings in the fine art of the Hitachi TEM, Pete Baldo without whom the irradiations would not have happened, Bernie Kestel for his invaluable experience in sample preparation (jet thinning), and finally Becky Videtic who helped me sort through various forms and other paperwork during my stay at Argonne. My time at Argonne was truly a life changing experience.

A number of PhD students at Salford University also need thanking, it has been an honour sharing an office with them. In particular I must thank Kerry Abrams, Amy Gandy, Jonathan Hinks and Matthew Werner, without whom I would certainly have not had as much fun as I have had. Many thanks also go to Duncan Riley, my coffee-drinking partner and the person responsible for collaboration on writing the computer code described in this thesis.

I must also thank friends and family for many things including their continued encouragement and for pretending to be interested in the finer details of ion implantation and electron microscopy. Thank you all Mum, Dad, Colin Fearon, Mike Pinder, Andy “Moonhead” Rain, Andy Mooney and Andy “Reggie” Reed –
thank you all for putting up with my extended periods of absence during my time in
the USA and my self-imposed exile that followed.

Finally, I would like to thank Mary – she knows why.
ABBREVIATIONS

a  lattice parameter
\(a-c\)  amorphous-crystalline
ANL  Argonne National Laboratory
a-Si  amorphous silicon
CRN  continuous random network
c-Si  crystalline silicon
\(d-c\)  damage-crystalline
\(\Delta a\)  lattice parameter deviation
DLTS  deep level transient spectroscopy
DSC  differential scanning calorimetry
E  energy
\(E_a\)  activation energy
\(E_d\)  displacement energy
\(E_f\)  fermi energy
\(E_g\)  band gap energy
EPR  electron paramagnetic resonance
HREM  high resolution transmission electron microscope
I  interstitial
IR  infra-red
IV  interstitial-vacancy
IVEM  intermediate voltage electron microscope
JEMS  java electron microscope simulator
k  Boltzmann's constant
k-MC  kinetic Monte Carlo
LVM  local vibrational modes
MC  Monte Carlo
MD  molecular dynamics
MEIS  medium energy ion scattering
\(N_d\)  number of displaced atoms
\(\phi\)  ion fluence
\(R_0\)  initial radius of damage cylinder
ROI  Region of interest
rpdf  radial pair distribution function
RBS  Rutherford backscattering
\(R_p\)  projected range
SACT  small angle cleavage technique
SEM  scanning electron microscope
SIMS  secondary ion mass spectroscopy
SPEG  solid phase epitaxial growth
T  temperature
<table>
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<tr>
<td>TB</td>
<td>tight binding</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope (&amp; microscopy)</td>
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<tr>
<td>V</td>
<td>vacancy</td>
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ABSTRACT

The work presented in this thesis describes both the thermal annealing of damage created in silicon due to low fluence ion implantation and the accumulation of that damage (to full amorphousness) at higher fluences. The technique utilised was *in situ* transmission electron microscopy (TEM). This technique allowed the entire life cycle of spatially isolated damage zones, generated at low fluence (~$1 \times 10^{11}$ ions cm$^{-2}$), to be followed and also enabled electron diffraction measurements on the build-up of damage levels (with increasing ion fluence) to be measured.

It is shown that, regardless of the implant species or energy, the spatially isolated damage regions thermally anneal over a wide range of temperatures from 50 to 500 ºC, regardless of the initial size of the damage volume – a very different behaviour from that of a planar amorphous-crystalline ($a$-$c$) interface. This indicates that the damage recovery process is different from the re-crystallization of the planar $a$-$c$ interface in that it cannot be assigned a single activation energy.

The ion beam induced amorphization at room and low temperature (50 K) has also been studied through *in situ* electron diffraction measurements and these results have been compared to a new numerical model. The results show reasonable agreement for the case of the low temperature irradiations. This indicates that the amorphization of silicon due to ion irradiation is not truly heterogeneous for both low and high mass ions (Si – 28 amu and Xe – 131 amu respectively) and all irradiations required a multiple overlapping of the damage zones in order to produce amorphous material.

The results from both sets of experiments lead to the conclusion that the zones produced within the collision cascade volume of the energetic ion are not
generally amorphous as previously thought. Through the work performed in the annealing experiments, one possible defect that may be formed during the implantation is the IV pair, and various forms and configurations of this defect in the zone provide a self-consistent explanation for almost all the experimental observations.
Introduction
Chapter 1: Introduction

1.1 BACKGROUND

The development of solid-state electronics followed the necessity to solve problems and this began, on one occasion, prior to the 1890 US census [1]. It was predicted that the 1890 census would take 10 years to condense and correlate through manual tabulation and that this length of time was unacceptable. As a result, the US census Bureau sponsored a contest to find a new method of processing all the census data. The winner was a mechanical tabulating machine devised by Herman Hollerith [1] that was capable of analysing the census data within six weeks.

This machine was a mechanical system driven by an electrical motor that introduced the punch card. As a result of this success, Hollerith went on to form the Tabulating Machine Company that eventually became the International Business Machine Corporation (IBM). This tabulating machine was one of the earliest computers and the technology of the computer continued to evolve during the 1930s through the use of electromechanical switches in computers.

Further development continued throughout World War II in which intelligent and fast machines were required to help crack secret codes. One of the machines developed during this time was the world’s first electronic computer, the Electronic Numeric Integrator and Calculator, ENIAC.

The ENIAC could not be farther from the modern computer in its design. It occupied around 3000 ft², weighed approximately 50 tons, generated a large amount of heat, required the services of a small power station, and came at a cost of around $400,000 (in 1940 dollars) [1]. To operate properly, ENIAC needed some 19,000 vacuum tubes along with thousands of resistors and capacitors. Although seemingly
crude in design, the construction of ENIAC led to the birth of the electronic era and the eventual launch of the information age in the 1970s.

There have been many inventions in the time since ENIAC leading to the laptop computers of today. A measure of this progress was the duplication in the mid 1970s of the entire ENIAC system onto a piece of silicon measuring 2.42 cm² that required less power than a light bulb and cost less than $20.

Probably the most important event in this transition from large machines that occupied large volumes to modern day compact computers was the invention of the solid-state transistor. Before the development of the transistor, the primary electronic device was the vacuum tube. A vacuum tube consists of three elements: two electrodes separated by a grid in a glass enclosure as is shown schematically in figure 1.1. Inside the glass enclosure is a vacuum, required to prevent burnout of the elements and to allow easy transfer of the electrons.

Vacuum tubes perform two important electrical functions, switching and amplification. Switching is the ability of a device to turn a current on or off whilst amplification is the ability of a device to receive a small signal (or current) and increase it while retaining the electrical characteristics. The use of vacuum tubes does, however, have several drawbacks. They are bulky, prone to loose connections and vacuum leaks, and fragile. They also require large amounts of power to operate and their elements deteriorate rapidly. Because of these limitations, tube-based computers were susceptible to limited operation times.

These limitations led to many research programs to seek out a replacement for the vacuum tube. On 23rd December 1947 at Bell Research Laboratories, three scientists demonstrated an electrical amplifier made from the semiconducting material germanium.
This device offered the same electrical functions of a vacuum tube, but with the advantages of the solid-state: no vacuum requirements (during operation), small in size, light in weight, low power requirements, and long lifetimes. Although first named the transfer resistor, the new device became known as the transistor.

The three scientists that developed the transistor, John Bardeen, Walter Brattain and William Shockley were awarded the 1956 Nobel Prize for physics “for their researches on semiconductors and their discovery of the transistor effect” [3], and figure 1.2 shows an image of their first transistor. During their Nobel Prize ceremony, one of the prize committee members, Professor E G Rudberg, included in his speech this quote [4] which in retrospect seems even more apt than it did on the day of their receiving the award:

“The summit of Everest was reached by a small party of ardent climbers. Working from an advance base, they succeeded. More than a generation of mountaineers had toiled to establish that base. Your assault on the semiconductor problem was likewise launched from a high-
altitude camp, contributed by many scientists. Yours, too, was a supreme effort - of foresight, ingenuity and perseverance, exercised individually and as a team. Surely, supreme joy befalls the man to whom those breathtaking vistas from the summit unfold. You must have felt it, overwhelmingly. This joy is now shared by those who laboured at the base. Shared, too, is the challenge of untrodden territory, now seen for the first time, calling for a new scientific attack.”

Of course, nowadays we can see that the development of the transistor was another “advanced base” from which many more summits have been reached.

The announcement in 1947 of the first solid-state transistor started the solid-state electronics age and the electronics industry. The electronics industry is divided into two parts, the semiconductor industry and the electronics industry. The semiconductor industry includes the making of solid-state devices and circuits using the manufacturing process of wafer fabrication.

By the early 1950s, the semiconductor industry was in full swing supply devices for transistor radios and transistor-based computers.

In this embryonic stage of the industry, discrete devices were produced in the form of separate transistors, diodes, resistors and capacitors. The term discrete device is used because there is only one device produced on each separate chip. The dominance of discrete devices came to an end in 1959 when a complete circuit was formed on a single piece of germanium.
This device comprised five components of transistors, diodes and capacitors and used the natural resistance of the germanium as the circuit resistor. This was the first successful integration of a complete circuit in and on the same piece of semiconducting material and this arrangement is better known today as an integrated circuit.

Since the development of the integrated circuit, the number of devices in a single circuit has continued to increase each year. In 1965 Gordon Moore, one of the founders of Intel, commented in Electronics Magazine [6] that the number of transistors on a chip would double every 12 months. This was revised in 1975 by Moore himself to the number of transistors would double every two years [7]. Today Moore’s law, as it is now more commonly know, is the industry benchmark for progress.

The semiconductor industry keeps track of the integration levels of these circuits through a scale ranging from small-scale integration up to ultra-large-scale
integration. Table 1.1 shows the number of components per chip in this integration scale.

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<th>Level</th>
<th>Abbreviation</th>
<th>Components per Chip</th>
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<tr>
<td>Small scale integration</td>
<td>SSI</td>
<td>2 – 50</td>
</tr>
<tr>
<td>Medium scale integration</td>
<td>MSI</td>
<td>50 – 5000</td>
</tr>
<tr>
<td>Large scale integration</td>
<td>LSI</td>
<td>5000 – 100000</td>
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<td>Very large scale integration</td>
<td>VLSI</td>
<td>100000 – 1000000</td>
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<tr>
<td>Ultra large scale integration</td>
<td>ULSI</td>
<td>&gt; 1000000</td>
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In order to generate integrated chips, there are four basic stages of manufacturing that must be performed: material preparation, crystal growth and wafer preparation, wafer fabrication, and packaging.

During material preparation, the raw semiconducting material is mined and purified up to semiconductor device standards. This material is then used in the crystal growth stage where, in the Czochralski process (the other typical growth process used in semiconductor wafer preparation is the float-zone process), the material is melted down in a crucible. At this stage dopant impurity atoms may be added to dope the material and influence the electrical resistivity of the final wafer. A seed crystal of a known crystallographic orientation is then dipped into the molten semiconductor material. The seed crystal is then carefully rotated and slowly pulled out in a very controlled manner to produce a single crystal, cylindrical ingot, from the melt. Using this technique, ingots of silicon (the main semiconductor material used in IC manufacture today) can be produced that are up to 400 mm in diameter and 1 to 2 m in length.
These ingots are then sliced and polished, either single side polished or double side polished, to form the final semiconductor wafer ready for the fabrication stage.

The fabrication stage is the stage where the integrated circuits are formed on the wafer surface. Up to several thousand identical devices may be formed on each wafer. The area on the wafer that is occupied by the device is called a chip or die.

During the fabrication stage, a wafer must undergo many processing steps – sometimes upwards of 100 steps. These steps include masking etching, doping and annealing of the wafers. These steps are performed for the purposes of generating
regions of differing conductivity on the wafer which in turn generate the desired electrical properties of the device. This is done through ion implantation where the dopant species are directed onto the wafer as a beam of energetic ions through a mask or aperture in a highly controlled and reproducible manner. Ion implantation is thus an indispensable tool in the microelectronic industry. As an unavoidable consequence, damage is formed around the ion tracks within the crystal that accumulates over the period of the implantation and, at the fluences required for device fabrication, may result in an amorphous layer in the crystal.

The amorphous phase in a semiconductor device is generally undesirable and its removal requires the extra processing step during the fabrication stage of thermal annealing. This step is required in order to allow the crystal to regain its periodicity and to activate electrically the implanted dopants by allowing them to reside on substitutional lattice sites. Thermal annealing, or re-growth, occurs in silicon, at an appreciable rate, at temperatures of 550 °C and above by solid phase epitaxial growth (SPEG). Crystallization by SPEG occurs through layer-by-layer re-growth at the amorphous-crystalline \((a-c)\) interface where atoms on the amorphous side of the interface use the crystal as a template to re-order themselves into the lowest energy configuration. This repeats through the layers until single crystal remains.

After wafer fabrication, the chips are complete but untested. Each individual chip is then electrically tested to ensure that it meets the specifications. The final stage in IC manufacture is packaging. Packaging is a series of processes that separates the wafer into individual chips and places them into protective packages. The chip package is necessary to protect the chip from contamination and abuse and to provide a durable and substantial electrical contact system which will connect the
chip onto a printed circuit board or directly into an electronic product, for example a memory card used in modern digital cameras.

Knowledge of the formation and removal of basic defects resulting from ion implantation, during the fabrication stage, is necessary in order to improve the models that are used in IC manufacture. This is an ongoing process even today, nearly 60 years after the development of the first transistor, and the importance is shown from this quote from the International Technology Roadmap for Semiconductors [10]:

“... more detailed understanding of implant damage, amorphization and subsequent re-crystallization is important, as these phenomena can critically affect dopant profiles ... extensive research and model development needs to be started immediately to develop improved models for damage creation and annealing, and for temperature dependent implantation”.

The main focus of the work presented in this thesis is the formation of damage during ion implantation and its subsequent removal.
1.2 Work Presented in this Thesis

This thesis explores both the annealing characteristics of very low fluence ion irradiated silicon and the accumulation of damage during ion irradiation. Chapter 2 will give a review of the subject of damage accumulation and thermal re-growth in silicon with chapter 3 detailing the experimental techniques that have been used in this study to explain them. Chapters 4 and 5 give the results of the experiments on the annealing of spatially isolated zones and the ion beam induced amorphization, respectively, and are outlined in more detail below.

1.2.1 Annealing of Spatially Isolated Zones

During ion implantation an amorphous layer is formed at fluences used in device fabrication and this layer can be removed through thermal annealing that is characterised with a well defined activation energy of 2.7 eV [11]. It has been shown that during low fluence irradiation (~\(10^{12} \text{ ions cm}^{-2}\)), the spatially isolated damage zones that are created do not anneal with such a well defined activation energy – in fact they anneal over an extremely wide range of temperatures, from 50 to 500 °C.

In chapter 4, the results of thermal annealing experiments will be reported. In these experiments, ions were implanted at low fluence \emph{in situ} in the transmission electron microscope (TEM) and then subjected to either isochronal or dynamic thermal annealing. Images were recorded onto both film negatives and to videotape.

A major and significant conclusion of the work presented is that the results show that the zones that are visible in the TEM are not necessarily amorphous as previously stated in literature, see for example [12], but zones containing various
concentrations of damage. TEM image simulation has also been utilised to show that zones with varying concentrations of defects do show the same form of contrast as seen in the experiments. By the end of the chapter, it will be contended that the defect mediating the re-growth of the damage zones is the IV pair. Through various concentrations and configurations of this defect, all the annealing characteristics can be explained, including the anomalous zone growth that occurs in approximately 10% of all the zones observed.

1.2.2 Ion-beam Induced Amorphization

At high fluence (~$10^{14}$ ions cm$^{-2}$) ion irradiation, a planar amorphous layer may be formed within crystalline silicon. The manner in which this amorphous layer is produced is the subject of chapter 5. The amorphization is thought to occur through one of three mechanisms: heterogeneous nucleation, homogeneous nucleation or through a nucleation limited process.

In this chapter, a damage accumulation model based on Monte Carlo (MC) methods is created and implemented through Fortran 90 computer code. The results of this are then compared to experimental results obtained through in situ TEM measurements. From these results, it is seen that the amorphization is neither homogeneous nor heterogeneous but occurs through an overlapping of the collision cascades.
Chapter 1: Introduction

1.3 REFERENCES

2 Background & Literature Review
2.1 INTRODUCTION

The invention of the transistor in the late 1940’s by Bardeen, Brattain and Shockley spurred extensive and intense research which has developed over time into the ever increasing semiconductor industry as we know it today. The main semiconducting material used in the industry is silicon, used for its high purity, thermal characteristics and stable surface oxide.

Silicon is found largely as oxides such as silica, quartz, rock crystal, amethyst, flint and jasper to name but a few. The silicon must then be isolated before single crystal growth can occur and subsequent doping is used to form the final microelectronic device.

One of the most common methods of doping is ion implantation. Although this method has advantages in that the dopant concentration and the depth at which the dopant atoms are implanted can be closely controlled, the major disadvantage is the introduction of lattice damage that must generally be removed for electrical activation of the device.

The damage that may be introduced into the lattice as a result of the ion implantation may take the form of simple point defects such as isolated vacancies and interstitials, through the dimers of these point defects to small vacancy and interstitial clusters up to completely amorphous, spatially isolated, zones.

In this chapter, silicon as a material, the technique of ion implantation, and the inevitable introduction of radiation damage and its subsequent removal by annealing will all be discussed.
2.2 **Silicon**

Si is a member of group IV in the periodic table. Group IV elements along with group III-V, group II-VI, and $^{1}$A$^{11}$B$^{14}$C$_2$ compounds have electrical properties that have allowed these materials to be utilised in electronic device technologies that have been developed over the past 50 – 60 years. It must be stated at this point that Si is the dominant semiconductor material in use today.

The main reason for silicon’s dominance in the semiconductor market is the formation of its native oxide, SiO$_2$ and this oxide’s use as the primary gate dielectric material in integrated circuits. Due to this prevalence of silicon, much work has been performed on the physical and electronic properties of Si in both its crystalline and its amorphous phases.

### 2.2.1 Crystalline Silicon

In a crystal, atoms are arranged in a periodic array with the exact geometry depending on the way in which the outer-shell electrons bond together. A characteristic of a crystal is the existence of long-range order. At normal pressures, silicon crystallises into the diamond-like structure, with an fcc Bravais lattice and a two-atom basis set [1]. The orientation of the silicon crystal can be described by three Miller indices that determine the direction of some plane or vector within the lattice. Figure 2.2 shows the three lowest order indexes of silicon. The bonding between the Si atoms is purely covalent with each atom being tetrahedrally coordinated and the valence electrons occupying the $sp^3$ hybrid orbitals resulting in a typical bond angle between two adjacent bonds of 109.47º at 300 K.
The unit cell for Si has a characteristic lattice constant, $a$, of 5.431 Å [1, 2] and contains 8 atoms and each atom has four nearest neighbours separated by a distance of $\frac{\sqrt{3}}{4}a$ equating to a bond length of 2.35 Å and a next nearest neighbour distance of 3.84 Å [3] at standard temperatures and pressures. The density of silicon is, for standard temperature and pressure, 2.329 g cm$^{-3}$ [4], which equates to $5.032 \times 10^{22}$ atoms cm$^{-3}$. 
2.2.1.1 Intrinsic Silicon

Intrinsic silicon is pure undoped silicon (except for the unwanted impurities introduced during the growth of the crystal). At finite temperatures, the valence and conduction bands are separated by a band-gap, $E_g$, which can be seen in figure 2.3. The figure shows that the maximum energy in the valence band and the minimum energy of the conduction band do not lie in the same direction (figure 2.3b) and hence silicon is an indirect band gap semiconductor. The band-gap energy is $\sim 1.17$ eV.

In order for intrinsic silicon to behave like a conductor, thermal energy must be introduced to the system to a point where some electrons are thermally excited from the valence band into the conduction band, at the same time leaving behind positively charged electron “holes” in the valence band. When an electric field is applied, the holes move acting as positive charge carriers. If an electric current is applied across the semiconductor, the electrons and holes will gain kinetic energy and a current will flow.

The probability of finding an electron at a given energy, $E$, is given by the Fermi-Dirac distribution

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)}$$  \hspace{1cm} (2.1)

where $k$ is Boltzmann’s constant and $T$ is the temperature in Kelvin. The Fermi energy, $E_f$, is defined as the energy at which the probability of finding an electron with that energy is 50%. A graph of the Fermi-Dirac distribution at different temperatures is shown in figure 2.4.
The equation given in 2.1 is a probability distribution function and is shown graphically in figure 2.4 for three different temperatures. At T=0 K the valence band is filled, the conduction band is empty and these bands are distinguishable from one another through a small energy gap between the top of the valence band and the bottom of the conduction band. At finite temperatures, the possibility of an electron being thermally “promoted” from the valence band into the conduction band increases (as shown in figure 2.4).

**2.2.1.2 Extrinsic Silicon**

In an intrinsic semiconductor, there are no dopant atoms in the crystal and the charge carriers are created thermally. It is also possible to add foreign atoms as dopants into the lattice. When the charge carrier concentration due to doping is greater than the thermally induced charge carrier concentration, the material becomes an extrinsic semiconductor.
Figure 2.4: Graph of the distribution of electron energies for different temperatures as determined by the Fermi-Dirac Equation.

The electrical conductivity of the crystal can be varied through carefully altering the dopant concentration in the semiconductor. Through doping with different atoms, an extrinsic semiconductor may become either $p$-type (the charge carriers are positively charged holes), or $n$-type (the charge carriers are negatively charged electrons). Indeed, in semiconductors where these two forms of extrinsic material meet, junctions are produced that form the basis of most semiconductor devices.

Atoms that are used to dope the semiconductor usually come from groups III or V from the periodic table. A group V atom will have five valence electrons available to bond with the atoms in the host matrix, four of which will bond covalently with the Si atoms in the surrounding matrix. The fifth remaining electron will have an energy lying within the band-gap just underneath the conduction band. When doped to the extent used in integrated circuit device manufacture, this has the
effect of shifting the Fermi level closer to the conduction band. For dopant atoms from group III, the opposite is the case with the Fermi level being shifted towards the valence band.

### 2.2.2 Amorphous Silicon

Crystalline silicon (c-Si) maintains long-range order and its characteristic six-membered rings, as seen for the (110) orientation shown in figure 2.2 above. a-Si loses its long-range order by distortions of the ideal tetrahedral bond angle. Amorphous silicon (a-Si) also incorporates five-, seven- and eight-membered rings mixed with the six-membered rings of the perfect crystal. X-ray diffraction studies on amorphous silicon [6, 7] have shown that the first peak at $r = 2.35$ Å, indicated in figure 2.5 has a peak height of 3.8 signifying that a-Si has nearly complete four-fold co-ordination. The existence of medium-range order in the amorphous phase has also been suggested through fluctuation electron microscopy experiments by Volyes et al and Gibson et al [8, 9].

One of the first comprehensive descriptions of the atomic arrangements in amorphous structures was developed by Zachariasen in 1932 [10] and this model is now better known as the continuous random network (CRN) model. In this model, the atoms forming the amorphous structure are held together by forces similar to those as in periodic crystals. As is the case with crystals, these forces ensure that each individual atom in the amorphous material oscillates about an individual, definitive equilibrium position.

In a crystal, the atomic positions of the component elements can be well described by the formation of a unit cell containing a small number of atoms.
Through the use of this unit cell, an atom several thousands of atomic planes away from a given origin may be described and located easily.

![Figure 2.5: X-ray diffraction results showing the most probable bond length is 2.35 Å and that amorphous silicon has almost four-fold symmetry [11].](image)

This is not true for the case of amorphous materials. Here the amorphous phase may be described as an infinitely large unit cell containing an infinite number of atoms that form an extended network that lacks both periodicity and symmetry.

The structure of $a$-Si produced by ion implantation is known to be modified by low temperature processes below the crystallisation temperature. This modification of the amorphous phase produces a relaxed form of $a$-Si. This relaxation has also been linked to both short range ordering and the annihilation of defects in the amorphous lattice [12-14].

Both the relaxed and unrelaxed phases of $a$-Si have identical densities, within experimental error [15]. Following this, since there is no measurable density difference between as-implanted and partially annealed wafers (by partially annealed it is meant that the substrate has not begun to fully recrystallize) this implies that the relaxation occurs without significant volume changes.
In addition, $a$-Si has been found to contain defects that do not have four-fold coordination for example dangling bonds and localised variations in the atomic density.
2.3 **ION IMPLANTATION AND ATOMIC COLLISIONS**

Ion implanters are machines in which ions of specific isotopes of elements can be selected and then accelerated towards a target material. An advantage of this is that implantation can be controlled easily and accurately by varying conditions such as ion energy, implantation angle and target orientation. By selection of these implantation conditions the introduction of the various dopant atoms can be carefully controlled and complex electronic devices may be formed.

Knowledge of the interaction of the energetic ions with the atoms of the crystalline target is of fundamental importance for understanding the behaviour of the dopant atoms and is extremely important for the prediction of the processing steps involved in the device manufacture. In this section, a simple review of the interaction between ions and solids will be given.

Much of the theory of particle-solid interactions began with the work of Bohr [16, 17]. He theorised that as an energetic particle is introduced into the solid, the particle interacts and collides with the lattice atoms. This is due to the complex forces resulting from the interaction between the two nuclei and between the two electron clouds and in the attraction between the nuclei and the electrons. As the particle (an ion in all cases described throughout this thesis) travels through the lattice, it loses its energy as a result of these interactions. This may occur through collisions of the nuclei (nuclear) or through energy loss to the electron clouds of the target atoms (electronic). In the keV energy range the former mechanism is predominant for heavy ions whereas the latter is the dominant mechanism for lighter ions. As a general rule, if the energy of the ion in keV is greater than the atomic mass, the energy loss via the binary collisions of the atomic nuclei dominates and
where the energy of the ion is less than the atomic mass, the energy loss mechanism through electron cloud interaction dominates [18].

Over the years, with a greater understanding of the interaction between the particle and the solid and with the advent of the digital microcomputer, computer codes have been written to calculate some of the processes that occur through the implantation process. These codes utilise the ability of computers to handle and manipulate large amounts of data to predict, with a good accuracy, the results of the ion implantation. Probably the most popular code is TRIM [19], but other ion implantation software packages are available such as SUSPRE [20] and MARLOWE [21].

### 2.3.1 Inelastic energy loss/Electronic stopping

During the process of ion implantation, the energetic ion passes through the target material. The slowing down of the ion by electronic energy loss is a result of the inelastic collisions between the electron clouds of the target atoms and the ion moving through it [22]. As the ion passes by, the electrons of the target atom will be slightly perturbed exciting the electrons of the atoms involved. In cases where the kinetic energy transfer to the electron in the solid is greater than the ionization energy of the electrons bound to the ion, the inelastic collision may cause the stripping of electrons from the ion.

These mechanisms of electron excitation and ionization lead to energy absorption within the system which may not, generally, be restored to either the kinetic or potential energy of the system resulting in inelastic energy loss. The variation of the electronic stopping power with ion energy is shown in figure 2.6 with the maximum electronic stopping power occurring at approximately 100 keV/amu.
2.3.2 Elastic energy loss/Nuclear stopping

Inelastic energy loss is the predominant energy loss mechanism for light ions (at medium to high energies) in the initial early part of the ion’s range i.e. before significant energy loss has occurred. For heavy ions and light ions at low energies, elastic energy loss (nuclear collisions) begins to predominate. The simplest approach to describe nuclear collisions is to treat the interaction between ion and target atom as a simple binary collision, i.e. a moving energetic ion (or primary knock-on atom) and a stationary target atom with no external perturbations. The primary knock-on atom here is defined as an atom displaced through a direct collision with the bombarding ion [23]. This is a valid assumption, providing that the mean free path is significantly larger than the interatomic spacing, considering the limited range of interaction of the two nuclei.

