DEFECT STUDIES OF
ION IMPLANTED
SILICON & SILICON-DIOXIDE FOR
SEMICONDUCTOR DEVICES

Matthew Da-Hao Lay

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To my wife Yani
Abstract

We have studied the introduction of defects in silicon wafers with low dose channeling ion implantation. Implants of 600 keV phosphorus into Cz-grown silicon to fluences between $2 \times 10^8 - 1 \times 10^9$ cm$^{-2}$ were performed. Implants were performed in the channeling orientation and at a tilt angle equivalent to a random orientation. Samples were then examined with Deep-Level Transient Spectroscopy (DLTS) and three defects were identified in samples: VO, $V_2^-$ and $V_7^-$/VP. No variation in point-defect species was observed as implantation angle was varied in contrast with work published by others. Defect concentrations were found to increase linearly with implant fluence over the range studied, channeling however leads to a slower increase as fluence is increased. The $V_7^-$/VP defect depth profile was also obtained with DLTS. A significant amount of surface enhanced annihilation was proposed to account for the deviation of measured profiles from Crystal-TRIM simulations. Simulations however, did show a good fit to the measured profiles deeper into the sample. This suggests the influence of surface enhanced annihilation extends up to 1 $\mu$m into the sample. Only 1.5% of vacancies predicted to be produced could be accounted for in measurements and this was less than the expected yield of 4-10% based on the literature.

The subsequent production of secondary extended defects upon annealing in medium dose implanted samples as a function of implantation angle was also examined. Samples were implanted with 75 keV phosphorus ions to fluences in the range $1 \times 10^{14} - 4.5 \times 10^{14}$ cm$^{-2}$ and annealed at 750°C for 10–15 minutes. It was found that channeling does not affect the formation threshold but does affect the size and population of defects formed. The threshold fluence at which extended defects would form was found to be reduced with an increasing annealing time. The effect of channeling on the formation of short rod-like defects is also presented for the first time.

Finally, the effect of localised medium dose low energy implantation on the surface potential of thin thermal oxides on silicon was studied with Kelvin-probe Force Microscopy (KFM). Samples with either 5, 15 or 50 nm oxides were implanted with 15 keV ions of either $^{10}$B, $^{28}$Si, $^{29}$Si or $^{31}$P. It was shown that KFM was clearly able to laterally resolve implanted areas and that implantation resulted in a either an increase or decrease in the surface potential. Results suggested that oxide and silicon substrate damage manifested itself as a reduced surface potential as a result of defects with a negative charge state. It was unclear however if the increased surface potential was due to interface states or carbon-stitching on the surface. The magnitude of the change in surface potential scaled with implanted ion mass and fluence. However, as fluence was increased beyond $1 \times 10^{13}$ cm$^{-2}$ the increase in surface potential began to reduce.
Declaration

This is to certify that:

(i) the thesis comprises only my original work towards the PhD except where indicated,

(ii) due acknowledgement has been made in the text to all other material used,

(iii) the thesis is less than 100,000 words in length, exclusive of table, maps, bibliographies, appendices and footnotes.

Matthew Da-Hao Lay
Publications

During the course of this project, a number of public presentations have been made which are based on the work presented in this thesis. They are listed here for reference.


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Introduction

Semiconductor devices have revolutionised the world in which we live and have become such an integral part of our everyday lives that we often take for granted that they can and will perform the task they were designed for. The requirement for extremely high quality semiconductor wafers and tight tolerances on processing parameters arise from the high sensitivity of modern devices to defects created during the various fabrication steps. This includes contamination from impurities and damage created by the bombardment of ions. As devices such as transistors are reduced in dimension there are fewer and fewer carriers. Also, with the advent of solid state quantum computing, the effect of defects are ever more important. The next-generation of electronic devices are expected to include semiconductor structures that depend on the storage and transfer of information described by quantum physics. Successful realisation of such devices will depend on a detailed knowledge of the defects introduced into the material during each processing step and the elimination of defects wherever necessary.

There are many factors that affect the types of stable defects and the concentrations of defects that remain after processing. These include parameters such as annealing temperature and duration. The interaction between defects and the role of the surface and impurity gettering are several less obvious factors that are also important. Defect engineering can in fact be utilised to deliberately reduce charge carriers or mobility in specific regions within samples to obtain the desired properties. A full understanding of defect formation, evolution and the complexities of the interactions involved are necessary if defects are to be tailored for a specific purpose.

Defects have two main deleterious effects on samples: they can directly affect the electronic properties, and they can affect the ability to accurately fabricate the required device structures. For example, point defects in the nominally crystalline structure of a silicon wafer can form deep energy levels that trap charge carriers. The dissolution of extended defects after thermal annealing has also been shown to lead to enhanced dopant diffusion, so called Transient Enhanced Diffusion (TED) which makes it difficult to achieve the required doping profiles.
Ion implantation is an important part of semiconductor device fabrication and is usually performed in the interest of modifying the electrical characteristics of the target material. The implanted ions interact with atoms in the substrate in a stochastic manner and the final resting place for the ions can only be specified with some probability. Implantation also results in the creation of defects in the substrate wafer. If it is to be used for nano-scale device fabrication, the subsequent post-implantation behaviour of the defects that are created must be better understood.