In a study of defects generated as a result of the ion implantation process, the nuclear-collision energy-loss mechanism is the more important energy-loss mechanism (except at very high energies) as through nuclear collisions, the energetic ion may impart enough energy to the lattice atom to remove it from its lattice site. The energy required for this to occur is known as the displacement energy, $E_{d}$, and for silicon has an average value of 15 eV [24]. If the incident ion imparts an energy less than this value, the target atom will not permanently leave its lattice site. If the energy transferred to the lattice atom is equal to the displacement energy, the target atom will then be removed from its lattice site and may then collide head on with another target atom passing its energy onto that atom displacing the second atom from its lattice site with the first atom replacing it on the lattice. This is known as a replacement collision.
Figure 2.6: The electronic and nuclear contribution to the stopping power as a function of reduced ion energy (reproduced from [18]).

If the energy passed to the target atom by the ion is greater than the displacement energy, the lattice atom may be removed from its lattice site and become permanently dislodged and come to rest at a non-lattice site becoming an interstitial type defect. At the original lattice atom position, a vacancy will be left. Thus, a vacancy-interstitial defect pair, or Frenkel pair, is created from a single displacement, although there is a statistical probability that the Frenkel pair may recombine. If this displaced atom has enough energy, it will go on to become a secondary projectile, a primary knock-on atom, and create more damage within the lattice through a series of more displacements thus losing energy, through electronic and nuclear interactions of its own, until it finally comes to rest.

2.3.3 Kinchin-Pease Model

Early in the development of models for radiation damage in materials, Kinchin and Pease [23] theorised that the damage created by radiation was proportional to the energy deposited into the lattice through nuclear collisions. In the case of ion implantation, they assumed hard sphere collisions were the dominant collisions creating the damage. Using this simple theory, it is possible to determine
the number of atoms, \( N_d \), that would be displaced in the collision cascade as the ion comes to rest. In the low energy portion of the cascade, the regime where the nuclear stopping is dominant, the number of displacements created by an implanted ion is given by the modified Kinchin-Pease equation [25]

\[
N_d = 0.4 \frac{E}{E_d}
\]  

(2.2)

where \( E \) is the implanted ion energy and \( E_d \) is the displacement energy of the target material. The constant of 0.4 accounts for the electronic energy loss that occurs during the implantation.

The distribution of the damage generated as a result of each individual collision cascade is highly dependent on the mass of the implanted ion [26]. Molecular dynamic (MD) simulations [24] have shown that the damage resulting from low mass ion implantation consists primarily of isolated Frenkel defects and small clusters within the collision cascade. High mass ion implantation results in large defect clusters and amorphous pockets, according to the authors [24]. This is shown in figure 2.7 for B and As ions having the same energy deposition and the different damage morphology of the cascade is clearly visible. As stated earlier, the nuclear stopping power of heavy ions is much greater than that of light ions in any lattice for the medium energy range used in this thesis.

During heavy ion implantation, the ion expends much of its energy into primary recoils which can then in turn create further displacements. Because of this, much of the damage created by heavy ions will be denser and over a much shorter depth range than that of damage created by light ions of the same energy. The
damage created by progressively heavier ions becomes denser and more complex [27].

2.3.4 Ion Ranges

As stated previously, energetic ions will lose their energy through a series of elastic collisions or inelastic interactions with the atoms of the lattice. Due to the statistical nature of the energy loss mechanisms, the final depth at which the implanted ions will come to rest will have a Gaussian-type profile centred about a certain range called the projected range $R_p$. Figure 2.8 shows a schematic diagram of the projected range. A sample distribution is shown in figure 2.9 for both a Xe and Si implantation into Si as result of a TRIM calculation. The profile of the implantation may be described more fully using the projected range, the straggling (distribution of the implanted ions about the projected range), the skewness (the asymmetry of the distribution) and the kurtosis (the distortion of the Gaussian distribution peak).

2.3.5 Ion Channelling

In a single-crystal solid, there may be large open channels [28]. If an ion, or any other energetic particle, is incident along a major crystallographic direction, it may undergo a series of small angle deflections and the ion is said to be steered or channelled [18]. In the case of silicon, the $<110>$ direction is a particularly large and open axis. If ions incident along one of these open channel axes it is very possible for a small fraction of the implanted ions to be channelled and the ion will come to rest at a considerably greater depth than predicted by models that do not include this effect.
Figure 2.7: Morphology of the damage created by different ion implantations as obtained from MD simulations for a) a 3 keV B ion and b) a 2 keV As ion. Both these implantations have the same energy deposition into the lattice (1.3 keV). The atoms displayed have a potential energy of 0.2 eV or greater than the other atoms in the crystal. It can clearly be seen that the B implantation creates mainly isolated Frenkel pairs and small clusters whereas the As implantation contains much more complex damage. From ref: [24].

Figure 2.8: Schematic diagram of the possible path lengths for an implanted ion in Si. It is possible for ions to be implanted deeply into the crystal, or to not penetrate deeply at all. The most likely depth to which the ion will be implanted is known as the projected range. The straggling (the distribution of the implanted atoms about the projected range) can also be seen in this diagram.
Figure 2.9: Results from TRIM [19] calculations showing ion trajectories for 100keV Si (a) and 400keV Xe (b), along with their implant profile for the Si implant (c) and the Xe implant (d). Also included in the profile graphs are the data for the projected range, straggle and kurtosis.

The effect of channelling may contribute to differences in the projected range and will be discussed next. Figure 2.10 shows three crystal orientations that have non-channelling and channelling possibilities. This is unwanted in device manufacture as the profiles of the implanted ion can be altered quite significantly therefore changing the predicted device characteristics upon electrical activation. Channelling may be avoided by tilting and azimuthally rotating the wafer during the implantation; by use of a pre-amorphizing implant of Si or an inert ion such as Xe; by implantation through a screen oxide which is a naturally amorphous surface oxide; or through self-amorphization by using, say, As to a high dose. Not all of the effects of ion channelling are unwanted.
Through analytical techniques such as Rutherford Backscattering (RBS) and Medium Energy Ion Scattering (MEIS), light ions are intentionally channelled in order to study damaged layers [30, 31].

2.3.6 Simulation of Ion Implantation using TRIM

Several computer simulation codes have been developed to predict certain outcomes such as ion range and number of vacancies produced during the process of ion implantation. Some of the more popular simulation codes are SRIM [19], SUSPRE [20] and MARLOWE [21]. Of these, SRIM is the most popularly used simulation code. SRIM is in fact a group of programs that calculate the stopping and range of the energetic ions in matter using a fit to a full quantum mechanical treatment of the ion-atom collisions. The most comprehensive of these programs is TRIM (TRansport of Ions in Matter). TRIM has been widely used to simulate the effects of ion implantation and has been used to compare experiment to theory especially in the case for depth profiles [30].
The interaction of energetic ions with solids is heavily statistical and for this reason TRIM uses Monte Carlo methods and a binary collision algorithm to simulate the ion trajectories of many energetic ions. In order to accurately simulate the implantation, many different variables can be altered with the TRIM program. This includes the ion mass, energy and angle of incidence; along with the target details which include the elements that form the target, the target density and the displacement energies. As well as single element targets, TRIM is capable of handling complex targets of compound materials and even includes a compound database within its program.

With a suitably high number of simulated ions injected into the target, TRIM will calculate the final three-dimensional distribution of the implanted ions as well as the phenomena of the ions’ energy loss, including target damage, sputtering, ionisation and phonon production. Some simple results of a TRIM simulation for Xe and Si implants into Si have been shown earlier in figure 2.9. Predicting the actual nature of the final damage configuration created during ion implantation is a much more difficult problem due to thermally activated processes not included in TRIM.
2.4 DEFECTS

Defects have a very strong influence on the structural and electrical performance of a semiconductor, generally being detrimental to the performance of the device.

To understand at an atomistic level the amorphization and re-crystallization processes, it is necessary to identify and understand the defects that may act as nucleation sites for the amorphous phase or as defects that induce re-crystallization. It is thought by some authors [32-35], that the re-crystallization occurring at the $a$-$c$ interface arises as a result of the formation and motion of defects generated at or nearby the interface. It has also been suggested [36, 37] that the breaking of bonds and network rearrangement is the responsible mechanism for the recrystallization of $a$-Si. In this section, defects will be discussed from simple defects to more complex defects. Although many forms of complex defects are created through the annealing of planar $a$-$c$ interfaces, they will not be extensively discussed here.

The understanding of the intrinsic defects in silicon represents the first logical step in the understanding of radiation damage in silicon as these are also the primary defects created by the incoming particle [38]. There are two fundamental native intrinsic defects in silicon, the lattice vacancy and the silicon interstitial, both of which are present in the crystal at any finite temperature but may also be produced during the implantation process. In addition, these defects may occur as isolated defects or as complexes with either other defects or impurities. Shown in figure 2.11 are some of the simple point defects that may occur in the silicon lattice.
2.4.1 Vacancy-type Defects

2.4.1.1 Vacancies

A lattice vacancy may occur when an atom leaves its lattice site and the site remains vacant.

Experiments have been performed through high energy electron irradiation at cryogenic temperatures which is the only method found to produce isolated vacancies and interstitials. Through this method of damage generation, the low mass of the electron gives rise to only simple damage since the displaced lattice atom receives little energy just above $E_d$. The cryogenic temperature is required to freeze in the displaced atoms. Point defect generation by electron irradiation also has the advantage that an electron is not an impurity and displacement of the lattice atoms occurs without implantation of additional atoms.

Through electron paramagnetic studies (EPR), the isolated lattice vacancy has been observed in both its single positive ($V^+$) and negative charge state ($V^-$) immediately following cryogenic electron irradiation. Indeed, the silicon lattice vacancy may take on any one of five different charge states ($V^{2+}$, $V^+$, $V^0$, $V^-$, $V^{2-}$)[39].

The charge states of the lattice vacancy arise through the reconfiguration of unsatisfied bonds following the generation of the defect. The dominant charge states for $n$-type, $p$-type and intrinsic silicon are the $V^{2-}$, $V^{2+}$ and $V^0$ respectively.

During 15 min isochronal annealing studies of single, isolated vacancies, peaks in the EPR spectra have disappeared at ~70 K in $n$-type, ~150 K in $p$-type, and ~200 K in intrinsic silicon [40]. This is thought to reflect the dominant charge states of the vacancy defect in the different materials.
Figure 2.11: Schematic diagram of the different simple defects formed in silicon. The defects are: a) a vacancy, b) a di-vacancy, c) an interstitial, d) an interstitialcy, e) an impurity interstitial, f) a substitutional impurity, g) a vacancy-impurity pair, and h) an impurity self-interstitial pair. From ref: [3]. Note the relaxation of the lattice around the defects.

In addition to the isolated vacancy, there may be occurrences where the vacancy is trapped by another defect or impurity atom. Through the trapping of the impurity or defect, the energy levels of the vacancy-defect/impurity are altered within the band-gap in comparison to that of the isolated vacancy. This, in turn, alters the thermal stability of the defects. The stability of the vacancy and several of the first generation vacancy defect pairs is shown in figure 2.12 resulting from ~15 – 30 min isochronal annealing studies [41].

2.4.1.2 Divacancies

Divacancies are produced readily in silicon through either electron or ion irradiation. The divacancy has been readily identified through EPR [42] and has an associated infra-red (IR) 1.8 μm absorption band [43].
Differential scanning calorimetry (DSC) measurements [44] have shown two clear peaks of heat release during a 40 °C min⁻¹ temperature scan, one at 140 °C and the other at 240 °C. This indicates two distinct annealing processes of the divacancy occur.

IR and positron annihilation experiments [45] have suggested that divacancies may be thermally annealed at 150 °C through recombination with mobile interstitials. At this temperature, the divacancy is still immobile. At 250 °C, the divacancies begin to become mobile and start to loosely associate with other divacancies. As the temperature is increased further, to 500 °C or higher, the associated divacancies may begin to agglomerate into larger defects.

### 2.4.1.3 Vacancy Clusters

As stated previously, during ion implantation, a large number of displacements may be produced in a highly localised region. As a result, aggregation of vacancies can occur and is expected to dominate over the interactions with more distant isolated impurity dopants [39]. This is not well understood but can be implied.
through EPR investigations of neutron-irradiated materials [46, 47]. These studies identify various vacancy aggregates.

The tri-vacancy, as with the divacancy, may interact with oxygen in the bulk material having the effect of stabilising the defect complex.

*Ab initio* [48] studies have shown that vacancies may form stable clusters and that as the cluster increases with the addition of one vacancy, the formation energy of the defect increases by 1 to 5 eV. The hexavacancy (V6) is particularly stable.

These vacancy clusters are expected to be the sources of released vacancies during the subsequent annealing at elevated temperatures.

### 2.4.2 Interstitial-type Defects

#### 2.4.2.1 Interstitials

As a lattice vacancy is formed, the lattice atom that is displaced through its formation must come to rest somewhere else in the lattice. If the atom comes to rest at a non-lattice site, it is said to be interstitial. This is the second component of the Frenkel pair. Generally, and especially in the case of ion implantation [38], there is a significant possibility of Frenkel pair annihilation by recombination. An impurity interstitial may also occur when an impurity does not take up a position on a lattice site.

As opposed to the vacancy, there has been little experimental evidence [49] for the existence of the individual interstitial despite irradiation at cryogenic temperatures (4.2 K) in *p*-type silicon. Here, only defects identified as interstitials trapped at impurities are observed. In *n*-type silicon, the defect survival rate is much lower at cryogenic temperatures, hence it is much more difficult to observe the
interstitial. There is evidence, however, that interstitial migration may occur at temperatures of ~150 – 170 K [50] where trapped interstitial configurations are observed. Through experimental evidence, migration energies ranging between 0.12 to 0.57 eV [51-53] have been obtained.

This indicates that the silicon self-interstitial is highly mobile at low temperatures and as such can travel long distance within the lattice until it either recombines with vacancies, reaches a surface, is trapped by impurities or other interstitials, or displaces other atoms from their lattice site [49, 54].

Much of the work done on the silicon self-interstitial has been theoretical due to the inability to observe stable isolated interstitials even at low temperature as previously described. Through these theoretical investigations, it has been determined that there are five different metastable structures for the Si self-interstitial, these being the [110] (X) and [100] (S) split sites, the tetrahedral (T), hexagonal (H) and bond-centred (B) sites [55]. These different structures are shown in figure 2.13. For silicon, the case of the [110] split self-interstitial is the most important structure as this gives the lowest possible energy configuration [56, 57] for the five possible charge states (I^{2+}, I^+, I^0, I^-, and I^{2-}).

Many theoretical investigations give rise to a migration energy for the silicon interstitial of approximately 0.78 eV (see for example [58-62]) – much higher than that found experimentally. Indeed an activation energy for migration of 0.78 eV would mean that the interstitial is immobile at room temperature, contrary to the experimental evidence.

In addition to the isolated interstitial, there may be occurrences where the interstitial is trapped by another defect or impurity atom.
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Figure 2.13: Interstitial configurations in their ideal positions: a) a [110] split interstitial, X, b) a [100] split interstitial, S, c) a tetragonal interstitial, T, d) the hexagonal interstitial, H and e) the bond centred interstitial, B. From [55].

Through the trapping of the impurity or defect, the energy levels of the interstitial-defect/impurity are altered in comparison to that of the isolated interstitial. This, in turn, alters the thermal stability of the defects.

The stability of the interstitial and several of the interstitial defect pairs are shown in figure 2.14 resulting from ~15 – 30 min isochronal annealing [63] as obtained from local vibrational mode (LVM) spectroscopy and by deep level transient spectroscopy (DLTS).
Figure 2.14: Schematic of the annealing stages of interstitial related defects (~15-30 min isochronal). The defects have been identified by DLTS (indirectly), EPR and LVM spectroscopy (directly). From ref: [39].

2.4.2.2 Di-interstitials

Di-interstitials may be formed by either rapid relaxation of the cascade immediately following an ion impact, or through the clustering of self-interstitials during early stages of the annealing process [64]. The di-interstitial has been observed in neutron, proton and ion irradiated silicon by EPR [65, 66] and has the P6 centre associated with this defect.

Three structures of the di-interstitial have been proposed: the so-called L [65], K [67] and C [68] forms although the K and C forms are very similar. Following from EPR experiments, it has been suggested [69] that the K form is not the di-interstitial associated with the P6 EPR centre (although it does have the lowest configuration energy), and that the L form is only metastable.

Various computer simulations (MD and tight-binding) of the di-interstitial have yielded migration energies ranging from 0.18 to 0.7 eV [64, 70-72], indicating that the di-interstitial may be even more mobile than the self-interstitial although a
migration energy of 0.7 eV is too high to allow migration at room temperature. Some \textit{ab initio} simulations \cite{73, 74} have also found indications for a relatively high mobility of the di-interstitial. The experimental evidence for the migration of the di-interstitial leads to the understanding that the activation energy for migration is larger than that of the mono-interstitial.

\subsection*{2.4.2.3 Interstitial Clusters}

During ion implantation, small interstitial clusters are formed during the fast relaxation of the highly disordered region contained within the collision cascade immediately following each ion impact. Another source is the clustering of the self-interstitial diffusing during the first stage of annealing.

Secondary Ion Mass spectroscopy (SIMS) experiments \cite{75} have been performed along with inverse modelling \cite{75} in order to infer the formation energies for clusters of varying size, ranging from 2 interstitials up to clusters containing 250 interstitials. The graph shown in figure 2.15 displays the formation energy as a function of cluster size as determined from these experiments. The strong minima that occur at \( n = 4 \) and 8, where \( n \) is the number of interstitials in the cluster, indicate that these are the most stable forms of clusters.

Molecular dynamics (MD) simulations have demonstrated \cite{64} that the \( n = 3 \) has a high migration energy, and as such does not migrate far in the crystal. Indeed, the migration is so slow that the \( n = 3 \) cluster diffusion is slower than the atomic diffusion. The migration energy of the tri-interstitial was found to be 1.6 eV in this study \cite{64}, but in other theoretical studies has been found to be as low as 0.23 eV \cite{76}.

EPR experiments \cite{69} have shown evidence for the \( n = 3 \) and 4 clusters.
Figure 2.15: Graph showing the formation energies of interstitial clusters as inferred by SIMS analysis and inverse modelling [75]. It can be clearly seen that the $n = 4$ and 8 clusters are easily formed.

The $n = 4$ cluster has been attributed to the B3 EPR centre which has been shown to be stable up to temperatures of 500 ºC.

Although not a great deal is known about interstitial clusters, it is thought that these clusters are the pre-cursors for more complex defects. In particular, the $n = 4$ has been suggested to be the main pre-cursor cluster for the nucleation of $\{113\}$ defects [75].

### 2.4.3 IV Pairs

During the modelling of self-diffusion and interstitial-vacancy recombination in silicon using the tight-binding (TB) simulation technique, Tang et al [77] encountered a new defect that has become know as the interstitial-vacancy (IV) pair. This defect has also been proposed as a possible contender to induce amorphization in Si.
Tang and co-workers found that as a vacancy approaches the X-type structure of the silicon interstitial (see §2.4.2.1 above), instead of an immediate recombination and annihilation, a metastable defect structure is generated.

Since the defect consists of a local rearrangement of bonds within the crystal without introducing an excess or deficit of atoms, the IV pair is also known as a bond defect. The atomic structure of an IV pair is shown in figure 2.16.

In figure 2.16 it can be seen that as a result of introducing an IV pair into the lattice, the five- and seven-membered rings that are characteristic of the amorphous phase are introduced whilst perfect four-fold co-ordination is still maintained.

Following the work of Tang et al using TB techniques, Stock and co-workers [78] modelled the formation of the IV pair through the use of molecular dynamics (MD) simulations. Using these MD techniques, it was observed that the IV pair may not only be generated through incomplete interstitial-vacancy pair recombination, but also through a pure ballistic process. This indicates that the IV pair may be the
primary defect formed by ion implantation and there is no need for the pre-existence of interstitials or vacancies within the lattice for its formation.

Theoretical lifetime studies of the defect performed by Tang et al [77] have showed that the IV pair is a stable defect at room temperature with a lifetime of the order of hours which is in contrast to work on the IV pair by Pelaz et al [35]. Further studies using \textit{ab initio} Hartree-Fock calculations by Cargnoni et al [79] have shown that the IV pair consists of a large nuclear distortion, compensated by a rearrangement of the electron charge. They also confirmed the stability of the defect.

Both the studies by Tang et al [77], and Cargnoni et al [79] discovered that the formation energy of the defect is comparable and even possibly lower than that corresponding to the typical point defects of Si. As a result of this, the equilibrium concentration should be equivalent to or greater than that of other forms of defects.

As yet, the existence of the IV pair has not yet been verified experimentally. This is due to the fact that the defect maintains perfect four-fold co-ordination meaning that there are no unpaired electrons which prevents its detection under typical experiments such as electronic paramagnetic resonance and electron nuclear double resonance. First-principle calculations have also shown that the IV pair hardly disturbs the band structure of the Si making detection by deep level transient spectroscopy impossible [80].

\subsection*{2.4.4 Dangling Bonds}

A dangling bond is a broken covalent bond and is generally found on the surface of most crystalline materials in the absence of any lattice atoms above them. At the surface of a (001) Si crystal, each surface lattice atom would have two
dangling bonds. Because these dangling bonds do not form the lowest energy configuration, the surface atoms tend to adsorb atoms to reduce the surface energy.

2.4.5 Dynamic Annealing

A direct result of the thermally induced migration of vacancies and interstitials is that damage may be removed by the annihilation of vacancies and interstitials during the collision cascade formed by implantation. This is a process known as dynamic annealing and is highly dependent on implant parameters such as the substrate temperature and the rate of defect generation (which, in turn is dependent on factors such as ion mass, ion energy and flux). The dynamic annealing of semiconductors decreases with flux and decreasing target temperature [81-84]. The explanation for the decrease in dynamic annealing with increased flux is that at sufficiently high fluxes the collision cascades produced can begin to overlap with each other before the defects generated within a single cascade are able to anneal. As a result, higher concentrations of stable defects are formed. At lower fluxes where the collision cascades do not overlap, an increase in target temperature leads to an increase in defect migration which in turn corresponds to a high rate of defect annihilation. Indeed it is possible to increase the target temperature to a situation whereby an amorphous layer may not be formed in the substrate depending on the ion species and fluence. As the temperature of the target is lowered, say to liquid nitrogen temperatures, the defect mobility may diminish to a point where the damage is “frozen in” and the dynamic annealing is greatly reduced.
2.4.6 Amorphization by Ion Implantation

During the process of ion implantation, each incoming energetic ion causes damage to the target lattice through the generation of defects as described earlier in this section and in §2.3.

Here we look at the possible processes whereby the concentration of defects introduced to the lattice by the energetic ions reaches a point at which the lattice can be considered to be amorphous and there is no medium to long range order in the structure.

2.4.6.1 Collision Cascades and Spike Phenomena

Through the process of ion implantation, the evolution of individual collision cascades can be divided into three phases: the displacement phase, the thermal spike phase and the relaxation phase. As described previously, as an energetic ion enters a target material it dissipates its energy through a series of nuclear and electronic collisions, and in semiconductors and metals it is the nuclear collisions that produce atomic displacements in the target lattice.

If the energy density remains below a certain value, the interaction between the energetic ion and the substrate may be described as a series of binary collisions involving the ion and the recoiling substrate atoms. This description is more commonly known as a collision cascade. Brinkman first suggested [85] that as the mean free path between the displacing collisions approaches the interatomic spacing of the substrate, the interaction can no longer be regarded as one involving independent binary collisions and this description breaks down.

At the point where the mean free path between the binary collisions approaches the interatomic spacing, a small highly disturbed region forms within
which the mean kinetic energy of the atoms may be up to several eV per atom. This
is known as the energy or displacement spike. After a period of approximately $10^{-11}$
seconds, the initial kinetic energy deposited in the spike may be shared in a relatively
uniform distribution throughout all the atoms enclosed by the spike region. Under
some conditions this may give rise to an effective rise in temperature within the spike
volume that is significantly greater than the temperature necessary to cause melting
of the substrate. As a result, the volume contained by the spike melts forming a
liquid-like distribution of atoms. What follows is a rapid quenching of the volume as
the high temperature is rapidly dissipated throughout the substrate effectively
freezing in the liquid-like distribution. This phase is referred to as the thermal spike.

The concept of the thermal spike has been the subject of much controversy.
This controversy arises from the small sizes and small timescales over which the
thermal spike occurs. The argument against the thermal spike states that the
quenching times may be too short and the cascade dimensions too small for
Maxwell-Boltzmann statistics to apply, necessary to equate a physical temperature to
the region. Although these possible arguments have been raised, work by Donnelly
and Birtcher [86] have clearly proved the existence of thermal spikes through their
work in metals.

Towards the end of the thermal spike phase, the cascade may continue to
relax. The time period over which the cascade continues to relax is much longer than
the time period of the thermal spike. During this relaxation, the Gaussian energy
distribution centred about the cascade volume begins to spread out and defects may
migrate during the time period over which the peak of the temperature distribution
remains above a critical temperature. During this short period of relaxation, it is
possible for defects to interact and agglomerate to form more complex and stable
damage. It is also possible for defects to annihilate each other and cause some recovery of damage.

There is also a considerable difference in the collision cascade formed as a result of heavy ion implantation and a cascade resulting from light ion implantation. The difference occurs due to the different manners in which the heavy, or light, ion deposits its energy into the lattice. Heavy ions will transfer their energy to the lattice atoms with a greater efficiency and, as the mean free path of the heavy ion is short, within a small volume. The light ion will not have an as efficient energy transfer to the lattice atoms and travels over longer distances resulting in larger but perhaps less dense cascades or even sub-cascades. This is shown schematically in figure 2.17.

2.4.6.2 Structure of Damage Zones

During energetic ion implantation into solid targets, collision cascades are formed within the target with the nature of the structure produced being dependent on several factors including ion mass, ion energy and target temperature. MD simulations by Caturla et al [24] have been used in the study of isolated cascade structures for B and As implantations at various implant energies. By varying the mass and the energy of the ion, they were able to compare the cascade structures for ions of different mass but the same $R_p$ or energy density as well as looking at the average total number of vacancies and interstitials and the maximum cluster size formed for each particular implantation. Figures 2.18 and 2.19 show the cascade structures produced in the cases of the same projected range and the same energy density, respectively, for both B and As implants. Also included in the figures is the number of displaced atoms in the clusters as defined as those atoms having a potential energy greater than 0.2 eV above the ground state energy 10 ps after the collision event.
Figure 2.17: Schematic diagram of collision cascades produced by light ion and heavy ions. For the case of the light ion, the predominant energy loss mechanism in the early stages of the cascade is electronic and, hence, few lattice atoms are displaced and there is minimal damage. The atomic displacements occur towards the end of the ion track when nuclear collisions begin to dominate. For heavy ions, nuclear collisions dominate over the entire ion track and numerous displacements occur from both the energetic in and from the primary knock-on atoms.

For the cascades resulting from implantation with ions having the same $R_p$ it can be seen that the As implantation results in large clusters whereas the B cascade results in much smaller clusters. The two-dimensional projection of the same cascades in figure 2.18b showing that while a number of isolated Frenkel pairs and small clusters are observed in the B cascade, large clusters of almost equal numbers of vacancies and interstitials are seen in the As cascade. When we compare the cascade structures of the two implantations where the damage energy is the same in both cases, as shown in figure 2.19, we see drastically different cascade morphology. Here, the As implantation results in two large clusters and a few isolated defects. The B cascade shows no large clusters but many isolated vacancies and interstitials and many small point defect clusters are formed.
Figure 2.18: Results from MD simulations of B and As implants with the same $R_p$. $N_p$ is the number of atoms with a potential energy greater than 0.2 eV above that of the atom in the ground state. Taken from [24].

When we view the two-dimensional plot it can be seen that many more isolated point defects are produced in the B case compared to the As case. A summary of the key results from this work is shown in table 2.1.

The authors conclude that the reason for this difference in the cascade morphology due to the two different ions is that in the high mass ion case, a local melting of the cascade core occurs resulting in amorphous pockets containing many more displaced atoms than would be produced in simple binary collisions.
Figure 2.19: Results of MD simulations for B and As implants with the same energy deposited in the cascade. \( N_p \) is the number of atoms with a potential energy greater than 0.2 eV above that of the atom in the ground state. Taken from [24].

For low mass ions, where localised melting cannot take place, the production of defects results from the early collisional phase of the cascade. Similar conclusions were also drawn from MD simulations performed by Diaz de la Rubia [38].

Some experimental work has also been performed in order to try and determine the cascade structure resulting from ion implantation. Techniques used include TEM [87-89], X-ray diffraction (XRD) [90] and RBS [91]. All of these
studies used heavy ions (ions with a mass greater than 130 amu) with the exception of the XRD experiments [90] that used Si\textsuperscript{+} and P\textsuperscript{+} ions.

The light ion XRD study [90] used the deviation of the lattice parameter, $\Delta a$, in order to determine the build-up of lattice damage as a function of dose. Through this, the authors were able to determine that cascades begin to overlap with each other at a fluence of $\sim 1 \times 10^{14}$ ions cm\textsuperscript{-2} and that individual clusters have a concentration of defects that is a maximum at the centre of the cascade and decreases outwards to the edge of the cascade.

Table 2.1: Table showing information regarding MD of collision cascades. Modified from [24].

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (keV)</th>
<th>Range (Å)</th>
<th>Damage Energy (keV)</th>
<th>Mean number of Vacancies and Interstitials</th>
<th>Maximum Cluster size</th>
<th>Defects in clusters &gt; 10 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1</td>
<td>49</td>
<td>0.4</td>
<td>28</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>83</td>
<td>0.8</td>
<td>61</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>130</td>
<td>1.3</td>
<td>76</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>As</td>
<td>2</td>
<td>36</td>
<td>1.3</td>
<td>144</td>
<td>63</td>
<td>72</td>
</tr>
<tr>
<td>As</td>
<td>5</td>
<td>64</td>
<td>3.4</td>
<td>376</td>
<td>225</td>
<td>73</td>
</tr>
<tr>
<td>As</td>
<td>10</td>
<td>100</td>
<td>7.2</td>
<td>655</td>
<td>270</td>
<td>71</td>
</tr>
<tr>
<td>As</td>
<td>15</td>
<td>125</td>
<td>10.8</td>
<td>1174</td>
<td>471</td>
<td>74</td>
</tr>
</tbody>
</table>

Thompson and Walker [91] used in situ RBS measurements of low dose, heavy ion irradiation to measure the number of displaced atoms per incoming ion at both room temperature and at 35 K. In this study they discovered that the amount of dynamic annealing of the isolated cascades depends on the energy density of the cascades with the ratio of number of displaced atoms per ion at room temperature to
that at 35 K approaches 1 when the energy density of the cascade is greater than or equal to 1 eV per atom. This suggests that at room temperature, some of the damage created within the cascade volume may dynamically anneal out for low energy density cascades but for high energy density cascades greater than ~1 eV per atom, the cascade volume is essentially amorphous and little or no dynamic annealing occurs.

TEM studies of high mass, low fluence implants have been performed [87-89] although only one of these studies [89] involved imaging of the zones in situ. The in situ experiments [89] showed that immediately following implantation, the contrast of the zones changed slightly with the weakest contrast disappearing and the stronger contrast being reinforced over a timescale of ~20 s. In the same study, high resolution transmission electron microscopy (HREM) was performed on the same samples, a substantial length of time post-implantation, and showed that at the centre of each of the visible zones the atomic fringes disappear and amorphous contrast is observed. It was also noted that there was no evidence of lattice distortion or dislocations in the immediate area surrounding the cascade core [89].

Other experiments involving offline TEM imaging of damage zones produced by low fluence, high mass ion implantation [87, 88] have studied the effect of the variation of energy density of the cascades. In this study, the authors used As, Sb and Bi ions in an energy range from 10 to 118 keV to vary the energy density from 0.02 to 2.69 eV per atom. They found that for energy densities greater than 0.5 eV per atom, single isolated cascades were formed. In the energy density range of ~0.25 – 0.5 eV per atom, single isolated cascades were still formed but there were occasions in which multiple cascades were formed – a sub-cascade structure. As the energy density was decreased further, the sub-cascade structure becomes much more
prevailing down to an energy density of ~0.1 eV per atom where many cascades are composed of multiple defects. This is in agreement to the MD work by Caturla et al [92].

Work also performed on the effect of the TEM imaging conditions [87] showed that whether imaged in bright-field, dark-field, or weak-beam dark-field, the damage regions all had essentially the same appearance and they concluded that the contrast was that of structure factor type, to be discussed in §3.3.5. It was also observed that the damage zones were not dislocation loops, stacking fault tetrahedral, or clusters of either vacancies or interstitials and that the strong structure factor contrast was that of amorphous material. However the same authors in a later paper [88] determined that although the zones showed strong structure factor type contrast, the zones were not necessarily in an amorphous state.

2.4.6.3 Heterogeneous Nucleation

Morehead and Crowder developed the theory and created a model [84] according to which small amorphous volumes are generated heterogeneously within each collision cascade during the stopping of the energetic ion. This model assumes that the disordered core surrounding the ion track is cylindrical in shape and vacancies, or other primary defects, may escape via thermal diffusion. This is shown schematically in figure 2.20. The final stable radius of this amorphous cylinder, \( R_0 - \delta R \), is heavily dependent on the original size of the damage cylinder \( R_0 \) and the temperature dependent out-diffusion of the primary defects which reduces the size of the cylinder by an amount \( \delta R \). The initial size of the damage cylinder, \( R_0 \), is determined by the energy lost by the implanted ion in terms of nuclear displacements per unit length. The damaged volume is thus larger for heavier ions due to the greater nuclear loss per unit length and a greater resistance to dynamic annealing effects.
The energy of the ion implanted determines primarily the width of the amorphous layer being produced [93], with the dose rate being a secondary effect.

This oversimplified model has been expanded upon further by Gibbons [26] to not limit it to the case of a heavy ion creating an amorphous volume. In this model, Gibbons assumes a damage cylinder is formed with each ion cascade (as in the Moorhead and Crowder model) and associated a plan-view area with each cylinder $A_d$. This area is, of course, the damage area one would see if viewing the implantation in a TEM viewing along the incident ion direction with the area being viewed given as $A_0$. Through a set of differential equations, Gibbons showed that the fraction of amorphous area, $A_d/A_0$, can be derived using the relation between the differential build-up of amorphous material with fluence, $dA_d/d\Phi$, to the amorphous cross-section created by the ion track, $A_i$. According to the model, the amorphous fraction is given by:
\[ \frac{A_i}{A_0} = 1 - \left( \sum_{k=0}^{m-1} \frac{(A_i \Phi)}{k!} \exp(-A_i \Phi) \right) \]  

(2.3)

where \( m-1 \) is referred to as the overlap number and \( m \) is the number of ions required to amorphize the overlapped region. This model has been used by several authors working with Si, GaAs and other III-V semiconductors [94].

In the case of Si, during heavy ion implantation, each ion produces an amorphous region (as predicted by Morehead and Crowder [84]) and as such no overlap is necessary [95]. For lighter ions, the damage contained within the cascades produced is not as severe as in the case for heavy ions. As a result of this, light ions require a number of cascade overlaps before turning the region amorphous. For a low value to the number of overlaps required to turn the crystal amorphous, a linear behaviour of the amorphous fraction versus dose is observed, but for large values of overlap number a sublinear behaviour is seen. For both these situations, heavy and light ions, as the ion fluence increases, the number of damage zones increases and begin to accumulate and overlap to form a continuous amorphous layer [84, 87, 96-98].

Some observations of the structure of the damage resulting from heavy ion implants supports the formation of the amorphous state along the ion track by heterogeneous nucleation [87, 88, 98, 99]. Many TEM experiments of heavy ion implants at low fluences have shown the existence of small apparently amorphous clusters within the crystalline matrix [87, 89]. Studies performed at cryogenic temperatures on the damage morphology and recrystallization kinetics of amorphous regions show a very discrete nature to the collision cascades [100, 101]. This behaviour has been attributed to the reduced diffusion of defects at cryogenic
temperatures so their position within the collision cascade volume after quenching is
maintained and any reaction between defects occurs only within the confines of the
cascade volume itself [100].

Some experiments performed using either molecular ions [102] or ion
clusters [103] have yielded different conclusions. The molecular ion experiments
[102] were performed at cryogenic temperatures using Bi or Bi$_2$ as the implant
species whilst keeping the incident energy per ion the same in both cases (0.5 and 1.0
MeV respectively). RBS-C analysis was then performed at differing fluence steps
and showed that a greater amount of lattice disorder was produced by the Bi$_2$
irradiation. The authors also concluded that in neither irradiation was the damage
produced in isolated cascades amorphous material. Experiments performed
irradiating silicon with Au$_n$ clusters where 1<n<7 [103], with the same energy per
incident ion (200 keV per ion), showed that the amount of lattice disorder produced
increased as n increased. High resolution TEM of samples irradiated to a low fluence
with Au$_7$ showed that a single ion track produced by this implant did produce an
amorphous region whereas smaller clusters did not.

2.4.6.4 Homogeneous Nucleation

The homogeneous nucleation model is based on the ion irradiation causing a
build-up of defects [104-106] homogeneously within the lattice up to a point
whereby the defect density in the lattice is high enough to cause a spontaneous
transition of the entire region from crystalline to amorphous. As the ion fluence
increases, the number of defects within the crystal increases and as a critical defect
density is reached, the lattice collapses into the more energetically favourable state of
the amorphous phase. The amorphous state is more favourable because the free
energy of this phase is lower than that of highly defected crystalline silicon.
Chapter 2: Background & Literature Review

The model is known as homogeneous nucleation because the amorphous silicon nucleates as a result of a homogeneous distribution of defects throughout the crystal produced within different collision cascades throughout the irradiated region. It has been reported that amorphization will occur in the crystal when the defect concentration is greater than $1.15 \times 10^{22} \text{ cm}^{-3}$ [107] and the onset of amorphization would be expected to occur abruptly and over a narrow dose range. This defect concentration, for silicon, translates to a lattice defect atomic fraction of 0.02 [105].

A major factor in the homogeneous nucleation of amorphous silicon is the effect of dynamic annealing. This is an extremely important consideration in the theory of homogeneous nucleation as dynamic annealing will reduce the overall number of defects present in the crystal. At room temperatures, the dynamic annealing will be in competition with the generation of the defects created through the ion irradiation and which must reach the critical defect density in order for the crystal to be rendered amorphous. At lower temperatures, the effect of the dynamic annealing is less, due to the “freezing in” of the defects and the crystal will become amorphous much quicker. As a result, this nucleation model is highly dependent on the initial implant conditions.

2.4.6.5 Nucleation Limited Model

Amorphization occurs preferentially at pre-existing damage sites such as amorphous defects [108] or a-c interfaces [109, 110] and for a constant flux irradiation, the fluence required to form a buried amorphous layer increases with temperature.

This suggests that the amorphization follows a two-stage nucleation process consisting of the production of suitable amorphization sites, through the
accumulation of residual defects, followed by the interaction of simple defects with these sites to produce the amorphous phase.

It has been suggested [111] that the kinetics of the amorphous phase formation follows the classical mechanism of nucleation and growth in which the process may be described by an Avrami-Johnson-Mehl equation for phase transformation given by

$$F = 1 - \exp\left( -K\Phi^n \right)$$

where $F$ is the amorphous fraction, $\Phi$ is the ion fluence, $n$ is an exponent for the three-dimensional growth and $K$ is a temperature dependent parameter.

The nucleation process can be associated with the initial part of the collision cascade. After the small amorphous volumes are formed within the confines of the cascade, long-lived defects generated during the irradiation may interact with the $a$-$c$ interfaces of the amorphous volumes and induce the growth or shrinkage of the volume depending on the substrate temperature and ion flux.

During the nucleation stage, defects remaining following the initial quenching of the cascade may accumulate to form complex defect structures and extended defects. As the ion fluence increases, so does the complexity of these defects, with residual defects accumulating until the free energy of the defected crystal reaches a level such that the amorphous phase is favoured and the crystal “collapses” into the amorphous state. It is at this point that the residual defects are thought to be similar regardless of the initial ion irradiating type [112].
2.5 **Annealing Processes**

If an amorphous layer is produced in a semiconductor such as silicon, it may be removed by annealing. This may include different treatments such as laser, ion bombardment or thermally induced re-growth – of which there are also different forms such as rapid thermal annealing (RTA), furnace annealing (FA), and spike annealing (SA). During this re-growth, the crystal remains in the solid phase unlike the float-zone process of removing impurities and defects in the crystal where a small section of the crystal is molten.

As the crystal grows in the solid phase, the amorphous material may re-grow using the underlying perfect crystal as a template. In the case of an amorphous layer extending to the surface of the crystal, the interface between the amorphous material and the crystalline material begins to move towards the surface at a given rate until either the annealing treatment is ceased or until the interface has reached the surface. If the amorphous layer is buried, i.e. there is no free surface; both of the amorphous/crystalline (a-c) interfaces will re-grow reducing the amorphous layer width until both interfaces meet. As a result of this, there may be a layer of complex defects left behind.

In this section we will discuss the concept of solid phase epitaxy and some of the factors that can affect it.

### 2.5.1 Solid Phase Epitaxial Growth (SPEG)

Solid phase epitaxial growth (SPEG) i.e. the re-growth to crystallinity of an amorphous layer, is an extremely important process during device manufacture and
was first reported by Mayer et al [113] in 1968. This process permits the removal of the majority of damage created during the ion implantation process and allows for the electrical activation of the dopant atoms. In SPEG, the atoms of the amorphous phase reorder themselves using the underlying crystal as a template for the re-growth. This occurs whilst the silicon crystal is still in the solid phase, hence the term solid phase epitaxial growth. During SPEG the \( a-c \) interface moves through the crystal as the amorphous phase is re-grown and this is shown schematically in figure 2.21. This re-growth may be induced through either thermal treatments [114] or through ion bombardment [115].

The crystallization due to heating occurs well below the melting temperature for Si (~1400 °C) and the velocity of the \( a-c \) interface, \( v \), can be described through an Arrhenius-type equation of the form

\[
v = v_0 \exp \left( -\frac{E_a}{kT} \right)
\]  

(2.5)

where \( k \) is Boltzmann’s constant and \( T \) is the temperature in Kelvin. The generally accepted values for the constants \( E_a \), the activation energy, and the velocity prefactor, \( v_0 \), are 2.7±0.02 eV and \( 4.64 \times 10^6 \) ms\(^{-1} \) respectively [116]. Through this equation, it can be estimated, quite accurately, that the sample will recrystallize at rates between 0.01 – 100 Ås\(^{-1} \) for temperatures in the range of 460 – 660 °C.

There have been attempts to correlate the activation energy for re-growth (2.7 eV) to triggering events. This will be discussed further in §2.5.5.
2.5.2 Orientation Dependence

For the case of amorphous layers produced by self-ion implantation into intrinsic silicon, it has been observed that the re-growth is highly temperature and orientational dependent.

The orientation dependence is inversely related to the atomic density of the different planes in the crystal. The re-growth rate of (111) Si is the slowest whilst (100) Si has the fastest re-growth rate [117]. In fact the re-growth rate of (100) Si is up to 25 times faster than that of the (111) Si re-growth rate. This is shown in figure 2.22.
Figure 2.22: Graph showing the re-growth rate of amorphous silicon as a function of the orientation. Clearly it is seen that the fastest re-growth orientation is the (100) and the slowest is the (111). From [117].

2.5.3 Dopant Enhanced SPEG

An interesting property of the kinetics of SPEG is its strong dependence on the impurity content. It is possible, through the addition of dopants, to enhance, retard, and even halt the re-growth.

This change in SPEG due to the introduction of dopants shows a very strong temperature and concentration dependence and is therefore very complex in nature. Early experiments on the enhancement of SPEG by phosphorous doping showed that the rate can be enhanced up to six times without changing the activation energy.

Further studies have shown that when the impurity concentration within the amorphous silicon layer is greater than 0.1 at.%, there is a marked effect on the kinetics of the SPEG. Csepregi et al first showed [118, 119] that group III and V dopants can greatly increase the rate of SPEG whereas non-doping impurities such as C, O, N, and noble gases can retard the SPEG rate [120]. It was subsequently discovered [121-123] that when \( n \)- and \( p \)-type dopants are both simultaneously
present in the $a$-Si, the SPEG is returned to a value that is characteristic of intrinsic Si.

As the impurity concentration begins to increase, and the concentration exceeds approximately 0.3 at.%, complex processes such as impurity segregation and precipitation can alter the kinetics further to such an extent that dopants that increase the rate of SPEG at lower concentrations begin to actually retard the re-growth rate [124, 125].

2.5.4 Solid Phase Epitaxial Growth Models

A number of models have been developed to describe the SPEG process and these models take a number of different approaches to describe the process. These different approaches can be broken down into three different sub-sections. The first that will be discussed is the atomistic approach in which it is considered how the atoms on the $a$-Si side of the interface are rearranged onto the underlying crystal template. Another approach has been to consider the kinematic effects occurring during re-growth. These models try to identify the rate limiting step in the SPEG process and derive equations to predict the SPEG rate as a function of the temperature and dopant concentration. More recent models attempt to correlate the SPEG rate with the electronic properties of the structure at the $a$-$c$ interface. The experiments that were performed for this thesis used noble gases and self-ion implants, and as a result the importance of electronic effects on the re-growth are diminished so this aspect will be only discussed briefly here.
2.5.4.1 Atomistic Models

To describe the SPEG process in an atomistic manner, it is first necessary to have a good model for the \( a-c \) interface. As described earlier, the amorphous structure of Si is composed of five-, six, seven- and eight-membered rings and this is reasonably modelled in the CRN model. Using this as a basis, many workers have developed models that can describe the movement of the \( a-c \) interface at an atomistic scale by considering the re-arrangement of atoms on the amorphous side onto the crystalline template. At the interface of these models, the structure maintains full four-fold co-ordination so the structure is in its lowest energy state. Defects may occur at the interface as distortions in bond angles and bond lengths.

Csepregi et al. [117] proposed that the re-growth occurred as a result of the propagation of [110] terraces in \{111\} planes and ledges. This occurs in these directions as it is assumed that for an atom to be attached to the crystalline phase it must have two nearest neighbours at the interface which are already in the crystalline phase.

Building on these ideas, it has been suggested that the SPEG process can be mediated by a bond breaking mechanism [36, 37]. In this model, the amorphous phase becomes re-grown onto the crystal template by bonds breaking and reforming along a [110] ledge and accounts for the observed activation energy.

Instead of a bond breaking mechanism mediating the SPEG process, Narayan [126] suggested that the re-crystallization process may occur as a result of a mass transportation of excess interstitials from the amorphous phase to the crystalline phase.
2.5.4.2 IV Pair Annealing

Using MD techniques, Stock et al [34, 78] showed that the IV pair is a characteristic structure of the a-c interface. As a result of these MD studies, the IV pair has been used as an elementary unit to describe amorphous material [35].

Following on from the MD studies, kinetic Monte Carlo (k-MC) studies have been performed on the annealing of IV pairs in bulk silicon. These k-MC studies assign activation energies to the extreme cases of 0.43 eV for an isolated IV pair (zero coordination) and 5 eV for an IV pair completely surrounded by other IV pairs (full coordination). The experimentally measured activation energy of the planar a-c interface, 2.7 eV [114], is used as the activation energy for the case when half the IV pair is surrounded by other IV pairs (half total coordination). The intermediate coordination numbers have interpolated activation energies.

The local characterization of the disordered atoms resulting from ion implantation has a direct consequence on the characteristic re-growth behaviour due to the different damage morphology lying within the interaction radius of the IV pair and is shown in figure 2.23. In this figure, each grey circle represents a single IV pair and the dashed lines the interaction radius. Isolated IV pairs such as that shown as “A” annihilate first as they do not have an IV pair neighbour. For IV pairs that have amorphous pockets within their interaction radii, the pockets begin to anneal with the outer IV pairs (B and C) as the inner pairs (F and H) have more IV neighbours. IV pairs at the extremities of elongated finger-like amorphous pockets (B) recombine first due to their low coordination number, followed by the IV pairs of more rounded pockets (C) that have a slightly higher coordination number.
Figure 2.23: Schematic of the damage/annealing morphology of the IV pair. See text for full description of the processes occurring. From [11].

For the case of the planar \( a-c \) interface, when an IV pair is either missing or spontaneously recombines, say between \( D \) and \( E \), both \( D \) and \( E \) have fewer surrounding IV pairs than \( G \) and thus the whole layer re-grows from \( D \) and \( E \).

Each amorphous region re-grows at a rate dependent on the local coordination of defects. For amorphous pockets approximately spherical in shape, re-growth occurs at a lower temperature than a planar \( a-c \) interface because the convex \( a-c \) interface would have fewer IV pairs surrounding it than is the case for the planer interface.

2.5.4.3 Kinetic Models

Perhaps one of the simplest and most effective models is transition state theory. Here SPEG is thought to be a thermally excited transition between the amorphous and crystalline phases that compete between each other during the re-growth. The transition may only occur if the system obtains enough free energy to overcome a potential barrier with a height determined by a given activation energy. During this period of re-growth, the amorphous-to-crystalline and the crystalline-to-
amorphous phase changes compete with each other, and it is assumed that the crystalline-to-amorphous phase change does not occur i.e. the rate at which the amorphous layer increases in thickness is zero.

2.5.4.4 Electric Field Models

Models that account for electronic processes are much more likely to explain the differences in SPEG rates for dopant enhanced/retarded regrowth. Since the experiments reported in this thesis used self-ion or noble ion implantation the electronic component of SPEG has been vastly reduced. As a result of this, some electric field models will be introduced here briefly for completeness.

2.5.4.4.1 Charged Vacancy Model

Following on from the work done by Csepregi, Suni et al [121, 123] proposed that the bond breaking mechanism described in §2.5.5.1 is mediated by vacancies diffusing from the amorphous side of the interface. Suni related the concentration of vacancies to the Fermi level which is altered by the dopant concentration. With a greater concentration of vacancies at the interface, SPEG will be enhanced.

A model based on the diffusion of charged vacancies at the interface from within the amorphous phase has been developed by Mosley and Paesler [127] and Licoppe and Nissim [128]. This differs from the model by Suni in that the concentration of defects at the interface changes with dopant concentration. On the amorphous side of the interface, the defects pin the Fermi level to the middle of the band gap, creating an electric field at the interface. The strength of this electric field increases with dopant concentration and Mosley and Paesler postulated that this increase in electric field attracts dangling bonds towards the interface to aid the
SPEG process. This model is believed inadequate in providing a large enough effect to match the data [129].

The possibility of vacancy assisted SPEG or the migration of defects to the interface has been ruled out through pressure-enhanced SPEG studies [129]. It is more realistic that mechanisms based on point defects residing at the interface are dominant.

These models have many parallels in other semiconductor processes where events are dictated by the concentration of defects through the electronic properties of the material.

### 2.5.4.4.2 Charged Kink-Site Model

The charged kink-site model [130] builds on the proposal of Spaepen and Turnbull [36] of considering a bond breaking process propagating along [110] ledges. It is assumed that the growth sites have electronic energy levels inside the band gap linking the structure of the material to shifts in the Fermi level. Thus, the growth, or kink, site can be visualised as some bond breaking event.

### 2.5.5 Annealing of Non-Planar a-c Interfaces

Although some work has been published on amorphous zones in the past, as described above, only two groups have recently looked at the annealing of amorphous zones. These groups are the Donnelly-Birtcher group from the University of Salford, UK and Argonne National Laboratory, USA who have looked at the evolution of the amorphous zones through thermal annealing; and the Jencic-Robertson group from Institute “J. Stefan”, Slovenia and the University of Illinois, USA who have looked at the evolution of zones due to electron beam annealing.
In this review, “amorphous zones” will be used to describe the damage regions in keeping with the terminology used in the referenced papers although it will be seen later in this thesis that the zones are not generally amorphous, but damaged.

2.5.5.1 Electron Beam Annealing of Damage Zones

A comprehensive study of the electron beam annealing of damage zones assumed to be amorphous in semiconductors has been performed and reported in a series of papers published by Jencic, Robertson and other authors [131-137]. These studies followed the electron beam annealing of spatially isolated zones created by room temperature Xe\(^+\) implantation with energies varying from 50 to 300 keV and doses between 5 \(\times\) 10\(^{10}\) and 2 \(\times\) 10\(^{11}\) ion cm\(^{-2}\) into Si, Ge, GaAs, GaP and InP. All these irradiations were performed at the IVEM-Tandem facility at Argonne National Laboratory on pre-thinned samples, but all the microscopy was performed off-line on a Philips CM30 TEM. The Philips TEM was equipped with an in-column Faraday cup allowing for accurate dosimetry of the electron beam. Imaging of the amorphous zones produced by the irradiation was performed in bright-field down-zone and two-beam dark-field conditions. In the analysis of the zones, the crystallization kinetics were evaluated through the areal density of the amorphous zones over the dose steps, and only in some cases were isolated zones tracked.

In all cases the electron beam induced a re-growth of the amorphous zones with the number of zones remaining in a given area decreasing linearly with electron dose as shown in figure 2.24.

Figure 2.25 displays a graph showing the disappearance rate of the amorphous zones with varying electron energy in both the bright-field down-zone and two-beam dark-field conditions. It is clear that in both cases the disappearance
rates show the same trend although the disappearance rate for the two-beam condition appears to be higher than the down-zone case. This was attributed to the difference in the defect resolution limit between the two imaging conditions which has been supported by the work of Bench [94]. It can also be seen from figure 5.25 that a minimum in the disappearance rate occurs at approximately 100 keV for silicon and it is for this reason that this energy is used throughout this thesis.

Figure 2.26 show the disappearance rate for three crystal orientations (001), (110) and (111) and it is clearly shown that there is no orientation dependence. This is contrary to the case for planar amorphous layers. This can be understood when it is considered that a spatially isolated amorphous zone will be effectively surrounded by all crystallographic planes.

The effect of the depth of the amorphous zones was also investigated in this paper by varying the energy at which the ion was implanted from 50 to 300 keV, and the result of this is shown in figure 2.27.

With the exception of the 300 keV result, varying the ion energy has little effect on the disappearance rate of zones in Si with the crystallization process being altered little by surface effects.

During the 300 keV implantation, some ions have a projected range greater than the specimen thickness meaning that a column of damage will be produced along the ion path creating smaller amorphous zones. This smaller zone size possibly explains the higher disappearance rates.

As well as obtaining disappearance rates by taking values of the areal density of the zones, several zones were tracked and an effective diameter assigned to each zone at each dose step.
This is shown in figure 2.28 for zones created in Ge. The electron beam energy is not given in the text [137], but this is of little consequence as this will alter only the rate at which the zones are annealed. From this figure, the annealing behaviour was categorized into four groups:

1) A constant linear decrease in diameter (zone 6),
2) An initial linear decrease in diameter, followed by a constant zone size (zone 5),
3) A linear decrease in diameter followed by a sudden disappearance (zones 2, 3, 4, 7), and
4) An initial linear decrease, a “plateau” of constant size, then a sudden disappearance (zones 1, 8).

From inspection of the curves, the authors stated that the curves are remarkably linear, within experimental error [137].

\[\text{Fraction Remaining} = \frac{1}{1 + \text{Electron Dose (x } 10^{21} \text{ electrons cm}^{-2})}\]

**Figure 2.24:** Figure showing the fraction of initial damage zones remaining in Si as a function of electron dose for different electron energies ranging from 25 to 250 keV. From [136].
It was then assumed [137] that the electron-solid interactions impinge on a certain region within a given time interval, and it is then possible to postulate the region in which the electron-solid interaction influences the zone re-growth.

The possibilities are:

1) interactions from the entire amorphous volume – the active region is the zone itself

2) interactions from a thin shell surrounding the a-c interface – the active region is the surface of the zone

3) interactions from the crystalline material surrounding the zone – the active region is much larger than the amorphous zone itself and can be assumed to be constant.

The annealing characteristics of these three statements can be represented in a graph as shown in figure 2.29. From this figure and the curves shown in figure 2.28, the authors came to the conclusion [137] that the annealing of amorphous zones as a function of electron dose is surface-dependent.
With all the evidence shown, the conclusions were drawn up that the re-growth of amorphous zones occurred as a function of electron dose, initiated by some mechanism at the $a$-$c$ interface. The proposed mechanism is as follows: for electron energies above $E_d$, re-growth occurs through a process of re-ordering atoms at the $a$-$c$ interface in which the energetic electrons have enough kinetic energy to ballistically displace the atoms causing the atoms to re-arrange themselves from the amorphous to crystalline configuration [137].

This mechanism still does not explain the minimum and increase in disappearance rate (shown in figure 2.25) that occurs below the threshold displacement energy. The decrease in disappearance rate down to a minimum at 100 keV for Si indicates that there may be a different displacement energy for crystalline and amorphous silicon and that ballistic re-arrangement of the $a$-$c$ interface may continue to this lower energy.
As the electron beam energy is decreased even further and the disappearance rate begins to increase again, the authors suggest that another mechanism begins to dominate. In this mechanism, as the low energy electrons pass through the $a-c$ interface, they excite valence shell electrons into anti-bonding levels causing a weakening or severing of the bonds. Each broken bond creates a defect that can be conceptualized as a dangling bond or an electron-hole pair. The two atoms that shared the now severed bond will shift positions locally as will their neighbours. Whilst in the excited anti-bonding state, the electrons and holes can move throughout the lattice. Due to the extra strain energy associated with the $a-c$ interface, these dangling bonds will propagate along the interface in a manner analogous to the Spaepen and Turnbull model [37]. The defects will eventually become trapped or recombine with each other forming a covalent bond.
Figure 2.28: Graph showing the behaviour of individual damage zones in Ge due to electron beam annealing. The electron beam energy is not given in the paper. From [137].

This mechanism for electron annealing below the electron energy required to permanently displace atoms from their lattice sites can also be used to describe the “plateau” type anneals shown in figure 2.28. Here, the atoms at the $a$-$c$ interface to accommodate their neighbours that have transformed from the amorphous to crystalline. As this occurs, the amorphous zone shrinks, but the structure within the amorphous material becomes more complex resulting in a period of stability which is maintained over a given dose step.

Eventually, when a critical bond is broken or when a certain sequence of bond breakages occurs, the amorphous structure becomes unstable again and collapses into the crystalline structure.
2.5.5.2 Thermal Annealing of Damage Zones

A recent study on the thermal annealing of zones assumed to be amorphous in silicon has been carried out by Donnelly et al [138] and is consistent with early work performed by Chadderton [104]. In this recent work, amorphous zones were created using 200 keV Xe$^+$ to doses of $1.25 \times 10^{12}$ ions cm$^{-2}$ \textit{in situ} using the IVEM-Tandem facility at Argonne National Laboratory with the TEM operating at 100 keV to minimize electron beam induced re-growth of the zones.

Analysis of 400 individual zones during isochronal annealing steps showed little or no correlation between the size of the amorphous zone and the temperature at which it re-crystallized, with each annealing step showing zones of every size disappearing. This behaviour is inconsistent with a single activated process for re-

Figure 2.29: Graph showing the schematic curves for the different models for the activation volume contributing to the zone re-crystallization. From [135].
growth and also contradicts findings of MD studies in which the activation energy increases with zone size.

Later papers by the same group [139, 140] showed that in some cases it was possible that the amorphous zone would increase in size – so called reverse annealing, and this was observed in approximately 2% of all the zones measured. This reverse annealing was attributed to a high density of point defects quenched into the Si surrounding the amorphous core of the zone becoming amorphous following thermal annealing thus allowing for the zone to increase in size.

This was not a spurious result for 200 keV Xe\textsuperscript{+} implantations as similar observations have been seen in the annealing of spatially isolated zones formed by implantation with 50 keV Xe\textsuperscript{+} in which reverse annealing occurred in approximately 11% of all the zones measured [141]. In this study, it was proposed that the reverse annealing effect occurred as a result of the IV pair and the configuration of interstitials and vacancies around the amorphous core of the zone. It was shown that certain configurations allowed for a percentage increase in effective radius of up to 43% [141]. This work will be discussed in more detail later in this thesis in §4.4.3.

In the 1981 paper by Howe and Rainville [87], they studied the thermal annealing of damage zones produced by a variety of heavy ion implantations to see the effect of variation of the energy density deposited in each cascade. It should be noted, however, that in this study the implantations were performed into a bulk sample from which the TEM sample was prepared post-implantation and this step involved a thermal treatment. As was shown by Donnelly et al [138-140], thermal annealing of amorphous zones may occur at temperatures as low as 50 °C and as such the results from the Howe and Rainville paper cannot be regarded as a fully accurate detail of the thermal annealing of damage zones. It is interesting to note that
during the thermal annealing experiments, the authors discovered that the damage contained within the zones did not convert to extended defects e.g. dislocation loops, following annealing. It was observed that the damage produced as a result of diatomic implants was more resistant to annealing and this was interpreted to be as a result of a larger damage zone when compared to atomic implants and that the damage resulting from the diatomic implantation was more highly amorphous [87] than the damage from atomic ions although the authors do not explain how a material can be amorphous to varying degrees.

2.5.6 Post-Annealing Defects

During the process of integrated circuit (IC) manufacture, the silicon wafer upon which the IC is to be constructed is implanted with dopant atoms to a high fluence and then the wafer is annealed in order to obtain the desired electrical properties. Although this annealing, as discussed in §2.5.5, removes the majority of the damage created as a result of the ion implantation, it does allow the evolution of extended defects through the implanted region. The defects that arise from the annealing are highly dependent on the implantation and annealing conditions and can be categorised into five individual categories that will be briefly summarised in §2.5.7.1, and are taken from Jones et al [142].

2.5.6.1 Classification of Post-Anneal Defects

The first category (type I) of defects is the sub-threshold type. These defects occur as a result of the annealing of the substrate following an implantation that has not formed an amorphous layer in the sample. Following annealing at temperatures \( \leq 800 \, ^\circ\text{C} \), \{113\} defects and dislocation loops may be formed, yet with annealing at
temperatures above 850 °C typically only dislocation loops are formed. Fluences of ≥7 x 10^{12} \text{ cm}^{-2} are required for \{113\} defect evolution while fluences of ≥2 x 10^{14} \text{ cm}^{-2} are necessary for dislocation loop formation. The defects are produced at the \( R_p \) of the implanted ion.

The second category (type II) of defects is the end-of-range type. These defects are so-called due to their formation just beyond the \( R_p \) of the implanted ion. The stable defects formed following annealing are the same as in category one type defects, although they evolve from a fully amorphous layer in this category. This type of defects will be expanded upon in §2.5.6.2.

Category three defects (type III) are re-growth related type defects. These forms of defects arise following the annealing of an amorphous layer and occur as a result of the imperfect re-crystallisation of the amorphous layer during SPEG. The defects formed in this category are stacking faults, micro-twins and hairpin dislocations.

The fourth category (type IV) of post-annealing defects is the clamshell, or zipper, type defects. The name clamshell or zipper arises from the fact that they are formed as a result of a mismatching of crystalline silicon following the SPEG annealing of a buried amorphous layer. At the point where the two \( a-c \) interfaces meet following the anneal dislocation loops are formed.

The final, and fifth, category of defects (type V) is the so-called solubility related type defects. These defects form when the solubility of the implanted species exceeds the solid solubility in silicon. Defects may take the form of precipitates, dislocation loops or partial dislocation loops following annealing at temperatures above 750 °C.
The schematic diagram in figure 2.30 shows the defect location with respect to the damage region following implantation.

### 2.5.6.2 End of Range Defects and their Evolution

End of range defects form just beyond the projected range of the implanted ion. These defects arise from an excess of interstitials within the crystal and evolve to reduce their excess energy which is possible through forming larger defects with lower formation energies. In this situation, smaller clusters dissociate and the released interstitials are attracted by larger defects which remain stable up to high temperatures.

During ion implantation and in the early stages of the annealing, most of the excess interstitials in the crystal may be stored as di-interstitials [27] that may grow into small interstitial clusters. Inverse analysis using an Ostwald ripening model has shown that interstitial clusters containing either 4 or 8 atoms form the most stable small clusters [75] (see also §2.4.4). During longer annealing times and higher annealing temperatures, these clusters may begin to condense and form extended defects.

Types of extended defects that may form are \{113\}s and dislocation loops. TEM images of both \{113\}s and dislocation loops are shown in figure 2.31. The \{113\}s are formed from smaller clusters (see §2.4.4) and become visible in the TEM at a length of approximately 2 nm [143].

The \{113\} defects are bundles of rows of Si di-interstitials that lie along the \{113\} plane and are elongated in <110> directions. Around the defect are five- and seven-membered ring arrangements which allow for the insertion of the interstitial planes without dangling bonds [144]. Following the initial nucleation of the \{113\} defect, further annealing allows larger \{113\}s to grow in length at the expense of
smaller {113}s thus also reducing the density of the overall {113} population within the crystal.

Another extended, end-of-range defect that may form following annealing is the dislocation loop and may take one of two forms – a perfect dislocation loop or a faulted dislocation loop. Dislocation loops are formed in the crystal when a small additional plane of interstitials is formed between two large planes. In cases where there is a mismatch in the atomic arrangement of the crystal following dislocation loop nucleation, a faulted loop is formed and where there is no lattice mismatch, a perfect dislocation loop is formed.

At annealing temperatures above 800 °C, the dislocation loops will act as sink sites for interstitials ejected from the {113} defects. In this process, the Ostwald ripening process, the density of the {113}s will decrease whereas the density of the dislocation loops will increase.

### 2.5.6.3 Bubbles and Voids

Following from hydrogen and noble gas ion implantation, bubbles may form in silicon. This may either occur as a result of extremely high fluences [145] or following annealing [146].

It is also possible, through different annealing schemes, for the gas contained within the bubbles to escape from the bubbles to leave a void. Figure 2.32 shows an example of bubbles as imaged in the TEM.
Figure 2.30: Schematic diagram showing the relationship between the damage density distribution (solid lines) and the amorphization threshold (dashed lines) leading to the different categories of defects. Taken from [147].
Figure 2.31: TEM micrographs showing \{113\} type defects (top image) and dislocation loops (bottom image). Images taken from [148].

Figure 2.32: Bubbles as imaged within a TEM. It can be seen that both large and small bubbles are formed [149].
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3 Experimental Methods
3.1 INTRODUCTION

Since the invention of the transmission electron microscope (TEM) by Ruska and Knoll in 1932 [1], it has become one of the most important and widely used instruments for the materials scientist. In the field of radiation effects in materials it has been of particular importance making many essential contributions to our understanding of how microstructures develop during irradiation. Of course as with all experimental techniques, TEM has its limitations that should be known and understood before useful information may be obtained. In this chapter, the practical techniques and equipment used to obtain the experimental results described in this thesis will be presented. Included will be the requirements for the preparation of good samples for the experiments and practical problems associated with preparing these samples, along with the imaging conditions that were used to record the images and, finally, the ways in which the results were analysed.
3.2 Sample Preparation

3.2.1 Introduction

All the results presented in this thesis have been obtained from in situ experiments performed on silicon. In this section, the techniques that were used to prepare samples ready for the in situ ion irradiation will be described. The silicon that was used throughout the experiments was <100> float-zone silicon wafers, 300 μm thick, p-type (B-doped) with 1 – 10 Ω cm⁻¹ resistivity.

One necessity of samples for in situ TEM experiments is that the sample is thin which may also cause some complications in the interpretation of the experimental results. The surface of the thin sample acts as a very strong sink for mobile point defects in the sample, and as a result, the damage may develop in a different manner to that of a bulk sample. Provided that this is taken into account when analysing the results from in situ experiments, the experiments can provide extremely useful insights into the damage mechanisms involved.

The experiments that were performed can be categorised into three different sections from a sample preparation point of view: 1) low energy (50 keV) amorphization experiments; 2) medium energy amorphization experiments (200 – 400 keV); and 3) annealing experiments. All three different types of experiments require different methods of specimen preparation and mounting in order to provide the best results. Two different sample preparation techniques were used during the course of the experiments: electrochemical thinning and the small angle cleavage technique (SACT). These sample preparation techniques were chosen rather than the common ion beam milling technique to avoid the unwanted radiation damage that
could be introduced into the specimen material during specimen preparation. The electrochemical thinning technique was used to prepare samples for the low energy amorphization experiments as a large, very thin area is required and this is unobtainable through the SACT method. The reasons behind this will be explained in a later section. For the medium energy amorphization experiments and the annealing experiments, the SACT method was used to prepare the samples but two different mounting methods were used which shall be fully explained in §3.2.2.1. As with all methods of sample preparation for TEM, it is necessary to produce a specimen that is representative and as free from artefacts as possible.

3.2.2 The Small Angle Cleavage Technique

The small angle cleavage technique (SACT) was first developed [2, 3] for the preparation of TEM samples in plan- or cross-sectional view of semiconductors. The technique has also been shown to be suitable in the preparation of thin films deposited on silicon [4]. Compared to the commonly used ion beam milling method, SACT has two distinct advantages when preparing samples for the TEM when investigating the nature of radiation damage. Firstly, and most importantly, ion milling may result in the introduction of artefacts [5] resulting from the interaction of the energetic ions with the material unless extreme care is taken. Low temperature milling may reduce the damage caused by the ions. Even then the sample may not be entirely free from radiation induced artefacts and a thin amorphous layer is almost always produced. When producing a sample for TEM viewing by SACT, the technique provides a good, clean viewing area of the sample when performed correctly. This technique also avoids foil bending problems as the specimen wedge angle of 18.4° is sufficient to provide a certain degree of rigidity. The only artefacts
that have been produced during this method of sample preparation are small steps in the sample which are easily discernable from the radiation damage that is introduced at a later stage in the study. This is a major advantage over ion beam milling.

Secondly, ion beam milling requires relatively complex equipment and sample preparation time may be measured in days especially for cross-sectional samples. This is extended if the sample is not elemental where preferential milling may result in a composition change. The equipment needed to produce samples by the SACT method are simple hand tools such as scribers, tweezers and common laboratory equipment such as a sample grinder, a low-power stereo microscope, a hot plate and a low-temperature oven. Another great advantage is that samples in both cross-section and plan view may be produced in little over an hour meaning that a sample may be, for example, implanted, prepared and imaged in the TEM all in one day. The procedure for producing samples by SACT is simple and consists of back thinning of the bulk sample, cleaving along the desired planes and mounting of the wedges produced in the correct orientation for the desired viewing arrangement – plan view or cross-sectional. The following describes the method to produce samples of (100) Si ready for mounting for TEM viewing. Descriptions to produce samples from (110) or (111) Si may be found elsewhere [2].

The small angle cleavage technique requires that a small sample of (100) silicon, approximately 5 mm x 5 mm, be mounted onto a polishing jig using a low temperature wax and then back polished using wet, 600 grade grit silicon carbide paper at an angle of ~18° to the [110] direction to a thickness of approximately 100 μm thick. Samples with thicknesses of between 80 and 120 μm can be used but it has been found that samples thinned to 90 μm produce the best samples. The 18.4° is chosen to correspond to the <120> direction of the cubic lattice and lines are scribed
along this direction using a diamond scribe to reduce the specimen thickness at the scribe line by approximately 10%, as shown in figure 3.1. Scribe angles of up to 30° have been experimentally found to also produce good TEM samples. After removing the thinned sample from the polishing jig using acetone, the sample is rinsed clean in acetone again several times. It is then cleaved along the scribe lines by placing the sample on a glass coverslip with the scribe lines parallel to the coverslip edge producing several Si strips, as shown in figure 3.2. Two pairs of tweezers are then used to cleave the sample, one pair is used to hold the sample in place, and the second pair is used to apply gentle downward pressure to part of the sample that is overhanging the glass coverslip. The sample will cleave along the scribed line to produce good sample strips for the next stage in the process.

The sample strips are then placed front surface side up in a plastic weighboat and immersed in ethanol. The ethanol prevents sample whiplash during the final cleave. Under a low-power optical microscope the sample strips are manually scribed, using a tungsten tipped scriber, and cleaved to produce small wedges with two cleaved sides. This final cleave is performed by scribing a small notch parallel to the standard \{110\} cleavage plane and then a small amount of pressure is applied to the region of the notch causing a cleave to propagate along the \{110\} up to the \{120\} cleaved plane, also shown in figure 3.2. As the two planes intersect, a triangular based pyramid tip is formed composed of the front surface and the two cleaved sides. It is around this area that the sample will be electron transparent. Not all wedges produced by this method will be electron transparent, only wedges with good sharp tips are selected for mounting and a 50% success rate is typical.
3.2.2.1 Mounting of Cleaved Samples

Samples that were produced by SACT were used in two types of experiments: annealing experiments and medium ion energy amorphization experiments. Both types of experiments required different sample mounting techniques. For the samples to be used for the amorphization experiments, the sample had to be held firmly in place to reduce any movement during ion bombardment whilst still maintaining a large clear target area for the ion beam. The samples used for the annealing experiments required a firm mounting again but because the sample was to be thermally annealed, it was preferable not to use conducting epoxy because of concerns about its high temperature stability. As a result of the two specifications that have just been described, two different methods...
of mounting the samples were used; one for the amorphization experiments, the other for the annealing experiments.

**Figure 3.2:** Silicon strips formed by the initial scribe and subsequent cleaving along the \{120\}. Also shown is the final cleave along the \{110\} (shown as a dotted line), and a tip produced after this final cleave.

Both of the mounting techniques use the wedges formed by SACT described earlier.

The samples for amorphization experiments were mounted on 600 or 800 \(\mu\)m Cu hole grids using a silver conductive epoxy. This was done by picking up the wedge using a small pair of tweezers and then placing the selected wedge onto a small amount of epoxy placed on the grid. The sample was mounted with the polished side up so it was in plan view \((100)\) orientation. It was also possible to mount the samples in a cross-sectional orientation, \((110)\), using this mounting method by simply mounting the \{110\} plane onto the grid. During the course of the experiments, only one wedge at a time was mounted onto each grid but it is possible to mount up to four samples onto one grid in any combination of plan view or cross-sectional views [4]. The epoxy was then cured in a low temperature oven for 30
minutes or left overnight at room temperature. Samples were then ready for use in
the TEM.

Samples that were to be used for annealing experiments had to be mounted so
the use of epoxy was eliminated so there would be no release of hydrocarbons into
the TEM column during heating. The solution to this problem was to mount the
wedges in a molybdenum oyster grid. This did cause some problems however. The
grid lines may shadow the sample from either the electron beam or the ion beam
causing the sample to be un-viewable, un-irradiated or both. Once the sample had
been mounted, it was checked in the TEM for suitability and good samples were then
heated to ~600 °C for approximately 30 seconds to remove stresses in the grid that
might cause movement of the sample during the annealing experiments. Figure 3.3
shows SEM images of samples mounted in both methods described.

3.2.3 Electrochemical Thinning

Samples that were to be used for the low energy amorphization experiments
had stringent requirements that could not be obtained by using the preferred
preparation technique of SACT previously described. Due to the low energy of the
implant, a shallow amorphous layer is formed in the sample. Using the high wedge
angle sample produced during the SACT technique, it was discovered that during the
amorphization of the sample, crystalline spots were always visible in the diffraction
pattern as a result of a combination of the high wedge angle and the relatively large
probe size used in the experiment i.e. the electron beam was always sampling thicker
parts of the wedge with un-irradiated material. This meant that a sample would have
to be produced that would allow an amorphous layer to form within the sample
resulting in no crystalline spots in the diffraction pattern for the probe size used. For
this reason it was decided to prepare samples using the jet polishing technique as this formed thin samples with a shallow wedge angle covering all requirements for a good sample for this type of experiment. What follows is a description of how the samples were prepared.

In order to prepare a good specimen by electropolishing for TEM viewing, a 3 mm disc must be first core drilled from the bulk sample. If the sample is already not thinned to the required thickness the sample must then be ground down to a thickness of approximately 150 $\mu$m. Once the desired thickness has been achieved, the disc may then be dimpled on both sides. This is a critical stage in the preparation of a good specimen. In order to make the best specimens possible the sample must be dimpled in the centre on both sides of the sample with the thickness at the centre of the disc being approximately 50 $\mu$m after dimpling.

The sample is then placed into an electro-polishing system. This polishing system contains a polishing nozzle that allows a cooled electrolytic solution to flow over the specimen. The electrolytic solution (a 30 – 50% HF solution in methanol [6]) is kept cool to solid carbon dioxide temperature in order to increase its viscosity during the flow over the sample. During this stage it is extremely important to keep the polishing temperature, current and voltage stable in order to ensure a controlled, balanced removal of the remaining material. The sample is polished until perforation is just achieved. At this point the specimen should be examined in the TEM for suitability for use in an experiment.
Figure 3.3: SEM images of the mounting techniques used. The mounting of the sample ready for amorphization experiments is shown in a) where the sample is mounted onto a hole grid using a silver conductive epoxy. Mounting of the sample for annealing experiments, where the sample is mounted in a Mo oyster grid is shown in b). Finally, c) shows the possibility of mounting four samples on one grid in different orientations – plan view and cross-sectional view.
3.3 Imaging in the TEM

3.3.1 Introduction

Transmission electron microscopy is a technique whereby an energetic beam of electrons is focused onto a specimen causing an enlarged version of the specimen to be detected on either a fluorescent screen, photographic film or a CCD camera.

In early studies of matter, light microscopes were utilised. However, the maximum resolution available in the image is determined by the wavelength of the beam that interacts with the sample. Visible light has a wavelength of 400 – 700 nm; generally much larger than many of the objects of interest to the materials scientist today.

Electrons behave as both particles and waves [7], and their wave-like properties means that a beam of energetic electrons will behave like a beam of photons in the analogous optical microscope. The wavelength of the electron beam is determined by its energy and thus can be adjusted by accelerating fields so that the wavelength is substantially smaller than that of light. Here the transmission electron microscope (TEM) and some of the different imaging mechanisms are introduced although much greater detail may be found in texts such as Transmission Electron Microscopy [1], Electron Microscopy in the Study of Materials [8], and Characterization of Radiation Damage by Transmission Electron Microscopy [9].

3.3.2 Transmission Electron Microscopy

A TEM consists of a tall column containing an electron gun (at the top of the column), an assembly of magnetic lenses and limiting apertures. This is shown
schematically in figure 3.4. Also shown in this figure are the specimen stage and the viewing area. The entire column is maintained under vacuum (to better than $10^{-4}$ Torr) to reduce the effects of the energetic electrons colliding with air molecules and deviating from their path. Keeping the system under vacuum is also essential to prevent the filament from burning out or contamination, but hydrocarbon build-up on the sample is a possibility when using “wet” pumps, such as diffusion pumps, rather than dry pumps e.g. ion pumps.

What follows is a brief description of the components that comprise a modern day TEM and their specific roles within the microscope.

### 3.3.2.1 The Electron Gun

The electron gun is the source of energetic electrons in the TEM and can be classified into two general forms: thermionic or field-emission guns. The TEM that was used throughout this study was a thermionic electron source and, as such, this is the only type of source that will be discussed here.

In a thermionic electron source, such as a W or LaB$_6$ filament, the filament is heated to a temperature so that the electrons have a sufficient energy to overcome the natural energy barrier. This barrier energy is termed the work function and materials such as LaB$_6$ that have low work functions are ideal materials to use in the formation of electron emitting filaments. The electron source filament is used as a cathode in a triode gun arrangement as shown in figure 3.5. The cathode is mounted in a Wehnelt cylinder that contains a small, axially aligned, aperture. The anode is a flat plate containing an axially aligned aperture.
Figure 3.4: Simplified ray diagram of TEM column operating in imaging (left) and diffraction (right) modes. The positioning and arrangement of lenses and apertures are clearly seen with respect to each other. The diagram is not drawn to scale.
A large negative potential is applied between the cathode and the anode (typically 100 kV or greater) whilst the Wehnelt has a slight negative bias placed upon it with respect to the cathode. As electrons are thermionically emitted from the cathode, they are slightly “focussed” by the Wehnelt before being accelerated by the potential difference between the cathode/Wehnelt and the anode. At some point between the Wehnelt and the anode, a crossover of the electron beam occurs and it is this crossover point that acts as the illumination source for the rest of the optical system.

3.3.2.2 Magnetic Lenses

In modern microscopes, the main types of lenses are magnetic lenses, the notable exception being the Wehnelt cylinder that acts as an electrostatic lens. The reason for this is that magnetic lenses are more reliable, have no electrical breakdown and have better aberration characteristics.

Magnetic lenses are constructed from a cylindrical core of a “soft” magnetic material, such as iron, with a hole bored through it. This assembly is known as the
polepiece. A coil of copper wire is wound around the core through which a current is passed inducing a magnetic field in the bore of the polepiece. By varying the current through the copper wire, the strength of the magnetic field can be altered.

Since the first magnetic lens was produced in 1926, although there have been many strides in progress to achieve better magnetic lenses, they are still far from perfect. The imperfections that are inherently produced during the manufacture of magnetic lenses all limit the resolution of the microscope. There are three main defects that substantially affect the performance of the microscope: spherical aberration, chromatic aberration and astigmatism.

3.3.2.2.1 Spherical Aberration, $C_s$

Spherical aberration occurs as a result of the inhomogeneous magnetic field acting on the off-axis electrons. The electrons further away from the optical axis of the microscope are more strongly deflected back and are focussed at different points along the optic axis. This has the effect of taking a curved wavefront (the electron beam illumination) and curving it further. When imaging point objects, this has the result of producing a disk of a finite size which ultimately reduces our ability to magnify any detail due to degradation of the image. Spherical aberration is most important in the objective lens because it degrades the image that is viewed in the TEM.

3.3.2.2.2 Chromatic Aberration, $C_c$

This form of aberration is related to the wavelength, and hence energy, of the electron beam – hence the term chromatic. Modern microscopes are supplied with very stable high voltage supplies meaning that there is very little deviation in the electron energy at the source leading to little chromatic aberration. It is safe to say
that as there is very little instability in the voltage supply, we have an almost monochromatic electron beam. The beam is not truly monochromatic as there is an inevitable spread of energies from the electron gun itself. This is true until a sample is placed into the path of the beam. Due to scattering effects, electrons with different energies exit the specimen’s exit surface resulting in a more chromatic beam than entered the specimen. This effect is worse for thicker samples emphasising the need, again, for thin samples.

3.3.2.2.3 Astigmatism

Astigmatism occurs due to a non-uniform magnetic field that affects the electrons during their path along the optic axis. The defect generally arises from either the inability to machine polepieces to be perfectly cylindrically symmetrical along the bore of the polepiece; or from inhomogeneities in the iron creating localised variations in the magnetic field strength. In older microscopes astigmatism could also result from electrically charged contamination on apertures.

Fortunately astigmatism can be easily corrected for through the use of small octupole magnets known as stigmators. The stigmators produce a compensating field that balances out the astigmatism from the main lenses.

3.3.2.2.4 Condenser Lens System

The condenser lens system consists of more than one physical lens and is located at the top of the optical column as shown previously in figure 3.4. The main role of the condenser lens system, in conventional TEM, is to form a focussed beam of electrons at the upper objective lens focal point to allow a near parallel electron beam to be incident upon the sample. A near parallel beam is preferred as the beam is
then as coherent as possible and this will produce the sharpest diffraction patterns and produce images with the best contrast.

3.3.2.2.5 Objective Lens System

The objective lens system is the most important element within a TEM. It is this lens system that takes the electrons emerging from the exit surface of the sample and forms a diffraction pattern in the back focal plane of the lens before reforming the image in the image plane.

The objective lens is a very strong lens with a short focal length producing a magnified image at its focal plane.

3.3.2.2.6 Intermediate Lens System

The intermediate lens is adjusted to allow either the diffraction plane or the image plane to be imaged by making either of these planes into its object plane. The image is magnified again at this stage. The back focal plane of this lens is set at the object plane of the final group of lenses in the TEM – the projector lens.

3.3.2.2.7 Projector Lens System

The projector lens system is a lens group that takes a magnified image in its object plane and reproduces this image in its back focal plane which is co-planar with the a viewing screen allowing the user to see the selected image. This system of lenses is also the main magnifying group of lenses and it is at this stage when the image may be magnified from several hundreds of times to several hundred thousand times.
3.3.2.3 Apertures

Apertures are often used in TEM and they have many different uses. Apertures are used in the condenser lens, the objective lens and the intermediate lens.

3.3.2.3.1 Condenser Lens Aperture

The condenser lens aperture is used to limit the convergence angle of the beam before it is incident on the specimen. As a result of this, the aperture controls the illumination of the beam.

3.3.2.3.2 Objective Lens Aperture

The objective aperture is placed in the back focal plane of the objective lens and its primary use is to select the electrons that will contribute to the final image. This aperture can be used to alter the contrast and the resolution of the final image.

3.3.2.3.3 Intermediate Lens Aperture

This aperture is better known as the selected area, or field limiting, aperture and is a very useful aperture in the TEM system. This aperture is used when the user wishes to take image or diffraction patterns from a certain area of the specimen. Obviously this cannot be done by placing an aperture around the specimen as the specimen itself prevents this possibility. The method that is used to bypass this problem is to place an aperture at a focal plane of the image thereby producing a “virtual” aperture at the specimen. When this is done correctly, i.e. the system is co-planar, only information within the aperture will be imaged, including the local diffraction pattern.
3.3.2.4 Electron/Solid Interactions

With an electron beam incident upon a solid target, the electrons of the beam are either transmitted as an undeviated beam or they are scattered becoming absorbed, reflected or transmitted in the process. In TEM information is obtained using the electrons that have been transmitted as either an undeviated beam or as scattered beams. In order for this to happen the target must be sufficiently thin (for the given electron beam energy) so that a significant fraction of the electrons are transmitted.

The electrons that are scattered within the sample may be scattered by either elastic or inelastic means. When elastically scattered the electrons do not lose any energy and only their path is changed. Electrons scattered inelastically transfer some of their energy causing excitation or ionization of the bound electrons, excitation of the (quasi-) free electrons or lattice vibrations and possibly heating or radiation damage of the specimen.

Atoms that make up the target material may scatter electrons differently depending on the target atoms and it is this difference in scattering which is utilised in the production of contrast in the TEM. The different forms of scattering events that occur in electron/solid interactions will now be introduced.

3.3.2.4.1 Elastic Scattering

During elastic scattering events, there is no energy transfer from the electron to the target atoms and only a change in momentum occurs. There are two forms of elastic scattering events that occur: incoherent and coherent scattering.

During incoherent scattering events, the scattering is random and as such there is a phase change in the scattered electron wave with respect to the incident
wave. This is the primary elastic scattering mechanism for amorphous materials and polycrystalline materials consisting of very small grains (\(\sim 2\) nm).

For materials that are polycrystalline with medium to large sized grains (2 – 10 nm) or fully crystalline materials, the main elastic scattering mechanism is the coherent scattering mechanism. All waves that are scattered coherently throughout the crystal have well defined phase relationships with each other and with the incident electron wave. This tends to interference over large angles and leads towards electron diffraction effects that will be discussed in §3.3.3.

3.3.2.4.2 Inelastic Scattering

During inelastic scattering there is an energy loss in the scattering event whereby energy is transferred from the incident electron beam to the sample as mentioned previously (§3.3.2.4). The most important of these losses is the plasma excitation of electrons, or plasmon generation. In this mechanism, the incoming electron causes the electrons in the valence band of the target material to oscillate collectively. The scattered electron produced following the generation of a plasmon contains no structural information and is scattered at very small angles (and hence cannot be removed through the use of an aperture) and as such produces a diffuse contribution to the diffraction pattern or image.

The mean free path for the generation of plasmons is \(\sim 100\) nm for incident electrons of 100 keV energy and it is highly probable for a large fraction of the transmitted electrons from specimens of the order of 100 nm thick to be inelastically scattered for 100 keV electrons. The production of inelastically scattered electrons can be reduced by increasing the electron beam energy or by using thinner specimens.
Scattering events such as excitation and ionization can be ignored as these interactions do not contribute much to the energy loss compared to the energy loss produced by plasmon generation, especially in specimens composed of light atoms. These scattering events also have comparatively large scattering angles and can thus be reduced through the introduction of apertures.

### 3.3.3 Electron Diffraction and Diffraction Patterns

Electron diffraction in the TEM uses a monoenergetic electron beam, incident upon a thin specimen to interfere and form an interference pattern comprising of many diffracted beams being imaged as a series of spots on the viewing medium (photographic film or the screen). The resulting diffraction patterns are very useful to the materials scientist and can be used to yield information such as the crystallinity of the sample i.e. is the sample crystalline or amorphous, the crystallographic characteristics of the sample such as the lattice parameter and symmetry, and the orientation of the sample. This ability to determine the crystallographic orientation is useful in aligning specimens into certain orientations for specific imaging conditions.

Electron diffraction occurs in crystals as a result of the elastic scattering of electrons off the atomic planes in the crystal. This is Bragg scattering and diffraction will be discussed here in terms of Bragg scattering off atomic planes and then expanded for the case of real crystals. Real diffraction patterns formed by silicon will then be discussed.

### 3.3.3.1 Scattering from Crystals/Bragg’s Law

In electron diffraction, planar waves of monochromatic electrons can be considered to be reflected off planes of atoms rather than being scattered from individual atoms.
What follows is a derivation of Bragg’s law and this is largely taken from Williams and Carter [1]. The simplified diagram in figure 3.6 shows an initial wavefront, $\omega_I$, being scattered by two planes of atoms to produce a deviated wavefront, $\omega_D$. Whether this deviated wavefront is truly diffracted or not depends on whether or not the atomic planes are scattering in phase which is determined by the angles between the incident beam, the diffracted beam and the atomic planes.

The diagram is easy to analyse if it is simplified and we introduce the notion of wave vectors, $\mathbf{k}$. At this point it is assumed that the wavefront is planar and that $\mathbf{k}$ is normal to this wavefront. Figure 3.7 defines the wave vectors $\mathbf{k}_I$ (incident wavefront), $\mathbf{k}_D$ (diffracted wavefront) and $\mathbf{K}$. Through vector addition we can write the equation:

$$\mathbf{K} = \mathbf{k}_D - \mathbf{k}_I \quad (3.1)$$

where $\mathbf{K}$ is the change in $\mathbf{k}$ due to diffraction. It should be noted that this holds for any $\mathbf{k}_D$ and, as such, for any value of $\mathbf{K}$ meaning that the angle $\theta$ is not necessarily the Bragg angle.

Provided that the scattering process undergone by the electron is elastic, it can be stated that:

$$|\mathbf{k}_I| = |\mathbf{k}_D| = \frac{1}{\lambda} = |\mathbf{k}| \quad (3.2)$$

and it can be written that, using simple trigonometry from figure 3.7
Figure 3.6: Scattering from two planes of atoms. $w_1$ is the incident wavefront and $w_D$ is the diffracted wavefront [1].

\[ \sin \theta = \frac{|\mathbf{k}|}{2|\mathbf{k}_i|} \]  

(3.3)

or, rearranged using equation 3.2 as

\[ |\mathbf{k}| = \frac{2\sin \theta}{\lambda} \]  

(3.4)

If this is now extended to the situation of scattering from two single points that can be considered to be two atomic sites, we have the situation as shown in figure 3.8. It should be obvious from this diagram that constructive and destructive interference may occur. We can now define two planes to be normal to the vector $\mathbf{CB}$, which has a length $d$. 


Figure 3.7: Analysis of wavefronts using vector notation. \( \mathbf{k}_i \) and \( \mathbf{k}_D \) are the incident and diffracted wavefront vectors respectively and \( \mathbf{K} \) is the resultant vector [1].

The distance travelled by ray \( R_1 \) is larger than that travelled by ray \( R_2 \) by a path distance of \( AC + CD \) and it can be seen, using simple geometry, that

\[
AC + CD = 2d \sin \theta \quad (3.5)
\]

The path length \( AC + CD \) is \( n\lambda \) where \( n \) is any integer giving

\[
n\lambda = 2d \sin \theta \quad (3.6)
\]

We can now define the Bragg angle, \( \theta_B \), to be the angle at which the electron waves will constructively interfere and we can replace this for \( \theta \) into equations 3.4 and 3.6 giving

\[
|\mathbf{K}| = \frac{2d \sin \theta_B}{\lambda} \quad (3.7)
\]

And
Figure 3.8: Scattering of two beams from two points lying on different planes. The beams travel different distances leading to a path difference of AC+CD [1].

\[ n\lambda = 2d \sin \theta_B \]  

(3.8)

Equation 3.8 is Bragg’s law of diffraction and can be related to the wave vector by combining and rearranging equations 3.7 and 3.8 to yield

\[ \lambda |\mathbf{K}| = 2\sin \theta_B \]  

(3.9)

and we can say that at the Bragg angle, the wave vector \( \mathbf{K} \) has the value, \( \mathbf{K}_B \), and its magnitude is related to the interplanar distance by

\[ |\mathbf{K}_B| = \frac{1}{d} \]  

(3.10)
and we define this vector, $\mathbf{K}_B$, to be $\mathbf{g}$ which may also be referred to as the Bragg vector.

Bragg’s law gives a useful physical interpretation of the diffraction process as the diffracting planes of the specimen behave as mirrors for the incident electron beam. For this reason, the diffracted beams (the visible spots in the diffraction spots produced) are called reflections.

If we extend the case above from two parallel planes to many parallel planes separated by distance $d$, it can be seen, as shown in figure 3.9, that not only one Bragg reflection will be seen, but a series of reflections periodically spaced along a line. Each of these reflections is equally spaced by $\mathbf{g}$ and this vector is always perpendicular to the diffracting planes.

These higher order reflections ($ng$ when $n \neq 1$) are extremely useful in TEM especially during weak-beam dark-field imaging which will be discussed in §3.3.4.4.

### 3.3.3.2 Real Diffraction Patterns

As stated earlier, in §3.3.2, the electrons that exit the back surface of the specimen form a diffraction pattern in the back focal plane of the objective lens in the TEM. The intermediate lens then uses the back focal plane of the objective as its image plane and magnifies the diffraction pattern onto the viewing screen. In this section, real diffraction patterns for silicon will be discussed. Although in the experiments performed throughout this thesis only (001) Si was used and the images and diffraction patterns presented were all taken along the [001] zone axis (the specimen was set up in diffraction mode to be aligned in the [001] direction), the three lowest order indices will be discussed.

The diffraction pattern arising from the [001] crystal orientation is shown in figure 3.10a.
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Figure 3.9: Scattering from a set of planes, each planes separated by a distance $d$. When set into the Bragg condition, the diffraction spots formed are displaced by vector $g$ apart normal to the diffracting planes [1].

Here the spots are arranged in a regular square pattern with a $A/B$ ratio of $\sqrt{2}$. This ratio, and the subsequent ratios for other indexes, can be used to accurately determine the correct crystallographic orientation if there is some ambiguity of the orientation.

Shown in figure 3.10b is the diffraction pattern that arises from a [110] orientation. The $B/A$ ratio in this case is 1.155. Figure 3.10c shows a [111] diffraction pattern and it can be seen that the diffracted spots are equidistant from each other (for each $n$) giving a ratio of unity.

3.3.4 Diffraction Contrast

When imaging in diffraction contrast, the defects are imaged through a deviation in the elastic strain field of the defect in question. In order to image in diffraction contrast, the crystal is set at some well-defined diffracting condition and
an objective aperture is used to form an image using one of the many diffracted beams.

Figure 3.10: Figure showing the three lowest order diffraction patterns for Si. Shown are the diffraction patterns for [001] (a), [011] (b) and [-1-11] (c). Each figure also shows the planes from which selected spots have arisen from.

In this condition, the image is sensitive to differences in the specimen thickness and distortion of the crystal lattice due to defects, strain or bending. In the case of
imaging defects, the main objective of this thesis, the defect strain field causes local distortions in the diffraction conditions by bending the diffracting planes causing changes in the diffracted beams’ amplitude which is then seen in the image. The size of the objective aperture used ultimately determines the information that may be determined in the image. In this section we will introduce different image conditions.

3.3.4.1 Bright-field Conditions

There are two basic modes of operation of imaging in the TEM: bright-field imaging and dark-field imaging. Probably the most widely used condition is the bright-field imaging as this is used extensively throughout materials and biological science. To obtain a bright-field image an aperture is placed into the back focal plane of the objective lens in such a manner that only the un-diffracted electron beam is selected for image formation. This is done in such a manner that both the un-diffracted beam and the objective aperture lie along the optical axis of the microscope, reducing astigmatism in the final image.

3.3.4.2 Dark-field Conditions

As is the case for bright-field imaging, an objective aperture in the back-focal plane is used to select an electron beam. For a dark-field image, this is a diffracted beam. Here only the selected scattered electrons contribute to the final image. Again, the dark-field image is set up so that the diffracted beam and the objective aperture are made to lie along the optical axis of the microscope – so-called centred dark-field imaging, this being done again to reduce the astigmatism in the final image. Dark-field images are less affected than bright-field images by the presence of other diffracted beams, thus generally have a higher contrast.
A commonly used extension of this condition is the weak-beam dark-field condition that shall be described in more detail in §3.3.4.5.

### 3.3.4.3 Down-zone Conditions

In order to image in down-zone conditions, the specimen foil is tilted into such a condition that zone-axis orientation is achieved and several of the diffracted beams are equally excited. The zone-axis orientation used is generally a low-order index zone. Images obtained in this condition are named “down-axis” or “down-zone bright-field” images and have historically been termed kinematical images.

### 3.3.4.4 Two-beam Conditions

The two-beam condition is useful in TEM as the contrast produced using this condition is sensitive to the weak lattice strains making it well-suited to the investigation of symmetry and sign of the long-range elastic strain fields produced by small clusters.

The two-beam condition is set such that one particular set of diffracting planes \((hkl)\) is at, or close to, the Bragg condition. This is achieved by tilting the foil very slightly so that both the un-diffracted beam and the diffracted beam from the \((hkl)\) planes are both strongly, and equally, excited. From this initial condition, both bright-field and dark-field images may be attained.

Under these strong two-beam conditions, there is a strong dynamical interaction between the two strongly excited beams and the resulting image characteristics may be complicated.
3.3.4.5 Weak-beam Dark-field Conditions

Weak-beam dark-field imaging is a dark-field image obtained using a weakly-excited beam. In order to obtain this condition, the sample is tilted to a relatively high angle to such an extent that the majority of crystalline diffraction planes are far from the normally desired Bragg condition. The contrast that appears as a result of the weak-beam dark-field condition arises from the regions close to defects where the local strain field may distort the diffracting planes close to the defect so that they may satisfy the Bragg condition. As the majority of the diffracting planes in the crystal are not satisfying the Bragg condition, the overall intensity of the image is very low. Around the defects where the Bragg condition is now being satisfied, there is a substantial enhancement of the intensity relative to the surrounding background, resulting in a local image peak of high relative – but low absolute – intensity. Weak-beam imaging has been successfully used to image line dislocations, dislocation loops and other small centres of strain.

From a practical standpoint it should be noted that the gun tilt of the microscope should be altered such that the highly diffracted beam that is to be used for the imaging is centred along the optic axis, along with the objective aperture used to select this beam. This is done so that the aberrations are minimised.

3.3.5 Structure-factor Contrast

Structure factor contrast was first fully described by Ashby and Brown [10] with regards to inclusions. This technique may be used in different modes such as, for example two-beam, but when utilized under the down-zone bright-field condition, the resolution of disordered/amorphous zones is maximized [11].
In order to observe the spatially isolated amorphous regions within the crystalline lattice, diffraction contrast is utilised. If we consider an inclusion in a crystal matrix having an extinction distance \( \xi_g \) different from the matrix extinction distance of the inclusion \( \xi_g \) (the extinction distance being a characteristic length for a given diffraction vector that is dependent upon the lattice parameters, atomic number and the electron beam acceleration voltage), a difference, \( \Delta I \), in transmitted intensity, \( I \), occurs at the inclusions [10].

The extinction distance is a function of the structure factor and for amorphous material becomes infinite. The difference has a maximum at the exact reflecting position given by:

\[
\frac{\Delta I}{I} = -\pi \Delta \left( 1 - \frac{1}{\xi_g} \right) \sin \frac{2\pi t}{\xi_g} \tag{3.11}
\]

where \( t \) is the foil thickness containing the inclusion of thickness \( \Delta t \). Amorphous zones created by ion implantation leads to \( \xi_g = \infty \)

\[
\frac{\Delta I}{I} = +\pi \Delta \frac{\Delta t}{\xi_g} \sin \frac{2\pi t}{\xi_g} \tag{3.12}
\]

This means for a wedge shaped foil, the amorphous zones should show as white or black zones at the edges of fringes produced in the wedge [10]. This is shown graphically in figure 3.11.

As stated previously, although structure factor imaging allows the zones to be seen with good contrast in many different modes, the most commonly used modes
are two-beam and down-zone. The down-zone condition is the optimum condition to use when viewing damage zones due to the increase in the gradient of the transmitted intensity oscillation profile i.e. reducing the effective extinction distance [11] which allows for smaller zones to be observed and a greater resolution of all observable zones. In general, the assumption has been made in the literature that heavily damaged (crystalline) regions would not exhibit structure-factor contrast, however, it will be shown in §4.4.4 that this assumption is incorrect.

**Figure 3.11:** Variation in transmitted intensity as a function of foil thickness for a wedged specimen (a). (b) shows how this transpires into a real image showing light and dark fringes with zones visible at the edges of the fringes. (c) shows a TEM micrograph of a wedged specimen with the fringes and zones visible.
3.4 IRRADIATION FACILITIES

3.4.1 In situ Irradiations

In situ irradiation experiments within the TEM have played a significant role in radiation damage studies. A side effect of using the TEM for radiation damage studies is the fact that the electron beam itself may cause knock-on damage if the electron energy is sufficiently high. The threshold energy for this knock-on damage is dependent upon the material and irradiation direction, the threshold energy ranging is generally accepted to be 145 keV for silicon [12] but in some studies has also been found to be up to 280 keV [13] but this is likely to be an instrument error as it seems extremely high. In high voltage electron microscopes (HVEM) operating at around 1 MeV, displacements are produced in all materials. In such microscopes, displacement rates of 0.01 dpa s\(^{-1}\) may be achieved which are much greater than possible rates achievable for typical neutron irradiations. Due to this large dpa rate, large doses can be achieved within a single day, for example a dose of 100 dpa may be reached in a single day’s irradiation in a HVEM – equivalent to almost 30 years within a nuclear reactor. Through selection of cooling or heating stages for the microscope, to regulate sample temperature, it is possible to perform systematic experiments to investigate the behaviour of defects during irradiation for a wide range of irradiation conditions, over a relatively short time scale. This damage may also be observed during the irradiation enabling the monitoring of defect behaviour in real-time, see for example [14].

Characteristically produced as a result of electron irradiation, point defects are formed, largely as isolated Frenkel pairs. The main interest throughout this thesis is the damage formed as a result of ion irradiation, which produces damage in the
form of cascades, see §2.4. Ions may be formed in a TEM through several mechanisms. They may be formed in the TEM at the filament accidentally or deliberately at the filament through the coating of the filament with an oxide layer. This “gun-damage” is generally unwanted and most modern instruments have been designed to avoid this problem. Some microscope/accelerator facilities have been constructed in order to fully exploit in situ ion irradiations under controlled conditions. One of these is the facility available at Argonne National Laboratory (ANL) and it was at this facility that all the experiments reported in this thesis were performed. This facility was originally based around a 1.2 MeV Kratos EM7 HVEM, but now is based around a higher-resolution 300 keV Hitachi H-9000 NAR intermediate-voltage electron microscope (IVEM). In the next section, this facility is fully described.

3.4.2 In situ Irradiation Facilities at Argonne National Laboratory

The microscope/accelerator facility at ANL consists of an IVEM interfaced to two ion accelerators to allow for in situ ion beam studies involving ion beam damage. The microscope is a Hitachi H-9000 NAR IVEM with accelerating voltages of between 100 – 300 keV. Point-to-point resolution at 300 keV is 0.25 nm, with image recording available through either Kodak SO-163 film or S-VHS videotape recording through a Gatan 622 image intensified camera. Specimen holders are available at this facility that allow for double-tilting of the sample over a temperature range between 15 K and 1000 ºC.

Interfaced with the Hitachi TEM are two ion accelerators that allow ion masses between H and Pb at energies from 20 keV to 4 MeV (when the ion is double charged) to irradiate the samples. The accelerators providing these ions and energies
are a 650 keV NEC Ion Implanter and a 2 MeV Tandem accelerator. The ion mass and energy are limited due to the bending magnet that directs the ions from the accelerators into the microscope. The ions enter the microscope at an angle of 30° to the electron beam. At the sample position, the ion beam has a diameter of ~1.5 mm and the dose is measured by a Faraday cup located at 2 cm from the specimen allowing an accuracy of the dose in the order of 10 – 15% [15]. Typically, the flux at the specimen is $1 \times 10^{12}$ ions cm$^{-2}$ s$^{-1}$. Figures 3.12 and 3.13 show the IVEM/accelerator facility with the ion beam interface whilst figure 3.14 shows a diagram of the Faraday cup with respect to the specimen rod and objective pole pieces.

Figure 3.12: Photograph of the IVEM/Accelerator at Argonne National Laboratory.
Figure 3.13: Close up photograph of the ion-beam - IVEM interface.

Figure 3.14: Diagram of the internal components of the ion-beam - electron-beam - specimen interface.
3.5 **Electron Beam Effects**

During viewing of the samples in the TEM, the electron beam may have unwanted effects on the sample that may distort results. The effects include electron beam heating and electron beam induced dynamic annealing of the disordered zones produced during ion implantation.

During viewing of a sample in an electron microscope, the electrons lose energy as they pass through the samples as a result of interactions with the atomic electrons [16]. During each interaction of the energetic electron with the atomic electrons, the energy transferred to the atom during the collision is very small. The most probably outcome is excitation of the atomic electrons resulting in an energy loss of a few eV from the energetic electron. The total energy loss of the energetic electron would then be as a result of a number of interactions as the electron passes through the sample. It is during this energy loss process that energy is passed through to the sample as activation of plasmons, as discussed in §3.3.2.4.2, vibrations [16] resulting in heating of the sample.

Fisher [16] developed a model for the heating of samples during TEM viewing in the energy range of 100 keV to 1 MeV based on the theory of Bethe and the model described by Gale and Hale. The resulting expression is given as:

\[
(T_m - T_0) = \frac{I_0 \Delta E a^2}{4kd} \left[v_0 + \log_e \left(\frac{b}{a}\right)^2\right]
\]

where \(T_m\) is the maximum rise in temperature, \(T_0\) is the temperature of a circular conductor (approximately 3 mm for a TEM sample), \(I_0\) is the beam flux at the
sample, $\Delta E$ is the energy loss, $k$ is the thermal conductivity of the sample, $d$ is the thickness of the sample in cm, $\nu_0$ is Euler’s constant, and $a$ and $b$ are the radii of the conductor and electron beam respectively.

The results presented by Fisher show that the temperature rise in metallic foils using reasonable illumination is $\sim 30$ K for samples under 1 MeV electron irradiation. This approximate rise in estimated temperature is highly dependent on the model which assumes that the sample is a cylindrical slice and a perfect conductor. Work done by Bench [17] shows that the effect of beam heating on GaAs samples for room temperature ($T = 300$ K) and at low temperature ($T = 30$ K) for different acceleration voltages. These are summarised in table 3.1 below. It is evident from this table that although the temperature rise may be significant, the rise in temperature should not affect the result of the experiments especially with the electron beam not being incident on the sample as is the case for the amorphization and isochronal annealing experiments performed. During the dynamic annealing experiments, the only experiments where the electron beam is incident upon the sample during the entire duration of the experiment, the percentage temperature rise is small and therefore it can be considered that the electron beam heating affect during this series of experiments does not affect the integrity of the results presented here. In fact, the thermal conductivity of Si is much better than that of GaAs and the maximum temperature rise would be expected to be less than that of GaAs.

Another problem associated with the electron beam is the re-growth of the disordered zones occurring below the displacement threshold energy of the sample [12, 18-22]. Jencic and Robertson [12] studied the behaviour of amorphous zones in Si, Ga and GaP as a function of electron energies ranging from 25 to 300 keV. In all
materials it was found that re-growth occurred at all energies with a minimum re-growth rate below the displacement threshold energy in each case.

Table 3.1: Maximum temperature rise in a GaAs sample for given ambient temperatures and electron energies. From [17].

<table>
<thead>
<tr>
<th>Ambient Temperature (K)</th>
<th>Electron Voltage (keV)</th>
<th>Maximum Temperature Rise (K)</th>
<th>Percentage Temperature Rise</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>300</td>
<td>11.2</td>
<td>3.73</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>19.7</td>
<td>6.57</td>
</tr>
<tr>
<td>300</td>
<td>50</td>
<td>31.4</td>
<td>10.47</td>
</tr>
<tr>
<td>30</td>
<td>50</td>
<td>&lt;4</td>
<td>13.33</td>
</tr>
</tbody>
</table>

For Si the minimum re-growth rate occurred at approximately 100 keV, as shown in figure 3.15, somewhat below the electron displacement threshold energy of between 145 and 280 keV [12, 13]. For this reason, an acceleration voltage of 100 keV was used throughout the experiments and where possible the electron beam was not incident upon the sample. It should be noted here that early experiments showed that it was not possible to amorphize the sample when imaging the sample simultaneously, even at low temperatures.

![Figure 3.15: Graph showing the re-growth rate of amorphous zones in Si as a function of electron energy.](image)
3.6 **IMAGING RECORDING**

Images were either recorded directly onto photographic film or onto S-VHS videotape. The photographic film that was used was the standard Kodak SO 163. This film is designed to allow microscopists to change the speed and granularity by changing the exposure and processing conditions to meet their needs and it gives the best compromise between speed and resolution. The film can be used to obtain good images from both stable and unstable specimens. With stable specimens, the electron exposure can be increased leading towards better density and contrast during processing, resulting in minimum granularity in the film and a better signal-to-noise ratio. With unstable specimens, shorter exposure time can be used with a good image being produced but with a less than optimum grain size in the image as a result.

Images were also recorded onto S-VHS videotape using a Gatan 622 camera and image intensification system. This system comprises a YAG crystal at the bottom of the TEM column fibre-optically coupled to an image intensifier which is again fibre-optically coupled to a television camera with a cadmium zinc telluride target giving high resolution and sensitivity plus extreme resistance to blooming and photocathode damage. The images were then recorded onto S-VHS videotape using an S-VHS video recorder with a frame rate of 30 frames per second.
3.7 IMAGE ANALYSIS

Images were either recorded on film or on S-VHS videotape as discussed previously. Real-space images were captured on both film and videotape whereas diffraction patterns were captured on film only.

Images that were caught on film were digitally scanned into a computer using an Epson Perfection 2450 Photo scanner at 600 dpi. The images were then imported into Adobe Photoshop 6.0 for analysis. In Photoshop, each image was enhanced by performing a high pass filter, adjusting the levels so the brightest pixel in the image is white and the darkest was black and then performing a Gaussian blur with a 1 pixel radius in order to remove high spatial frequency noise before individual amorphous zones were drawn around manually on a separate layer. Then, using additional filters in Photoshop, the area of each individual zone was measured.

Films of the diffraction patterns obtained were scanned in and imported into Photoshop as described above. Using tools within Photoshop, intensity line scans were taken through the central spot of the diffraction pattern to past the region of the second amorphous ring (using Photoshop as a densitometer). The results of the line scan were then exported into Microsoft Excel. In Excel, the background of the intensity profile was removed giving the intensity profile of the amorphous rings only. The area beneath these intensity peaks was then integrated and normalised to the fully amorphous ring intensity and plotted as a function of ion dose.

Images that were captured on videotape were digitised by frame averaging through a Nippon Avionics Co., Ltd. Avio Image Sigma-II Realtime Digital Image Processor. Annealing experiments were digitised with an 8 frame average whilst amorphization experiments had a 32 frame average. The video was captured on a
computer using Adobe Premiere 5.0 and individual frames were captured for analysis in Photoshop as described previously.

3.7.1 Analysis of Debye-Scherrer Rings

During the amorphization experiments, diffraction patterns were recorded onto film negatives with various exposure times at different fluence steps. The developed negatives were scanned into a PC at a resolution of 600 dpi and saved as tiff files. Using Adobe Photoshop CS, a 15 pixel wide intensity profile was taken (using plug-ins available from the Image Processing Handbook [23]) across the width of the negative, ensuring that the profile passed through the central spot but avoided diffracted beam spots (as shown in figure 3.16) to measure the intensity of the amorphous ring as it begins to appear. The width of 15 pixels was chosen to give a reasonable signal-to-noise ratio whilst enabling diffracted spots to be avoided.

The intensity profile was then exported to Microsoft Excel. Using MS Excel, the background intensity was removed using a simple exponential function after which the amorphous peaks were integrated. An example of the background removal and the region of interest that is integrated is shown in figure 3.17. After obtaining the integrated intensities for all the fluences, each fluence step was then normalised to that of the completely amorphized intensity in order to generate amorphous fraction curves as a function of ion fluence. This was done for all exposures.

When analysing the diffraction patterns taken during the experiments, several assumptions are made. With regards to the actual recording of the diffraction pattern onto film negatives, it is imperative that the exposure of the amorphous ring is in the linear response portion of the exposure-intensity curve. The film used in the investigations presented in this thesis was Kodak SO-163 film and work by Bench
[17] on the linearity of this film during various exposure times has shown that as long as the most exposed regions recorded onto the film are not represented in the digitised negatives by pixels values of $\leq 6$ (when the negative is digitised with 16-bits leading to 256 levels, with 0 being black and 255 being white and in-between values being varying shades of grey), a linear response is ensured. It is also possible, using this type of film, to vary the contrast in the image by changing the processing conditions and for this reason, all the exposures taken in any given experiment were all processed at the same time to ensure that there was no change in contrast due to small changes in the processing step.

Another assumption is made during the actual digitisation of the negatives. The negatives were digitised using an Epson Perfection 2450 Photo scanner equipped for high quality scanning of negatives. It is assumed that the response of the scanner is linear and that there is no loss of image quality during the digitisation process.

Figure 3.16: Figure showing the scan region from which the intensity profile of the amorphous rings was obtained.
Figure 3.17: Graph showing a typical intensity profile through an amorphous diffraction pattern as obtained through the method described in the text.
3.8 REFERENCES


4 Annealing of Isolated Damage Zones
4.1 INTRODUCTION

In this chapter, we describe the results of annealing experiments performed on spatially isolated damage zones produced by low fluence ion irradiation of silicon. Two different types of annealing experiments were performed: isochronal and dynamic.

Through detailed analysis of the results from these experiments, the structural configuration of the zones produced is inferred, with TEM image simulations also used to confirm the results.

By the end of the chapter, it will have been indicated that the different annealing curve characteristics shown in the results may be explained in terms of the IV pair or “bond defect” in various configurations and concentrations.
4.2 BACKGROUND

In §2.5.6 we discussed the literature available on research regarding the annealing of non-planar $a$-$c$ interfaces. In this chapter we will be presenting and discussing the results obtained on the thermal annealing of small damage zones that arise through low fluence ion bombardment. In the literature discussed previously, it was shown that there have been two sub-sets of experiments that have been performed on the damage zones produced by low fluence irradiations: thermal and electron beam annealing; both of which are extremely relevant to the work described in this chapter.

The work done on the electron beam annealing [1-6] of the isolated zones formed by the low fluence irradiations are extremely important from an experimental methods point of view as it is necessary, when using an electron beam to image the zones, to reduce this effect. In order to reduce the effect, it was determined that the optimum electron beam energy was 100 keV and this is the energy that was used throughout the work reported in this thesis. Also during this work, it was determined that the interaction region that resulted in the re-crystallization of the zones was the surface of the zone.

The thermal annealing of zones (assumed to be amorphous) was performed in situ at Argonne National Laboratory, USA [7]. During these experiments, it was also observed that the zones did not re-crystallize in a manner similar to that of planar $a$-$c$ interfaces – a result that had also previously been observed through ex situ experiments [8]. Instead of annealing with a single, well-defined, activation energy, the zones annealed with a variety of activation energies implying that the zones were re-crystallizing under a different mechanism than planar $a$-$c$ interfaces, or that the
defect responsible for initiating the re-crystallization was different to that of the planar interface case. Perhaps the most interesting observation reported by the authors [7], was that of an anomalous growth of the zone which occurred in a small number of cases. The authors postulated that the responsible defect in this case was the IV pair.

The IV pair has been discussed in detail in §2.4.4 where it was shown that the defect may be formed from purely ballistic means and that at a concentration of ~25%, the radial pair distribution function is essentially the same as that of amorphous silicon formed by quenching molten silicon.

At this point it is necessary to state that all the previous work done [1-11] has been performed on the annealing of damage, that has been produced by irradiation with relatively heavy ions (Xe ions and heavier), bounded by non-planar $a$-$c$ interfaces.
4.3 EXPERIMENTAL METHODS

In this section, the relevant experimental details pertinent to the experiments detailed in this chapter will be discussed in more detail than in chapter 3.

4.3.1 Sample Preparation and Mounting

Samples were prepared for TEM imaging from a <100> float-zone silicon wafer using the small angle cleavage technique [12-14] described in §3.2.2. Samples were then mounted within Mo oyster grids so as to avoid the use of any glues thereby reducing the contamination in the TEM.

Once mounted, the sample was placed into the TEM and imaged to ensure that no shadowing of the electron beam from the grid bars occurred. Samples that met this criterion were then thermally annealed at 600 °C for 5 minutes to reduce the movement in the grid during anneals. Movement of the grid, and hence the sample, occurred due to the annealing of strains induced in the grid during sample mounting.

Once the sample had returned to room temperature it was implanted in situ to a dose of 6.25x10^{11} for 400 keV and 50 keV Xe^+, 2.50x10^{12} for 275 keV Kr^+ and 6.25x10^{12} for 100 keV Si^+. These particular ion energies were chosen as the $R_p$ as predicted by TRIM [15] and hence the surface effects, if any, that occur during the irradiation should be similar for all the ions. At these doses, approximately the same areal density of damage zones was visible in each case.
4.3.2 Annealing Schemes

4.3.2.1 Isochronal Annealing

Once implanted to the fluences required, images were recorded onto photographic film at room temperature. Images were taken in bright-field down-zone at focus, down-zone bright-field underfocus, two-beam bright-field at focus and two-beam dark-field at focus. The different imaging conditions were used to see if there were any differences in the size of the zones observed although no differences were found. After the images had been recorded the electron beam was blocked so that it was not incident upon the sample. This was done to reduce the effect of electron beam induced re-crystallization [1, 3-6, 10] during the thermal annealing. With the electron beam not incident upon the sample, the thermal annealing of the sample was begun.

Thermal annealing was performed on the sample by the use of a Gatan double-tilt heating holder capable of attaining temperatures of up to 1200 K. This holder was controlled using a Gatan SmartSet model 901 controller. Using this equipment the sample was heated from room temperature up to 50 °C as quickly as possible (typically 1 minute) and maintained at this temperature for 10 minutes. After 10 minutes, the temperature was reduced to room temperature as rapidly as possible (typically 1 minute). Once the temperature had stabilized at room temperature, a series of images were recorded as before. This process was then repeated for a series of temperatures up to 600 °C.

4.3.2.2 Dynamic Annealing

Following implantation, the sample was imaged under down-zone bright-field conditions. During the anneal, the electron beam energy was set to 100 keV to reduce
the effect of e-beam annealing. The images were recorded directly onto videotape as the sample was subjected to a slow temperature ramp of 5 °C min⁻¹ using the same equipment as outlined above. The sample was ramped up to a temperature of approximately 400 °C whilst maintaining the same region of interest in view at all times allowing for the analysis of a few zones for each experiment.
4.4 RESULTS AND DISCUSSION

In this section, the results of the thermal annealing of spatially isolated damage zones produced by low dose ion implantation will be presented and discussed. The ions used were 50 or 400 keV Xe\(^+\), 275 keV Kr\(^+\) and 100 keV Si\(^+\), implanted to fluences of 6.25 x 10\(^{11}\) ions cm\(^{-2}\) for the Xe implantations, 2.50 x 10\(^{12}\) ions cm\(^{-2}\) for the Kr implantations, and 6.25 x 10\(^{12}\) ions cm\(^{-2}\) for the Si implantations. These fluences were chosen to produce a similar areal density of damage zones in each case, a reasonably large number of visible (in the imaging conditions used) zones and minimum occurrence of cascade overlap occurred.

The overall statistical and individual behaviour of damage zones following annealing was then monitored by tracking approximately 400 individual zones through the various isochronal annealing steps. In addition to the isochronal annealing, some dynamic annealing experiments were carried out in which the temperature of the sample was increased slowly at a rate of 5 °C min\(^{-1}\), the results of which were recorded onto videotape. During these dynamic annealing experiments, only a few individual zones can be followed due to the small size of the CCD detector allowing for a small field of view being recorded onto the videotape.

An interesting observation, made during the course of the experiments described in this section, was that when a pair of samples which had been irradiated with Si and Kr was left overnight in a darkened room at ~25 °C, the zones that had been observed only 18 hours previously had all re-crystallized.

This observation reinforces the need for *in situ* experiments to be performed in this subject area and highlights the importance of having such research facilities available.
4.4.1 Isochronal Annealing – Statistical Data

When looking at the statistical data of the annealing of the zones, we are only looking at whether a zone is present or not following each isochronal annealing step – not at the fine detail of the individual zone annealing. Figures 4.1 and 4.2 show the statistical data results for isochronal annealing for the four irradiations carried out for this thesis.

In figure 4.1, the statistical data results for the annealing of the Xe irradiations are shown along with the data obtained by Donnelly et al [7] for the purposes of comparison. In this graph there are several forms of annealing behaviour on display. In the case of the specimen irradiated with 400 keV Xe\(^+\) ions there is an apparent linear decrease (within the experimental error) from room temperature up to 450 °C at which point a change in gradient occurs and the remaining zones anneal in an approximately linear fashion once more.

Both the 50 keV and 200 keV Xe\(^+\) irradiations show a similar trend in that there is a plateau in the annealing behaviour. In both cases there is an initial decrease in the number of remaining zones followed by a plateau (extending over 100 °C and 150 °C for the 200 keV and 50 keV Xe irradiations respectively) after which further annealing of the zones occurs. The existence of the plateau can be inferred from the images shown in figure 4.3.
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Figure 4.1: Graph showing the statistical annealing for zones formed by Xe irradiations. Also included in the graph are the results obtained by Donnelly et al. [7] shown in maroon. The lines are included for guidance only.

Figure 4.2: Graph showing the statistical annealing data for the Kr and Si irradiations. The lines are for guidance only.
Figure 4.3: Figure showing images of the damage zones as viewed in down-zone bright-field conditions following isochronal annealing steps. a) As implanted, b) 200 °C, c) 300 °C, and d) 500 °C.

One interesting feature of these annealing behaviour curves is the increase in the number of remaining zones that occurs in the 200 keV Xe irradiation at ~125 °C and in the 50 keV Xe irradiation at 450 °C. Although this is a strange result, it has been noticed before in the case of another heavy ion, Bi, during TEM observations [11]. This effect may simply be due to difficulties in determining whether small patches of contrast are damage zones.

If we now look at the statistical annealing of the damage created by the lighter ions used in this thesis (Kr and Si) as shown in figure 4.2, we see that in both cases there is an approximately exponential decrease in the number of zones remaining following each annealing step.

It is generally accepted in the literature that the contrast seen in the TEM in isolated regions, as a result of low fluence ion irradiation, is due to the amorphous nature of the damage within these areas. Indeed, if this were the case, then it is to be expected that the re-growth of the zones would be thermally activated with an activation energy similar, if not the same, as that of a planar $a$-$c$ interface (2.7 eV). If
this were the case, then it is reasonable to expect that the number of zones would remain essentially constant until the annealing temperature rose to approximately 550 °C after which the number of remaining zones would rapidly decrease. Donnelly et al [7] have shown this not to be the case and this is confirmed by the observations in the present work. This leads us to believe that the zones resulting from ion irradiation may not be amorphous in nature for all the irradiation cases shown in this study.

If the zones are not amorphous in nature then it is assumed that they are damaged. Given the imaging conditions used in the TEM, this is not an unreasonable assertion as the structure-factor contrast condition used may show any variance from the structure-factor of the crystal surrounding the zone as regions of contrast. There appears to be no scientific literature on the variation of structure-factor contrast with defect concentration in small regions of crystal. However, simulation work to be presented later in this chapter will show that damaged (but crystalline) silicon also yields altered contrast under structure-factor imaging conditions.

Looking at a typical zone size distribution for the ions as shown in figure 4.4, it is seen that it takes the shape of a skewed Gaussian distribution. If we now assume that the damage-crystalline, d-c, interface moves with a constant velocity (regardless of zone size or shape), how does this affect the zone size distribution and the number of zones remaining after each annealing step? Because the d-c interface moves with a constant velocity, zones of similar sizes will re-crystallize at approximately the same rate, regaining perfect crystallinity after the same period of time. If this were to occur, the effect on the zone size distribution, and hence the characteristic annealing curve as obtained by the statistical data, would become very complex, and as such no information about the annealing mechanisms can be extracted.
In order to fully establish the operative annealing mechanisms, the statistical behaviour of the annealing of the zones does not provide any real answers and only shows that the annealing behaviour of the spatially isolated zones is vastly different to that of a planar $a$-$c$ interface. As such, we must turn our attention to the thermal annealing of individual zones in order to establish the annealing mechanisms occurring.

### 4.4.2 Annealing of Individual Zones

Although the statistical information described above gives some insight into the annealing of spatially isolated damage zones, we need to follow the behaviour of many individual zones to gain further understanding into the mechanisms that occur during the re-crystallization. Whilst following the annealing characteristics of more than 400 individual zones, certain characteristic curves were observed.
Figures 4.5 to 4.8 show, in each case, some typical isochronal annealing curves for 50 keV Xe, 400 keV Xe, 275 keV Kr and 100 keV Si ions and in each graph the initial effective radius is approximately the same. It can be seen there is a large diversity of annealing behaviour that does not depend on the initial size of the zone, in keeping with previous results [7].

**Figure 4.5:** Figure showing three typical annealing curves resulting from isochronal annealing of spatially isolated damage zones formed by low fluence irradiation of 50 keV Xe⁺.
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Figure 4.6: Figure showing three typical annealing curves resulting from isochronal annealing of spatially isolated damage zones formed by low fluence irradiation of 400 keV Xe$^+$. 

Figure 4.7: Figure showing three typical annealing curves resulting from isochronal annealing of spatially isolated damage zones formed by low fluence irradiation of 275 keV Kr$^+$. 
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Figure 4.8: Figure showing three typical annealing curves resulting from isochronal annealing of spatially isolated damage zones formed by low fluence irradiation of 100 keV Si$^+$.  

In figures 4.9 to 4.11 some examples are given displaying typical ways in which zones of different sizes, produced by the same ions, re-crystallize. It can be seen that, again, there is a variety of ways in which the zones may anneal and that this appears to be independent of the initial size of the zone. It can be seen that in some cases the zone anneals show a continual, monotonic, decrease in the effective radius and can fully anneal back to crystallinity at temperatures as low as 100 °C, and in other cases the zone may actually increase in effective radius before fully crystallizing.
Figure 4.9: Graph showing zones of differing sizes annealing in a relatively continual manner.

Figure 4.10: Graph showing zones of differing sizes annealing in a step-like manner.
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Figure 4.11: Graph showing zones of differing sizes showing a growth in effective radius before annealing.

![Graph showing zones of differing sizes showing a growth in effective radius before annealing.]

Figure 4.12: Images of the same region following two consecutive annealing steps. Different zone behaviour can be seen in the images, with zones A, B and C shrinking whilst zone E remains virtually unchanged. Zone D is observed to grow significantly. Note that the zones marked “x” have disappeared. The zones were created by 200 keV Xe⁺.

![Images of the same region following two consecutive annealing steps. Different zone behaviour can be seen in the images, with zones A, B and C shrinking whilst zone E remains virtually unchanged. Zone D is observed to grow significantly. Note that the zones marked “x” have disappeared. The zones were created by 200 keV Xe⁺.]

10nm
Figure 4.12 shows a typical TEM image of the damage zones in a sample as-implanted and following several annealing steps. It can be seen that the larger zones which are not initially circular in projection tend towards a more circular shape suggesting that the zone is becoming more spherical in three dimensions, with regions where the $d$-$c$ interface has a small convex radius of curvature recrystallizing first. It can also be clearly observed in the figure that one zone increases in size following some annealing steps.

In addition to the isochronal annealing experiments performed, dynamic annealing experiments were also conducted on low fluence irradiated samples. During these dynamic annealing experiments, the temperature was ramped up slowly (~5 °C min$^{-1}$) to reduce the development of thermal gradients within the specimen and thus to minimize the thermal drift within the TEM. A small area was kept in view at all times. For all the irradiations, the same characteristic annealing curves were observed and an example of this is shown in figure 4.13. In general, zones shrink over periods which may be as short as a few seconds and then may remain unchanged over periods of minutes.

In both the isochronal and dynamic annealing experiments, there were rare observations of residual defects remaining following thermal anneals of up to 600 °C. Some examples of these are shown in figures 4.14 and 4.15. It is important to note that the observance of residual defects was an extremely rare occurrence, with less than 1% of all zones observed resulting in residual defects following annealing.
Chapter 4: Annealing of Isolated Damage Zones

To summarise the observations of the isochronal and dynamic annealing experiments: we have seen that the damage zones resulting from single ion impacts re-crystallize at temperatures well below that required for the re-crystallization of a planar $a$-$c$ interface and the zones re-crystallize over a wide range of temperatures; zones of similar initial effective radii may re-crystallize at different rates; zones do not necessarily re-crystallize in a continuous manner, but in a step-like manner with extended periods of stability interspersed with short timescales during which the zones anneal rapidly. It was also seen that regions of small radii of curvature re-crystallize first, and that, occasionally, zones actually grew during an annealing step. Finally, in very few instances residual defects are left after a zone has re-crystallized.

![Figure 4.13: Effective radius as a function of temperature for a slow ramp anneal (10 °C per minute) for a single zone produced by a single ion impact of a 50 keV Xe$^+$ ion at room temperature. The lines are included as a guide.](image)
Recent MD and k-MC modelling of ion beam induced amorphization and re-crystallization of Si by Pelaz et al [16] have provided a convincing argument for the thermal re-crystallization in terms of the IV pair as described in §2.4.4. The
characteristic annealing curves that have been observed during isochronal and dynamic annealing will now be discussed in terms of the IV pair.

### 4.4.3 Discussion

We have seen in the previous section that the regions of contrast produced in silicon as a result of ion impacts thermally anneal in a variety of ways. If we now look at the cases of the zones re-crystallizing over a wide range of temperatures (always below that required to re-crystallize planar amorphous silicon) and where regions of a small radius of curvature re-crystallize first, we can explain these observations in terms of the stability of the IV pair.

Following the work of Marques et al [17], we know that the stability of the IV pair is dependent on the number of surrounding pairs – its co-ordination. For an isolated IV pair with a co-ordination of zero, the activation energy for recombination has been calculated to be 0.43 eV. As the number of local IV pairs increases, so does the calculated activation energy for recombination and this can be described mathematically by [17]:

\[
E(n) = 0.6 + 0.2n + 0.0012n^3
\]  

(4.1)

Where \( n \) is the (integer) number of IV pairs at the first neighbour distance from the IV pair of interest, and this may vary from 1 to 12 (an IV pair completely surrounded by other IV pairs). For the case of a planar \( a-c \) interface, the co-ordination will be 7 [17] and this yields a value of the activation energy for
recombination of 2.4 eV, close to the value of 2.7 eV which is the experimentally observed value for the re-crystallization of a planar \( a-c \) interface.

Figure 4.16 shows a schematic diagram of two spatially isolated zones of drastically different effective radii with a concentration of IV pairs such that, within the zone, the material is amorphous. In the smaller zone on the left of the figure we can see that there is a small radius of curvature compared to the zone on the right (large radius of curvature). Although the figure is only in two dimensions, it is easy to see that, for a single IV pair at the \( a-c \) interface, where spontaneous recombination of IV pairs may act as the trigger for re-growth, there is a greater number of surrounding IV pairs in the large radius zone (from within the zone). This is due to the larger volume of crystalline material neighbouring any point on the small radius of curvature zone.

By using equation 4.1 and through the use of the equation for the volume intersected by two spheres [18], it is possible to interpolate the variation of activation energy for recombination as a function of zone radius. This is fully derived in Appendix B, but the graph showing the change in activation energy is shown in figure 4.17. It can be seen from the graph that as the zone radius increases, so does the activation energy for recombination before becoming asymptotic at 2.4 eV for radii of \( \sim 100 \) Å and above. As has been shown, zones are formed that are sub-100 Å (generally 5 – 60 Å) and it can be seen in figure 4.17 that this encompasses activation energies ranging from \( \sim 1.1 – 2.3 \) eV. Although this is just an interpolation, it shows that there is a strong dependency on the radius of curvature on the annealing of the zones. This also extends to the annealing of protuberances emanating from zones which are seen to anneal at lower temperatures than that of the circular region of the zone.
As well as the variation of zone radius having a strong influence on the annealing characteristics, so does the shape of the zone itself. k-MC modelling has been performed by Marques et al [17] on zones containing the same concentration of IV pairs within similar volumes of different shapes and this showed that a cube will anneal more rapidly than a sphere. This can be explained in terms of the co-ordination of the IV pairs at the corner of the cube as at this point it will be much smaller than at any point on the surface of the sphere. This leads to a lower activation energy for recombination and as such a cubic volume will begin to anneal more readily than a sphere.

As we have seen above in the treatment of varying the zone radius, the resistance to re-crystallization of a zone is theoretically highly dependent on the co-ordination of the IV pair that spontaneously recombines, initiating the annealing (this IV pair will now be referred to as the *initiating IV pair*). As the radius of the zone increases, the initiating IV pair has more IV pairs to which it may become more stable. If we maintain the radius of the zone and begin to reduce the concentration of IV pairs within the zone from ~25%, the number of IV pairs with which the initiating IV pair may become co-ordinated with reduces.
Figure 4.17: Graph showing the variation in activation energy for recombination of an IV pair as the surface of an amorphous zone of varying radius.

With this lowering comes a reduction in activation energy for recombination and as such we should observe zones annealing at lower temperatures. Indeed, in the case of annealing zones formed by 100 keV Si$^+$ ions, it was seen that some zones anneal at very low temperatures (<100 °C). The most probable reason for this is that, at IV pair concentrations of <10%, the IV pair begins to annihilate through direct interstitial-vacancy recombination within the bulk of the zone rather than at the d-c interface for higher concentrations [19] and as such will anneal at much lower temperatures.

We have shown that zones of small radii of curvature are less stable than larger zones and that zones of similar sizes may anneal at different rates. We therefore suggest that for zones of containing an equal IV pair concentration (>10%), the radius of curvature plays an important role in the annealing of the zones. The initial shape of the zone itself also plays an important role in the annealing
characteristics although this cannot easily be studied due to the plan-view nature of TEM imaging.

If we now consider the step-like annealing that has been observed, there are several possibilities that can account for this form of annealing. Firstly there is the possibility that the core of the zone has a higher concentration of defects surrounded by a shell of defects with a slightly lower concentration of defects. Because the outer shell of the zone contains a lower IV pair concentration it would begin to anneal at a lower temperature. As the \( d-c \) interface moves towards the centre of the zone it would encounter the higher concentration core of the zone at which point the annealing would halt because of the higher activation energy for recombination at this stage. The size of the zone will now be maintained until a temperature is reached at which the zone may resume re-crystallization.

Another possibility that explains the step-like annealing behaviour observed is the possibility of the zones becoming more stable due to the formation of more stable IV pair complexes. This has been observed during MD modelling [20] in which plateaus, similar to those observed experimentally in this study, have been formed through interaction of several IV pairs creating stable complexes. In the same study [20], it was shown that this occurred regardless of the defect concentration of the zone.

Another possibility for the step-like annealing is the existence of finger-like protuberances emanating from the central spherical region of the zone – see figure 4.18 for an example of this. Because the ends of the “fingers” would have a very small radius of curvature compared to the central region of the zone, the activation energy for recombination of the initiating IV pair would be lower than that of the
central spherical portion of the zone and as such the fingers would anneal at lower temperatures.

![Image of finger-like protuberances from zones](image)

**Figure 4.18:** Image showing the existence of finger-like protuberances from zones

When seen in a projected view as used in the TEM, we would observe the fingers re-crystallizing down to the circular area of the zone at which point the radius of curvature would be larger and the zone would be more stable at low temperatures and hence the re-crystallization would take the form of a step-like curve.

In order to explain our observation of damage zones annealing with a step-like characteristic, it is suggested that some zones become more stable following annealing steps. This stability may arise by the annealing of unstable finger-like protuberances, through the annealing of a less damaged shell surrounding a more damaged core, or through the generation of more stable IV pair complexes forming through the interaction of the IV pairs.

Probably the most unusual and unexpected result is that of the increase in effective zone radius seen during annealing. In this re-growth mechanism, the zone is seen to actually increase in projected area before reaching a maximum size before re-crystallization in a normal manner. Again this form of re-crystallization can be described in terms of the IV pair.
k-MC modelling simulations [21] have shown that for certain defect configurations, based on the IV pair, growth of a damage zone is possible. The modelling is based around a central amorphous core surrounded by a shell of vacancies which in turn is surrounded by three shells of interstitials. The concentration of the interstitial shells was varied to see the effect this would have on the growth of the zone. The results of the simulations are summarised in figure 4.19 and it is evident from the graph that through varying the defect configuration and concentration surrounding the amorphous core, it is possible to generate zone growth of up to ~43%.

This increase in effective radius occurs due to incomplete recombination of the surrounding vacancies and interstitials. As the vacancies close to the already amorphous core begin to recombine incompletely with the outer shell interstitials, the resulting IV pairs increase in concentration up to a point where they become visible in the TEM. Although work has been published on this effect, the results from the JEMS simulations show that the surrounding shells of interstitials and vacancies would be visible in the TEM under the structure-factor conditions and as such this method of growth in zone radius seems unlikely.

Another possibility which could occur that would account for the increase in effective radius could be a form of ripening process whereby IV pairs migrate from one zone to another. This, however, seems unlikely as there have been no theoretical studies to date in which the IV pair has been shown to migrate. There is a possibility that interstitials or vacancies may leave other zones and incompletely recombine on the amorphous core of the zone that grows.
Figure 4.19: Graph showing the effect of different defect configurations and concentrations on the amount of zone growth during thermal annealing.

This would be a ripening process of sorts, although the temperatures at which the zones have been observed to grow are lower than the migration energies for the isolated vacancies and interstitials and as such seems unlikely to occur. Given the JEMS results, this is the most probably method under which the zone could possibly grow.

The three options which have been proposed for the mechanisms of the growth of the zones are that a defect configuration surrounding the zone post-formation incompletely recombine with each other forming IV pairs on an amorphous core resulting in growth, a ripening process based on the migration of IV pairs, and a ripening process based on the migration of isolated interstitials and vacancies. As there is no evidence for the migration of the IV pair to date, it seems unlikely that this is the process occurring during the growth of the zones. The most
probable mechanisms are the incomplete recombination of defects already surrounding the zones, or a ripening process based on the migration of interstitials and vacancies to the zone.

In some cases during the annealing, even at temperatures of up to 600 °C, small regions of contrast (as shown in figures 4.14 to 4.15) are left within the images at positions where zones had previously been observed at lower temperatures.

Although not characterised during the experiments, it is possible that these small regions of contrast show the existence of point defect agglomerates that develop during annealing. This was a very rare occurrence, happening in approximately 1% of all the zones tracked.

The structure-factor contrast that is used to image the damage zones in the experiments [22] may also show contrast for other types of defects such as dislocation loops (with specific Burgers vectors) or rod-like defects. Because of this, the linear type feature shown in figure 4.14 may be a defect such as a dislocation loop or rod-like defect that is formed as a result of the release of excess vacancies or interstitials from the zone itself. The rare observation of this type of defect leads us to believe that the majority of damage zones either does not have a significant excess of vacancies or interstitials or that the excess interstitials and vacancies from nearby zones recombine or diffuse away. Residual defects have been observed to result from annealing during MD simulations [23].

4.4.4 JEMS Simulations

Earlier the concept of damage zones containing varying concentrations of IV pairs was introduced. Given that structure-factor imaging conditions are used throughout this thesis, an important question that we must ask is how would zones of
differing concentrations of IV pairs actually be imaged in the TEM under down-zone structure factor contrast? To answer this question we must employ electron microscope image simulation techniques.

Simulation of TEM images involves numerically calculating the images using detailed descriptions of both the specimen and the microscope. Simulating the images is useful in that it can be used as an aid to the interpretation of the true TEM image including what features in the image are due to artefacts produced by aberrations in the microscope and what are true features in the specimen.

There are two general groups of image simulation types: one involving Bloch waves, the other group involving slicing the specimen along the beam direction and then propagating the wave through the periodic potential of the thin slice (the multislice method). The Bloch wave method is good at handling small crystalline unit cells (specimens) and providing an insight into the scattering processes whereas the multislice method is excellent at dealing with large cells or cells containing defects. As we want to simulate specimens that include defects the multislice method is the simulation type that is required in this case.

The multislice method involves slicing a specimen containing many atoms into many thin slices. Each slice is then converted within the simulation program into a phase grating using the atomic potential of all the atoms within the slice. These phase gratings are then “stacked” on each other with a vacuum gap between each of the gratings. An electron wave is then incident upon the top grating and experiences a phase shift due to the periodic atomic potential lattice described by the phase grating. As the electron wave exits the top grating, it propagates and interferes with itself producing a new electron wavefront. This new wavefront is then the input wavefront for the next phase grating in the stack. This method is then continued for
the entire stack of phase gratings and the exit wave function at the last phase grating is operated on by a Fourier transform to obtain a transmitted wave function [24]. This transmitted wave function is then convoluted with the transfer function of the objective lens of the TEM in order to attain the image wave function at the back focal plane of the objective lens [24]. An inverse Fourier transform is then used to generate the final image.

The image simulation software package that has been used in this thesis is the JEMS package produced by P A Stadelmann. This is an extension of the popular EMS package by the same author [25], but converted for use on a Java platform enabling use on a standard PC. The input cells that were simulated using MD techniques were provided by L A Marques [26] at the University of Valladolid, Spain and were received as files containing the \( x \), \( y \), and \( z \) atomic co-ordinates. The cells were 10.37nm x 10.37nm x 10.32nm in the X, Y and Z directions respectively with the Z direction being the \(<100>\) direction. Centred in the cell is a sphere with a radius of 3nm. The entire cell volume contained 55404 atoms. Within the 3nm radius sphere, IV pairs were generated in concentrations of 5% (35 IV pairs), 10% (71 IV pairs), 20% (141 IV pairs) and 30% (212 IV pairs). To prepare the input cells for use within JEMS, a program was written in Fortran 90 that read in the atomic co-ordinates of the input cells, slicing the cell into the user defined number of slices and outputting as sliced files ready for implementation into JEMS. This involved slicing the large cell into the given number of slices and then normalizing the atomic co-ordinates in each slice. The normalized atomic co-ordinates were then outputted in the correct format in text files ready for use in JEMS, including the atomic form factors and thermal vibrations. An example of the file is shown below. The files were
then used in the JEMS supercell multislice sub-program to simulate the images of the
damage zones.

**An example of a JEMS input file.**

```plaintext
file|30%iv_1.txt
system|triclinic
superCell|true
HMSymbol|1|1|0|0| P 1
rps|0|x,y,z
lattice|0|10.370
lattice|1|10.370
lattice|2|0.272
lattice|3|90.000
lattice|4|90.000
lattice|5|90.000
atom|0|Si,a,0.00926,0.00927,0.24928,0.005,1.000,0.0350
atom|1|Si,a,0.00926,0.04631,0.24935,0.005,1.000,0.0350
atom|2|Si,a,0.00925,0.08334,0.24943,0.005,1.000,0.0350
.
.
atom|1455|Si,a,0.99080,0.89820,0.74917,0.005,1.000,0.0350
atom|1456|Si,a,0.99080,0.93524,0.74921,0.005,1.000,0.0350
atom|1457|Si,a,0.99079,0.97228,0.74926,0.005,1.000,0.0350
aff|0|Si|2.129,57.775,2.533,16.476,0.835,2.88,0.322,0.386|Doyle-
   TurnerActaCryst.A24(1968),390

aff|0|Si|0.120120145,70.63101,1.0649803,1.0460037,0.1822563,0.8688869,0.0306
   0761,0.2147628,1.1086769,3.6920595,1.5825809,9.931198|EarlJ.Kirkland,Ad
   vancedComputinginElectronMicroscopy

nsi|0|Si|0.415

aff|0|Si|0.0567,0.0582,0.3365,0.6155,0.8104,3.2522,2.496,16.7929,2.1186,57.6767|L

aff|0|Si|6.2915,2.4386,3.0353,32.3337,1.9891,0.6785,1.541,81.6937,1.1407|XRay::R
   HF::
```

174
Figure 4.20: Figure showing the results of the JEMS simulations for varying concentrations of IV pairs.

Shown in figure 4.20 are the results of the JEMS simulations for differing concentrations of IV pairs within a spherical region. It can be seen that there is a difference in contrast and apparent radius as the concentration of IV pairs is changed in the zone. It is known that as the concentration of IV pairs reaches approximately 25%, the radial pair distribution function of the crystal essentially becomes that of amorphous silicon [20] so in the cases simulated, only that of the 30% IV pairs case is a true amorphous zone, the other concentrations being varying levels of damage. This is an extremely important result as contrast resulting from single ion impacts experimentally imaged in this mode has always been referred to as amorphous zones in the literature yet it is shown here that this is clearly not the case. It is possible to have concentrations of defects that are well below that required to produce amorphous material, see for example the 5% IV pair concentration and for these zones to show contrast in the structure factor condition. This implies that many or all observations of amorphous zones in silicon in the literature may not actually be amorphous zones.
4.5 SUMMARY

It has been shown that ions of differing masses produce zones of contrast that re-crystallize at temperatures well below that of a planar $a-c$ interface. During isochronal annealing experiments, detailed inspection of many zones showed that zones of similar initial effective radii anneal in a variety of ways, including linear-type, step-like and re-growth-type annealing. Dynamic annealing experiments of individual zones showed that zones produced by the different ions all annealed in a similar manner: periods of stability lasting of the order of minutes, followed by rapid re-crystallization (timescales of seconds).

All these results have been shown to fit with the “bond defect” or IV pair. Although never observed experimentally, this defect has been shown in MD and k-MC simulations [16, 17, 19, 20] to have an activation energy for recombination that is highly dependant on the concentration, or co-ordination, of the defect. Different concentrations of this defect can explain the different annealing mechanisms that are seen in the experiments and as we have shown, it is not possible to distinguish in the TEM between zones containing 30% IV pairs and 10% IV pairs – which have vastly different annealing characteristics when simulated through MD modelling. This includes the extraordinary growth of zones before their “normal” re-crystallization in which incomplete recombination of interstitials and vacancies results in the increase of IV pair concentration surrounding an amorphous core containing approximately 25% IV pairs. As the IV pair concentration surrounding the zone increases, so does the projected area of the zones as seen in the TEM with increases up to 43% possible. This now seems to be an unlikely method of growth as the interstitial and vacancy shells required to initialise growth would be seen under structure-factor imaging conditions. The most probably method for growth is a ripening process in which
interstitials and vacancies migrate from one zone to another incompletely recombining at the core of another zone causing the zone to grow.

Other results of note are the appearances of other extended defects very close to, or at the location of zones. This indicates the possibility that very few zones have, and can eject, excess vacancies or interstitials.
4.6 REFERENCES


[26] L. A. Marques, Private communication
Ion Beam Induced Amorphization
5.1 INTRODUCTION

In this chapter the results of \textit{in situ} TEM amorphization experiments are presented. In these experiments, thin samples of Si were irradiated at constant flux until the sample was amorphized.

The amount of amorphous material is inferred through the intensity profile of the Debye-Scherrer rings formed by amorphous material as taken by nano diffraction patterns. A numerical method to model the amorphization of the silicon crystal based on Monte Carlo simulation principles is also presented and compared with the experimental results.

It will be shown that the numerical model is in good agreement with the low temperature experimental results and that the damage zones produced by ion implantation are not always in a uniquely amorphous phase and that in most cases, an overlapping of the damage zones is required to produce the amorphous phase in silicon.
5.2 Models of Damage Accumulation

In this section, a brief summary of the damage models described in detail in §2.4.6 will be given. After the summary, a newly implemented damage model will be described in detail.

5.2.1 Review of Damage Models

During the process of ion implantation, the incoming energetic ion causes damage to the lattice through a series of collisions with the target atoms of the crystal. As the incoming ion loses its energy, a collision cascade is formed around the track of the ion. This has been described in detail in §2.4.6.1. As the mean free path of the displacing collisions is reduced to that of the interatomic spacing, small highly perturbed regions are formed within which the mean kinetic energy of the target atoms may be increased by several eV – this is the displacement spike [1]. The kinetic energy deposited by the spike is dissipated uniformly over all the atoms in the spike region leading to a localised heating in the spike region. This may lead to a melting of the substrate within the spike volume that is rapidly quenched, possibly freezing in the liquid-like distribution. Although the thermal spike is a subject of much controversy, the work of Donnelly and Birtcher has shown the existence of thermal spikes in metals [2].

During the thermal spike phase, the peak in the Gaussian energy distribution centred about the cascade volume begins to spread out and defects may migrate during the time period over which the peak of the temperature remains over the temperature at which the defects have significant mobility. In this short period of
time it is also possible for defects to interact and agglomerate to form more stable defect complexes.

After the thermal spike and its associated relaxation phase have occurred, a damage zone may be left in the crystal. Molecular dynamic simulations have been performed by Caturla *et al* [3] in the study of isolated cascade structures of B and As implantations at various energies. In this study, the As implantations resulted in large clusters being formed with a few isolated defects. For the B implantations, no large clusters were produced but many isolated vacancies and interstitials along with many small point defect clusters were formed. This difference in cascade morphology was attributed to the high mass ion causing a localised melting of the cascade core resulting in an amorphous pocket whereas in the light ion case localised melting was unable to take place and the defects were produced as a result of the early collisional phase of the cascade. Diaz de la Rubia also drew the same conclusions in a separate study using MD [4] and some experimental observations using TEM [5, 6] are also in agreement.

As the ion fluence increases, there is an increase in the number of collision cascades that, assuming that the fluence is higher than a critical value, produce an amorphous layer within the crystal. The two most popular models for the nucleation of the amorphous phase are the heterogeneous and homogeneous models.

In the heterogeneous model of nucleation, each ion that enters the target substrate produces an amorphous zone and, as the fluence increases, the individual zones begin to overlap with each other producing an amorphous layer. This was first suggested and modelled by Morehead and Crowder [7] and is fully described in §2.3.7.3. Whilst this simple model is reasonable for heavy ions where amorphous
zones may be produced with each collision cascade, it is inadequate when extended to intermediate and light ions.

In order to take into account this problem Gibbons created a model [8] based on the model of Morehead and Crowder. In this modified model (described fully in §2.3.7.3) Gibbons accounted for the possibility that the energetic ion does not generate an amorphous zone and instead cascades must overlap with each other in the same region to turn the crystal amorphous.

The homogeneous nucleation model is based on the ion irradiation not generating discrete zones of amorphous material with each ion but instead the irradiation causes a build-up of defects in the substrate [9-11] to a point whereby the lattice becomes unstable and spontaneously collapses into the amorphous phase. If this were the mechanism by which the crystalline to amorphous transition were to occur, it would be expected to do so over a narrow fluence range.

Another model that has been used to describe the crystalline to amorphous transition is the nucleation limited model as described in §2.3.7.5. This model assumes that the crystalline to amorphous transition follows the classical mechanism of nucleation and growth as described by the Avrami-Johnson-Mehl equation for phase transformation [12]. Here, small amorphous cores are formed within the confines of the collision cascade. Long-lived defects generated during the irradiation may then interact with the \( a-c \) interfaces of the amorphous volumes and induce the growth of the amorphous volume. This form of nucleation has recently been used to describe the formation of amorphous layers resulting from low energy implantation of As and Sb into Si [13].
5.2.2 Simple Monte Carlo Model of Amorphization

A simple Monte Carlo (MC) model to describe numerically the amorphization of silicon due to ion irradiation has been developed. The model requires two inputs from the program TRIM [14]: the cascade volume and the damage distribution of each of the ions used in the study.

Figure 5.1 shows a flow diagram of the processes involved in the program. The first step is reading the user defined input file into memory. In this input file, parameters are defined ready for the program’s use. These parameters consist of the output file name, the name of the probability input file (as determined by TRIM), the total number of ions to be simulated, the total cell size (given in $x$, $y$ and $z$ lengths), the cell resolution, the cascade radius (as determined by TRIM), and the total number of results to be outputted.

The next stage in the program is to set up an array consisting of all the voxels that have been defined from the input file (a voxel is a small 3-dimensional volumetric element analogous to a 2-dimensional areal element that is known as a pixel). Following these setting up procedures, the program is now ready to “implant” the ions.

The implantation simulation procedure is relatively simple: a random $x$ and $y$ co-ordinate is picked then a weighted-random $z$ co-ordinate is chosen to determine the depth at which the collision cascade is formed. The term weighted-random is used for the $z$ direction co-ordinate as the random number generated to determine this co-ordinate is weighted by a factor defined by the damage probability file. After the cascade occurrence point has been determined through the generation of the $x$, $y$ and $z$ co-ordinates, the cascade sphere is centred about these co-ordinates using $r$ as obtained by TRIM and then defined in the input file.
Figure 5.1: Flow diagram showing the steps followed by the damage accumulation program as described in the text.

At this point the program now checks all the voxels to determine which voxels have their centre within the cascade radius. The voxels encompassed by the cascade
volume (and hence determined to have been “hit”) now have their “hit” count incremented by 1 which is then stored in the array.

After the specified number of ions have been simulated, the array is printed to a file. This file contains the total number of ions that have been simulated up to that point, the number of voxels that have not been “hit”, the number of voxels that have been “hit” at least once, at least twice, at least three times, at least four times and at least five times. After the specified total number of ions has been simulated, the program also prints out the input parameter data to the same file. This file can then be used to plot a graph showing the percentage amorphous material as a function of ion fluence and an example of this is shown in figure 5.2.

It can be seen from figure 5.2 that as the number of “hits” that is required to turn the crystal amorphous increases (this is equivalent to the number of overlaps required), the gradient of the amorphous fraction curve becomes steeper.

![Numerical Model Results - 400 keV Xe⁺](image)

**Figure 5.2:** Example of the results obtained from the MC amorphization model.
5.3 EXPERIMENTAL METHODS

In this section, experimental details pertinent to the experiments detailed in this chapter will be discussed.

5.3.1 Sample Preparation and Mounting

In general, samples were prepared for TEM imaging from a <100> float-zone silicon wafer using the small angle cleavage technique [15-17] as described in §3.2.2. Samples were then mounted in a plan-view orientation onto Cu hole grids using a silver epoxy.

The exception to this sample preparation scheme was those samples that were required for the 50 keV Xe⁺ irradiation. The samples used for this experiment were made using the jet thinning technique described in §3.2.3. This technique was used over the SACT method in order to produce smaller wedge angle samples thus ensuring that the entire thickness of the sample was amorphized during the irradiation.

5.3.2 Amorphization Schemes

Two different series of amorphization experiments were performed: room temperature and low temperature irradiations. For the room temperature irradiations, the samples were held in a Gatan dual-tilt holder whilst the low temperature samples were held in an Oxford Instruments dual-tilt cryogenic sample holder with the temperature maintained at 50 K. Irradiations were performed using 50 keV Xe⁺, 400 keV Xe⁺, 275 keV Kr⁺ and 100 keV Si⁺ with the ion flux maintained at
approximately $1.25 \times 10^{12}$ ions s$^{-1}$. The 400 keV Xe$^+$, 275 keV Kr$^+$ and 100 keV Si$^+$ energies were chosen so that the $R_p$ of each of the ions are approximately the same.

Before irradiating, a diffraction pattern was taken of the virgin sample using the nano-beam mode of the TEM. This mode alters the lens settings of the TEM to produce a much narrower beam. By using this mode, small spot sizes of $\sim$8 nm are possible ensuring that a small sampling region was used through the experiments. On wedge-shaped specimens, the small spot-size enables the electron beam to sample only the thinnest area of the specimen which will be entirely damaged by the ion beam.

Once the initial diffraction pattern was recorded, the strength of the condenser lens was not altered so as to ensure that the number of electrons contributing to the diffraction patterns did not vary greatly during the irradiations for a given exposure time. Any variation in the number of electrons contributing to the diffraction patterns (assuming the condenser is not altered) would be due to instabilities in the power supply which are known to be below 1 part in $10^5$.

During irradiations, the electron beam was not incident on the sample as this had been previously found in early experiments in this study to inhibit the full amorphization of the samples. Nano-beam diffraction patterns were recorded onto photographic negative at each fluence step at several exposure times to check for linearity of the response of the negative to changes in electron flux.

### 5.3.3 Data Analysis

The developed negatives were scanned into a PC at a resolution of 600 dpi and saved as tiff files. Using Adobe Photoshop CS, a 15 pixel wide intensity profile was taken across the width of the negative, ensuring that the profile passed through
the central beam spot but avoided diffracted beam spots to measure the intensity of
the amorphous ring as it began to appear. The width of 15 pixels was chosen to give
a reasonable signal-to-noise ratio whilst enabling diffracted spots to be avoided (see
figure 3.16).

The intensity profile was then exported to Microsoft Excel and here the
profile in the region of the amorphous peaks was integrated. After obtaining the
integrated intensities for all the fluencies, each fluence step intensity was normalised
to that of the completely amorphized silicon in order to generate amorphous fraction
curves as a function of ion fluence. This was done for all exposures.
5.4 Results

In this section of the chapter, the experimental electron diffraction results will be presented. Following this, these results will then be compared with the results of the numerical model that was described in §5.2.2. The results obtained for the 50 keV Xe\(^+\) irradiation are omitted here as the thickness of the electron diffraction sampling volume could not be determined accurately, and thus the MC modelling could not be performed allowing for comparison between the model and the experiments.

5.4.1 Electron Diffraction Results

In situ TEM experiments allowed measurements to be taken on the amorphization of silicon due to different ion irradiations. In the cases presented here, 400 keV Xe\(^+\), 275 keV Kr\(^+\) and 100 keV Si\(^+\) were the ions used and irradiations were performed at room temperature and at 50 K. During the irradiations, the electron beam was bent off the sample by means of a shutter, below the gun. This procedure was followed as early results in this study showed that the sample was unable to become amorphous when irradiated with both the ion beam and the electron beam incident on the sample at the same time, regardless of substrate temperature or ion mass.

During the irradiations, nano-diffraction patterns (NDPs) were taken and an example of some NDPs taken during a typical amorphization series are shown in figure 5.3. Using these NDPs, the fraction of amorphous material present in the crystal was determined as outlined in the experimental methods (§5.3), the results of
which are shown graphically in figures 5.4 – 5.6 for the same ions at low and room temperatures. Shown in figures 5.7 and 5.8 are the results for all the ions at room temperature and at 50 K respectively.

Figure 5.3: Figure showing nano-beam electron diffraction patterns during in situ heavy ion (400 keV Xe⁺) irradiation into silicon. Fluences are a) virgin, b) 8E13, c) 1E14, and d) 2E14 ions cm⁻². More NDPs were taken during the experimental run in order to obtain more data points. The camera length was 1.0 m.
Figure 5.4: Graph showing the results from in situ TEM NDP measurements for irradiation with 400 keV Xe\(^+\) ions.

Figure 5.5: Graph showing the results from in situ TEM NDP measurements for irradiation with 275 keV Kr\(^+\) ions.

Figure 5.6: Graph showing the results from in situ TEM NDP measurements for irradiation with 100 keV Si\(^+\) ions.
Figure 5.7: Graph showing the results from in situ TEM NDP measurements for irradiation with all ions at room temperature.

Figure 5.8: Graph showing the results from in situ TEM NDP measurements for irradiation with all ions at low temperature.
It can be seen that in all cases that the amorphous content of the sample increases as the ion fluence increases. This corresponds to a conversion of crystalline material to amorphous material with increasing fluence.

In all cases, the 50 K irradiation fully amorphized the sample at a lower fluence than the room temperature irradiation as is shown in figures 5.4 to 5.6. The reason for this is almost certainly that the dynamic annealing is reduced at lower temperatures resulting in more damage being retained per ion.

The graphs showing the results for the different ions at room and low temperature presented in figures 5.7 and 5.8 show that in both cases the Xe irradiations amorphize the samples at a lower fluence than the Kr irradiations which in turn amorphize the samples at a lower fluence than the Si irradiations. This indicates that as the mass of the ion increases, more stable damage is being produced by each impinging ion and this is the case for both room and low temperature irradiations.

5.4.2 Monte Carlo Model Results

Shown in figures 5.9 to 5.11 are the results for the different ions simulated in the Monte Carlo model described in §5.2.2. Shown in table 5.1 are the different parameters that were used in the simulations.

Some simulations were performed with different voxel sizes of 0.25 and 1.00 nm as well as 0.5 nm and it was determined that a resolution of 0.5 nm was the optimum resolution to use in terms of computational time and precision. It was determined in these tests that there was no precision gain in increasing the resolution to 0.25 nm when compared to the 0.5 nm resolution whereas the reduction in computation time was significant.
Figure 5.9: Graph showing the results of the Monte Carlo model simulation for 400 keV Xe\(^{+}\) ions.

Figure 5.10: Graph showing the results of the Monte Carlo model simulation for 275 keV Kr\(^{+}\) ions.
Chapter 5: Ion Beam Induced Amorphization

Figure 5.11: Graph showing the results of the Monte Carlo model simulation for 100 keV Si\(^+\) ions.

Table 5.1: Parameter values used in the Monte Carlo model for the various ions simulated.

<table>
<thead>
<tr>
<th>Cascade Radius (nm) (obtained from TRIM)</th>
<th>Xe</th>
<th>Kr</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13.8</td>
<td>10.4</td>
<td>7.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total number of ions simulated</th>
<th>1.0E7</th>
<th>1.0E5</th>
<th>1.0E5</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Cubic Voxel size (nm)</th>
<th>0.5</th>
<th>0.5</th>
<th>0.5</th>
</tr>
</thead>
</table>

The results of the model show a similar pattern in all cases. As the number of cascade overlaps are increased (labelled as “Hit” in the graph legends) it can clearly be seen that the slope of the amorphization curve becomes steeper and the fluence between successive “hit” curves to reach 50% amorphous material decreases.
5.4.3 Experiment versus Model Comparisons

In order to fully quantify the Monte Carlo model, it is necessary to compare the results obtained by the model to those obtained experimentally. The results are seen in figures 5.12 to 5.14. From the graphs it can be seen that the low temperature data lies in the region of the theoretical curves but the room temperature results do not. In all cases there is no correlation between the single hit (Hit 1+) curve that corresponds to direct amorphization – the heterogeneous model. There is a closer agreement, for the low temperature cases, of multiple hits (cascade overlapping) producing amorphization for all the ions studied.

5.4.4 Discussion

From the graphs shown in figures 5.12 to 5.14, it was seen that the results from the simulation are in better agreement with the low temperature experimental results than the room temperature results. In no cases is there a complete overlapping of the modelled curves with the experimental data.

The results from the Monte Carlo modelling have also shown that the gradient of the linear portion of the amorphization curve produced increases as the number of overlaps required to produce the amorphous phase increases.

When the experimental results are compared to the modelling results, the following observations can be noted: 1) the low temperature irradiations are closer in agreement (although not in complete agreement) with the modelled curves, and 2) in most cases, multiple overlaps are required to generate the amorphous phase in silicon – the exception being the room temperature 100 keV Si⁺ irradiation that appears to form amorphous silicon through homogeneous nucleation.
Figure 5.12: Graph showing the results for the experimental Xe irradiation compared with the MC model results.

Figure 5.13: Graph showing the results for the experimental Kr irradiation compared with the MC model results.
The fact that the low temperature irradiations are a better fit to the MC model is due to the reduction in dynamic annealing effects that occurs as the substrate temperature is reduced. The MC model takes, as one of the input parameters, the cascade volume as determined through analysis of TRIM calculations. As TRIM does not take into account any dynamic annealing effects during the implantation, the TRIM cascade volume would be larger than that expected for irradiations taking place at temperatures in which significant dynamic annealing could occur. It can be seen through analysis of the different curves produced in the model by the Si and Xe that this does not have a pronounced effect on the curves. This is also true for the MC model – the cascade volume is defined by a single effective radius that is fixed. Due to the simplicity of the MC model, there are no dynamic effects included that allow for the model to reduce the cascade volume at high temperatures.

Another implication of the dynamic annealing occurring is that the defects diffuse out of the immediate cascade volume and accumulate homogeneously so that,
at room temperature and above, the behaviour moves much closer to the homogeneous model of lattice instability thus yielding steeper curves in the experimental data than in the MC model. These defects could either be IV pairs that diffuse out from the cascade volume or interstitial and vacancy complex that diffuse out but then subsequently form IV pairs.

During irradiation at finite temperatures, there are dynamic annealing effects occurring that result in the slight reduction in the cascade volume. By reducing the temperature to 50 K this effect is significantly reduced and there is little, if any, dynamic annealing occurring during the irradiations. In reducing the effect of the dynamic annealing in this manner, the experimental results become more comparable to the MC model.

With this taken into account, it can be seen that the low temperature experimental curves still do not exactly correspond to the results obtained from the MC model. This is for several reasons. Although we have reduced the effect of dynamic annealing by reducing the substrate temperature to 50 K, there will still be some dynamic annealing effects occurring during irradiation even at this low temperature. As well as dynamic annealing effects, ion beam induced annealing could also occur [18] in which the overlapping of cascade volumes at high fluxes could cause the cascade volumes to interact with each other in such a way that annealing occurs and the final, stable cascade volume is reduced.

Another factor that may account for the deviation between the model and the experiments is the variation in cascade volume itself. In the model we have a fixed cascade volume as defined by a radius given in the input file. During the experimental irradiation, it is known that there is a distribution of cascade radii (as seen in §4.4) and that distribution has a skewed Gaussian shape to it. This size
distribution could cause a discrepancy in the amorphization curves as smaller or larger cascade volumes than are modelled may occur resulting in a difference in damage volume being produced by each incoming ion. Because the damage volume produced by each incoming ion has a variance to it, then the amount of amorphous material produced will also have a variance to it although it is most likely that the effect will be small and as such will not have a pronounced effect on the amorphization curves.

From the curves shown in figures 5.4 to 5.6, we can also see that in no case is the amorphization due to heterogeneous nucleation. If the sample were amorphized under heterogeneous nucleation conditions, the experimentally obtained amorphization curve would follow the “Hit 1+” curve produced by the MC model and an amorphous layer would be produced by the accumulation of amorphous volumes as described by Morehead and Crowder [7]. This model is generally accepted to be the mechanism that produces amorphous layers in silicon due to heavy ion bombardment, but as can be seen from figure 5.12 for the Xe irradiation, this is not the case here. Upon close examination of the low temperature Xe irradiation, it can be seen that the modelled curve that most closely resembles that of the experiment is the “Hit 3+” curve. This curve corresponds to a volume only becoming amorphous if the volume has been encompassed by a cascade volume at least three times – an overlapping of the cascades is required to render the region amorphous.

If we now look at the low temperature irradiation with Kr when compared to the results obtained by the MC model, as shown in figure 5.13, we can see that the experimental data initially agrees with the with the “Hit 2+” curve up to a fluence of $1 \times 10^{13}$ ions cm$^{-2}$ before deviating from this curve and then approximating the “Hit
3+” curve. Again, this corresponds to an overlapping of the cascade volumes that is required to occur before the crystal can be rendered amorphous.

For the case of the Si irradiation and modelling, as shown in figure 5.14, we can see that the low temperature experimental data more follows the “Hit 5+” modelled curve. This indicates that at least four cascade overlaps are required in order to produce the amorphous phase in silicon irradiated with Si.

In all cases, it is seen that the room temperature irradiations do not agree well with the modelled amorphization curves. As stated, this is likely to be due to the effect of dynamic annealing that occurs during the experimental irradiation that is not accounted for in the model. Although absolute information cannot be obtained for these irradiations, some information may be taken from the modelled curves with respect to the room temperature experimental data. Although the room temperature experimental data does not transpose directly onto the modelled curves, we can infer the number of overlaps required to generate the amorphous phase from the gradient of the linear portion of the amorphization curves.

Now considering the gradient of the Xe room temperature amorphization curve, it can be seen that the gradient of this curve is similar to the curve of the low temperature irradiation. Looking at the Kr irradiation curve, it can be seen that the gradient of the room temperature curve is increased compared to the low temperature irradiation. This is indicative of an increase in the number of overlaps of the collision cascades that are required to produce the amorphous phase in the crystal. Analysis of the gradients, reveals that overlaps of four and five cascades, for Xe and Kr respectively, are required to produce the amorphous phase.

The silicon irradiation at room temperature produces the greatest variation in the gradient of the amorphization curve when compared to the low temperature
irradiation. In the low temperature case, it has been shown that at least four overlaps of the collision cascades are required to form the amorphous phase. When looking at the room temperature irradiation, it appears that the gradient is very steep, with a rapid increase in amorphous material occurring at $3 - 4 \times 10^{14}$ ions cm$^{-2}$. This would indicate that the amorphization mechanism acting in this case would be the homogeneous nucleation mechanism, characterised by a rapid increase in the amount of amorphous material over a very narrow fluence range. Closer, numerical, inspection of the gradient reveals, however, that there is a finite gradient to the curve leading to a number of overlaps required to turn the substrate amorphous of at least four. This is the same as the low temperature irradiation for the same ion.

For all irradiations performed through this study, it has been shown that neither homogeneous nor heterogeneous nucleation occurs and this is evident from the amorphization curves experimentally obtained when compared to the MC model results. The experimental results are more akin to the overlap model of Gibbons [8] in which cascades must overlap with each other in order to produce the amorphous phase in the crystal. In the Gibbons model, cylindrical volumes were used instead of more realistically shaped volumes and as such this is a major flaw in this model. Through the development of the MC model described earlier in this chapter, the use of more realistic volumes has been implemented into an extension of Gibbons’ model. Using this model, it is easy to envisage that as an energetic ion is incident upon the sample, it produces a damage volume within the confines of the collision cascade itself although it is not amorphous at this point. As the fluence is increased, there is a possibility that another collision cascade will overlap with the damage volume and that, within this overlap volume, the crystal will become either more heavily damaged or amorphous depending on the mass of the implant species – the
more massive the implant species, the fewer overlaps are required to render the crystal amorphous.

This, obviously, suggests that even ions that are relatively heavy such as Xe do not necessarily produce the amorphous phase within the confines of a collision cascade produced by a single ion impact as previously thought and accepted in literature. However, when looking at the damage produced in silicon as a result of molecular ion irradiation (see for example [19, 20]), it can be seen that the damage created by a singular incoming molecular ion increases with the increasing number of atoms in the molecule. This is true for both room temperature and low temperature irradiations and has been attributed to the spatial overlapping of the collision cascades produced by the atoms which form the molecular ion. This clearly indicates that an impact with a single heavy ion does not produce amorphous material. If this were the case, overlap of cascades by, for instance, a diatomic molecule could not produce a greater amorphous volume than that produced by two individual impacts.

During experiments in which Au clusters were irradiated into silicon at room temperature, it was seen that even for clusters containing five Au atoms, amorphous material was not produced. As the number of Au atoms in the cluster was increased to seven, amorphous material was generated with the confines of the collision cascade produced by the cluster. These results are in agreement with the work presented here.

It has been shown that for ions ranging from Si to Xe in mass and for substrate temperatures from 50 K up to room temperature, amorphous material is not generally produced in the collision cascade produced by single ion impacts.
5.5 SUMMARY

It has been shown that a new model has been developed to describe the amorphization of silicon due to ion irradiation and that this model is based on Monte Carlo techniques. The results of this model have been compared to experimental data as obtained through in situ TEM measurements.

The results have shown that the data that were in best agreement to the MC model were those obtained during low temperature irradiations rather than the room temperature experiments. This is due to the dynamic annealing effect that is much more dominant during the higher temperature irradiations.

The most interesting result from the experiments presented in this chapter is the result that even for relatively heavy ions implanted into a silicon substrate held at low temperatures, multiple overlaps are required to induce a phase change from crystalline to amorphous material. This is contrary to the generally accepted view that for relatively heavy ions, amorphization occurs as a result of a heterogeneous nucleation mechanism.

The results obtain through this analysis are completely consistent with the results obtained in chapter 4 in which we saw that regions of contrast that were previously described as amorphous are not always amorphous.
Chapter 5: Ion Beam Induced Amorphization

5.6 REFERENCES

Summary and Conclusions
6.1 SUMMARY

Two aspects of the Si-based fabrication processes have been examined throughout this thesis; namely ion beam induced amorphization and the annealing of damage regions produced as a result of low fluence ion irradiation. The experiments and theory that contributed to these aspects were presented in chapter 4 (annealing of damage) and chapter 5 (ion beam induced amorphization). The main insights of these chapters are summarised in the following sections.

6.1.1 Annealing of Damage Zones

Chapter 4 presented the work done on the thermal annealing of damage generated by low fluence ion irradiation with various ions. The damage zones were imaged in a TEM under down-zone structure-factor conditions which showed the damage zones as isolated regions of contrast. Two different annealing schemes were utilised: isochronal annealing and dynamic annealing with images being recorded on both photographic film and videotape.

For all the ions used in this thesis (Xe, Kr, and Si), similar results were obtained. In all cases a wide variety of characteristic annealing curves were observed regardless of the ion or of the initial effective radius. It was observed that the damage zones resulting from single ion impacts re-crystallized at a temperature well below that required for re-crystallization of a planar \( a-c \) interface, the zones re-crystallized over a wide range of temperatures, zones of similar initial effective radii re-crystallized at very different rates, and they re-crystallized in steps – not continuously, on occasions some zones were observed to actually grow and there
were rare observations of residual defects left following re-crystallization of the zones.

It is proposed that these different characteristic curves can be explained in terms of the bond defect or IV pair whose stability is highly dependent on the local co-ordination with other IV pairs while the rare observation of residual defect following annealing indicates that very few zones have an excess of vacancies or interstitials.

Through use of multi-slice image simulations (JEMS), it was also shown that the zones of contrast that had previously thought to have resulted from amorphous material result also from damaged (but not amorphous) material and that regions containing a number of disordered atoms can also be observed using the down-zone structure-factor contrast mechanism. This is an important observation as all previous literature in which authors had observed regions of contrast resulting from single ion impacts had assumed that the regions were amorphous.

6.1.2 Ion Beam Induced Amorphization

Chapter 5 presented the work done on the in situ amorphization of Si due to bombardment with various ions at both room temperature and at 50 K. The amount of amorphous material present in the specimen was inferred through analysis of the Debye-Scherrer rings formed by amorphous material. In addition to the experimental work performed, a model to describe the build up of amorphous material within the sample was developed based upon Monte Carlo principles and the results of this model was then compared with the experimentally obtained results.

When comparing the Monte Carlo model and the experimental results it was seen that the low temperature (50 K) experiments were in closer agreement to the
model than the room temperature results. It was suggested that this discrepancy is
due to the degree of dynamic thermal annealing that occurs during the room
temperature experiments that is reduced during low temperature irradiation.

Through analysis of the gradients of the curves obtained, it is suggested that
in no case was the amorphization due to heterogeneous nucleation and that in all
cases an overlapping of the cascade volumes was required to produce amorphous
material. This is contrary to the current accepted view that all regions of contrast
produced as a result of single ion impacts in silicon and then imaged in a TEM are
amorphous.
6.2 Conclusions

From the work that has been presented and discussed in chapters 4 and 5 it is suggested that the damage formed within the volumetric confines of the collision cascade is not generally amorphous. This conclusion is found by looking at the differences between the expected and observed behaviour resulting from the experiments performed.

In the ion beam induced amorphization experiments, it was found that in no case did the fraction of amorphous material increase with ion fluence in the manner expected from heterogeneous nucleation considerations. In all cases it was observed that an overlapping of the cascades was required to produce amorphous material. This suggests clearly that the material enclosed within an isolated ion cascade is not amorphous.

The annealing of the spatially isolated zones has also shown characteristics that are somewhat at variance with those to be expected if the zones observed were to be amorphous. In the detailed analysis of the annealing of the zones, it was observed that there was a variety of ways in which the zones could anneal, including the unexpected growth of the zones. The different ways in which the zones can anneal can be modelled through the IV pair and its co-ordination with other localised IV pairs.

Electron microscopy simulation has also shown that varying concentrations of IV pairs within a fixed volume show the type of contrast seen in the experiments further leading to the conclusion that the zones are not generally amorphous in nature and that they may contain concentrations of IV pairs that account for the wide variety of annealing behaviours observed.
6.2.1 Recommendations for Further Work

In this thesis, the choice of the energy of ions was determined through the projected range, $R_p$. The exception to this was the use of the 50 keV Xe$^+$ ion.

The effect of the variation of the energy density of the cascades produced by a single ion species would also be of interest. This would involve using a relatively heavy ion such as Xe and then varying the implant energy from low energy (say 50 keV) up to high energies (approximately 1 MeV). This would produce a series of experiments in which the energy density would vary as would the cascade structure itself – ranging from a single cascade structure to a sub-cascade structure.
Appendices
APPENDIX A – NUMERICAL DAMAGE MODEL

Here the computer code, written in Fortran 90, is given along with a sample input file.

A.1 Computer Code

PROGRAM ion_implant

IMPLICIT NONE
INTEGER, PARAMETER :: rk = SELECTED_REAL_KIND(15,50)
INTEGER, PARAMETER :: ik = SELECTED_INT_KIND(6)
INTEGER:: j, k, s1, s2, s3, sample, points, c1, c2, c3
INTEGER(KIND = ik):: n, rows, i
REAL(KIND = rk):: xr, yr, zr, a, b, c, r, dummy, depth
REAL(KIND = rk), DIMENSION(3):: centre_point, hit_point
REAL(KIND = rk), DIMENSION(:), ALLOCATABLE:: z_prob
INTEGER, DIMENSION(:,:), ALLOCATABLE:: grid
INTEGER, DIMENSION(:), ALLOCATABLE:: counter, bin
CHARACTER(LEN=100):: filename, prob_file

!Read data from input file
OPEN(10, FILE = 'inputfile.txt')
READ(10,*) filename
READ(10,*) prob_file
READ(10,*) n
READ(10,*) a
READ(10,*) b
READ(10,*) c
READ(10,*) s1
READ(10,*) r
READ(10,*) rows
CLOSE(10)

! Read Probability Distribution into z_prob
ALLOCATE(z_prob(0:100))
z_prob = 0.0_rk
OPEN(10, file = prob_file)
READ(10,*)
DO i = 1, 100, 1
  READ(10,*) dummy, z_prob(i)
END DO
CLOSE(10)

! Start Randomnumber generation from a random seed.
CALL RANDOM_SEED()

! Setup Grid array
s2 = INT((b/a)*s1)
Appendix A: Numerical Damage Model

\[ s_3 = \text{INT}(\frac{c}{a}s_1) \]
\[ \text{ALLOCATE(grid}(0:s_1-1,0:s_2-1,0:s_3-1)) \]

points = 5 ! Number of Columns in Output
\[ \text{ALLOCATE(counter}(0:n), \text{bin}(100)) \]
\[ \text{OPEN}(10, \text{file} = \text{filename}) \]
\[ \text{WRITE}(10, '(A98)') ' Ions Not Hit Hit 1+ Hit 2+ Hit 3+ Hit 4+ Hit 5+' \]
\[ \text{grid} = 0.0_ik \]
\[ \text{bin} = 0 \]

DO sample = 0, rows, 1
! Generate random numbers for x, y and z
IF (sample > 0) THEN
DO i = 1, n/rows, 1
CALL RANDOM_NUMBER(depth)
CALL RANDOM_NUMBER(xr)
CALL RANDOM_NUMBER(yr)
CALL RANDOM_NUMBER(zr)
zr = zr / 100.0_rk
DO j = 1, 100, 1
IF ((depth >= \text{SUM(z_prob}(0:j-1))).AND.(depth < \text{SUM(z_prob}(0:j)))) THEN
\text{bin}(j) = \text{bin}(j) + 1
zr = (REAL(j-1)/100.0_rk) + zr
END IF
\text{hit_point} = (/xr*a, yr*b, zr*c/)
DO c1 = MAX(0,\text{INT}((xr*s_1) - r) - 1) , MIN(s_1 - 1,\text{INT}((xr*s_1) + r) + 1), 1
DO c2 = MAX(0,\text{INT}((yr*s_2) - r) - 1) , MIN(s_2 - 1,\text{INT}((yr*s_2) + r) + 1), 1
DO c3 = MAX(0,\text{INT}((zr*s_3) - r) - 1) , MIN(s_3 - 1,\text{INT}((zr*s_3) + r) + 1), 1
! Checks if centre of grid cell is less than Re away from hit point
centre_point(1) = c1*(a/(2.0_rk*REAL(s_1))) + (a/(2.0_rk*REAL(s_1)))
centre_point(2) = c2*(b/(2.0_rk*REAL(s_2))) + (b/(2.0_rk*REAL(s_2)))
centre_point(3) = c3*(c/(2.0_rk*REAL(s_3))) + (c/(2.0_rk*REAL(s_3)))
IF (\text{SUM}((\text{hit_point} - \text{centre_point})**2) < r**2.0) THEN
grid(c1,c2,c3) = grid(c1,c2,c3) + 1
END IF
END DO
END DO
END IF
! Count number of hits in each cell
counter = 0
DO i = 0, s_1 - 1, 1
DO j = 0, s_2 - 1, 1
DO k = 0, s_3 - 1, 1
\text{counter(grid}(i,j,k)) = \text{counter(grid}(i,j,k)) + 1
END DO
END DO
END DO
DO i = 1, points, 1
\text{counter}(i) = \text{SUM}(counter(i:n))
Appendix A: Numerical Damage Model

END DO

! Output to file
WRITE(10,'(I14)',ADVANCE = 'NO') sample*(n/rows)
DO i = 0, points, 1
  IF (i < points) THEN
    WRITE(10,'(I14)',ADVANCE = 'NO') counter(i)
  ELSE
    WRITE(10,'(I14)') counter(i)
  END IF
END DO
END DO

WRITE(10,*)
WRITE(10,'(A12,I14)') 'Total Ions: ',n
WRITE(10,'(A6,3F9.4)') 'Cell: ', a, b, c
WRITE(10,'(A6,3I5)') 'Grid: ', s1, s2, s3
WRITE(10,'(A15,F9.4)') 'Damage Radius: ', r

! Check distribution of zones by depth

WRITE(10,*)
WRITE(10,*) '  Prob output'
WRITE(10,*)
DO i = 1, 100, 1
  WRITE(10,'(I5,I8)')  i, bin(i)
END DO

CLOSE(10)

END PROGRAM ion_implant

A.2 Sample Input File

Si_out.txt !output file
Dam_prob.txt !prob file
1E8 !number of ions
500 !a, nm
500 !b, nm
100 !c, nm
1000 !cells in a-direction
7.9 !radius, nm
10000 !lines of output
APPENDIX B – IV PAIR POCKET STABILITY –

DEPENDENCE ON RADIUS

Zones that contain the same concentration of IV pairs will anneal at different temperatures when the zones are of differing sizes i.e. smaller zones will anneal faster than larger zones for a given concentration of IV pairs within the zone. This happens because of the change in co-ordination of the IV pair at the surface of the zone as the radius of the zone varies. For an isolated IV pair, the co-ordination is zero and has a pair re-combination energy of 0.43 eV. As the co-ordination of the IV pair varies, so does its re-combination energy and this is given as:

\[ E(n) = 0.6 + 0.2n + 0.0012n^3 \]  

Where \( n \) is the co-ordination number and this varies from 1 (two neighbouring IV pairs) to 12 (an IV pair completely surrounded and paired with other IV pairs). For the case of isolated zones, the co-ordination number will never exceed 7, the co-ordination of a planar interface, if the radius of the zones reaches infinity.

To find the re-combination energy of a zone of particular radius \( r \) we assume that a single IV pair at the zone interface recombines with an energy that is a function of the radius of the zone, \( E(r) \). In order to solve this problem, we look at the volume of two intersecting spheres. We know that the volume, \( V \), of the two intersecting spheres is given by:

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Appendix B: IV pair Pocket Stability

\[ V = \frac{\pi (R + r - d)^2 (d^2 + 2dr - 3r^2 + 2dR + 6rR - 3R^2)}{12d} \]  

where \( R \) is the radius of a fixed sphere, \( r \) is the radius of a sphere distance \( d \) from the origin of the fixed sphere. If we state that the radius of the fixed sphere \( R \) is the distance between two nearest neighbour IV pairs, \( \sim 7 \text{ Å} \), we can find the volume of the intersecting spheres as a function of the radius of the zone as it increases towards infinity. We always want the defect that initiates the re-growth to be at the origin of the fixed sphere \((0,0,0)\), and as such we must set the radius of the zone to be equal to the distance from the origin of the fixed sphere i.e. \( r = d \). When we plot a graph of the volume as a function of \( \frac{1}{r} \), we obtain a straight-line graph as show in figure B.1. Also shown on the graph is the line of best fit and its associated equation.

As we can see from the graph, the fractional co-ordination number of the defect at the origin of the fixed sphere increases with increasing radius up to 0.5 (a co-ordination number of 7) when the radius of the zone reaches infinity.

We can now use the line of best fit to obtain an effective co-ordination number as a function of the radius of the zone and put this value into equation B.1 to obtain a recombination energy for an amorphous zone of a given radius \( r \). A graph of the recombination energy as a function of zone radius is shown in figure B.2.

As we can see from this graph, the zone becomes more stable as its radius increases, eventually becoming asymptotic to 2.44 eV, the activation energy of recombination of an IV pair at a planar interface\(^3\). From this graph and related equations, we can now obtain activation energies for recombination of zones containing a concentration of 25% IV pairs or more (the value of IV pairs that give a

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radial pair distribution function the same as for an amorphous matrix) for zones of varying sizes.

**Figure B.1:** Graph showing the fractional coordination number as a function of the inverse radius of the amorphous zone. A line of best fit and its equation are shown.

**Figure B.2:** Graph showing the recombination energy as a function of the amorphous zone radius. The clear dependence on the radius of the zone is shown.
APPENDIX C – SLICING CELLS FOR JEMS, THE COMPUTER CODE

Given here is the computer code, written in Fortran 90, used for generating input files for JEMS.

C.1 Computer Code

PROGRAM slice_convert !

IMPLICIT NONE
INTEGER, PARAMETER :: ik = SELECTED_REAL_KIND(15,50)
INTEGER:: i, j, slices, atoms, axis
REAL(KIND = ik), DIMENSION(:,,:), ALLOCATABLE:: coords
REAL(KIND = ik):: cell_a, cell_b, cell_c, slice_width
CHARACTER(LEN=100):: filename, file_no

PRINT*,’Program to Slice coordinate files along a cartesian axis direction'
PRINT*,’and write JEMS input files and xyz files ’
PRINT* 
PRINT*,’Enter full name of coordinate file: (including path if not in this directory)' 
READ(*,*) filename 
PRINT* 
PRINT*,’Enter the cell dimensions a b and c in nm pressing enter after each ’
READ(*,*) cell_a
READ(*,*) cell_b
READ(*,*) cell_c
PRINT* 
PRINT*,’Pick an direction to slice the cell ’ 
PRINT*,’1 for x, 2 for y, 3 for z ‘ 
READ(*,*) axis 
PRINT* 
PRINT*,’Enter no of Slices: ‘
READ(*,*) slices
PRINT*

! Determine width of each slice
IF (axis == 1) THEN
slice_width = cell_a / slices
cell_a = slice_width
END IF
IF (axis == 2) THEN
slice_width = cell_b / slices
cell_b = slice_width
END IF
IF (axis == 3) THEN
slice_width = cell_c / slices
cell_c = slice_width
END IF
WRITE(6,'(A20,F8.4)') 'Slice Width = ',slice_width

OPEN(10, FILE = TRIM(filename))

atoms = 0 ! Initialize atom count
DO
  READ(10,*,end = 100)
  atoms = atoms + 1
END DO

100 CONTINUE

atoms = atoms - 1
ALLOCATE(coords(0:atoms,3))  ! Set coords array to atoms x 3
REWIND(10)

DO i = 0, atoms, 1
  READ(10,*) coords(i,:)
END DO

DO i = 1, slices, 1  ! Set output file names and sort coords into them
  WRITE(file_no,*) i
  OPEN(10+i, FILE = filename(1:LEN_TRIM(filename)-4)//'_'//file_no(VERIFY(file_no,''):LEN_TRIM(file_no))//'.txt')
  DO j = 0, atoms, 1
    IF ((coords(j,axis) >= (i-1) * slice_width) .AND. (coords(j,axis) < i * slice_width)) THEN
      WRITE(10+i,'(3F15.9)') coords(j,:)
    END IF
  END DO
  REWIND(10+i)   ! Reset File
END DO

CLOSE(10)
DEALLOCATE(coords)   ! Close array so it can be used again

! Covert new slice files into JEMS input

DO j = 1, slices, 1
  WRITE(file_no,*) j
  OPEN(11 + slices + j, FILE = filename(1:LEN_TRIM(filename)-4)//'_'//file_no(VERIFY(file_no,''):LEN_TRIM(file_no))//'.xyz')
  atoms = 0     ! Initialize atom count
  DO
    READ(10+j,*,end = 200)
    atoms = atoms + 1
  END DO

200 CONTINUE

! Writing .xyz file
WRITE(11 + slices + j,'(I6)') atoms
  WRITE(11 + slices + j,'(A22, I5)') 'Silicon Slice number: ',j
  atoms = atoms - 1
ALLOCATE(coords(0:atoms,3))  ! Set coords array to atoms x 3
REWIND(10+j)
DO i = 0, atoms, 1
    READ(10+j,*) coords(i,:)
    WRITE(11 + slices + j,'( A5,3F17.6)') 'Si',coords(i,:)
END DO
REWIND(10+j)

! File Header (JEMS input file)
WRITE(10+j,'(A5,filename(1:LEN_TRIM(filename)-4)//'_//file_no(VERIFY(file_no,'')://LEN_TRIM(file_no)))
WRITE(10+j,*) 'system|triclinic'
WRITE(10+j,*) 'superCell|true'
WRITE(10+j,*) 'HMSymbol|1|1|0|0| P 1'
WRITE(10+j,*) 'rps|x , y , z'
WRITE(10+j,*) 'lattice|0|',cell_a ! Cell Parameters
WRITE(10+j,*) 'lattice|1|',cell_b
WRITE(10+j,*) 'lattice|2|',cell_c
WRITE(10+j,*) 'lattice|3|90.000'
WRITE(10+j,*) 'lattice|4|90.000'
WRITE(10+j,*) 'lattice|5|90.000'
coords(:,axis) = coords(:,axis) - ((j-1) * slice_width)
DO i = 0, atoms, 1   ! Write out atoms info (atom symbol, Wickhoff notation, x, y, z, Debye-Waller, occupancy, absorption)
    WRITE(10+j,'(A5,I4,A6,F8.5,A1,F8.5,A19)')
        'atom|',i,'|Si,a,',coords(i,1)/cell_a,',',coords(i,2)/cell_b,',',coords(i,3)/cell_c,',0.005,1.000,0.0350'
END DO

! see http://cimewww.epfl.ch/people/stadelmann/jemsWebSite/BuildingFirstCrystal.html
! Write File Ending
WRITE(10+j,'(A101)') 'aff|0|Si|2.129,57.775,2.533,16.476,0.835,2.88,0.322,0.386|Doyle - Turner
Acta Cryst. A24 (1968),390'
WRITE(10+j,'(A189)')
WRITE(10+j,'(A14)') 'nsl|0|Si|0.415'
WRITE(10+j,'(A85)')
CLOSE(10+j)
DEALLOCATE(coords)
END DO

PRINT*, 'Files in same directory as input.'
PRINT*, 'Remove all spaces from JEMS files using text editor'
PRINT*, 'Press Enter to Continue'
READ(*,*)

END PROGRAM slice_convert