The trend towards the fabrication of shallow junctions in modern micro-electronic devices has also led to the use of low energy ions that have a larger channelling fraction. Implantation of low energy ions through high aspect ratio masks, a suggested step in constructing solid-state quantum computers may also involve channelled ion implantation. It has been known for some time that channeling ion implantation reduces the amount of implantation damage, but our understanding of the effect of channeling on defect formation is not complete. There have also been few experiments that have directly examined the profiles of defects created by channeling and none that have directly examined the effect of axial channeling on point defect formation.

As device dimensions are reduced higher implant fluences are also required, this increases the dopant concentration so that a large number of carriers can be maintained. This results in a higher concentration of defects created and can also lead to the creation of secondary defects after annealing. In particular, interstitial atoms can form extended defects, such as rod-like defects and dislocation loops. Their presence in silicon is technologically important from a fabrication standpoint because of their role in releasing interstitial atoms when they dissociate at elevated temperatures leading to TED.

There is also some interest in implantation after gate oxide growth. This may be used to adjust threshold voltages for MOSFET's and is also being used as a means for fabricating single donor arrays for solid-state quantum computing. Through-oxide implantation avoids the dopant diffusion that would occur if thermal oxidation was performed after implantation. It is expected that through oxide implantation will create defects in the form of sub-surface charge in the oxide or at the oxide interface, the presence of which may affect the operation of electrodes in quantum devices. However, there are few techniques that can examine implantation damage in thin-oxides implanted with a medium or high fluence of ions while also providing the capability to laterally resolve damaged regions in a sample; a growing need as the trend in reducing device dimensions is
continued. Scanning probe techniques such as Kelvin-probe Force Microscopy are ideally suited for this task, however there have been few studies of its potential use.

This project is the continuation of work by the many who have sought to understand the effect of ion implantation on single crystal silicon, and the associated silicon dioxide layer. In broad terms this work is a step towards understanding the impact of various implantation and annealing parameters on the local structure of silicon and thin oxide layers on silicon. Although defect studies in silicon have been the subject of much examination, there nevertheless remains areas to be explored. In particular, the effect of implantation angle on the profile of vacancy-related defects in ion implanted silicon has not been studied in detail, nor the effect of implantation on thin oxides on the small-scale. Furthermore, there is still some debate about the formation mechanisms of extended secondary defects in silicon.

A review of research on implantation related defects in silicon is presented in Chapter 1. Studies into the effect of damage density on the types of stable defects that can form and the effect of the proximity to the sample surface for example will be reviewed. Chapters 2 & 3 detail the main experimental techniques and equipment used for this work.

Subsequent chapters in Part II examine the effect of implantation on silicon and silicon dioxide thin films under various conditions. In Chapter 4, the effect of ion channelling on the profile of vacancy-related defects is studied with Deep-Level Transient Spectroscopy. Chapter 5 explores the effect of ion channelling and annealing duration on the formation of extended secondary defects. Chapter 6 explores the use of Kelvin-probe Force Microscopy to examine the effect of ion implantation on the surface potential of thin oxides on silicon, and attempts to correlate this with implantation damage. The main outcomes of these studies and suggestions for further work are presented in Chapter 7.
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Part I

Background
Chapter 1

Implant Damage & Ion Channelling

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1.1 Implantation Damage in Si

1.1.1 Primary Defect Structures - Point Defects

Frenkel Defects

It is well established that ion implantation introduces damage into the sample being implanted [1, 2]. In particular, Frenkel pair defects are created in implanted crystals as a result of the collisions between the implanted ion and atoms in the
sample lattice. The Frenkel defect consists of a host atom that has been knocked off its (substitutional) lattice site into an interstitial position (i.e. between crystal lattice sites) leaving a vacancy behind [2]. It should be noted that many early studies of defects in silicon were conducted on electron irradiated samples in which Frenkel defects are produced through the energy deposited to the lattice atoms via Compton scattering. Electron irradiation however produces less dense defect cascades due to the more uniform penetration of electrons into the sample compared to heavier ions.

Frenkel defects are known to readily annihilate at non-cryogenic temperatures. The silicon interstitial is highly mobile and if it encounters a vacancy can return to a substitutional lattice position, thereby annihilating the defect. This has been shown to be effective down to 4.2 K, although the efficiency of defect retention has been shown to be highly dependent on the presence of group III dopants which are said to trap the interstitial [3]. In trapping the silicon interstitial the dopant is shifted into an interstitial site [3, 4]. Isolated vacancy retention is thus more efficient in p-type silicon, although counter doping n-type silicon with p-type dopants also increases defect retention [3]. Substitutional carbon (C\(_s\)), which can exist with concentrations up to 10\(^{17}\) cm\(^{-3}\) in Czochralski (Cz) and Float-Zone (FZ) silicon, also traps interstitial silicon to form interstitial carbon (C\(_i\)) [5]. Interstitial carbon however becomes mobile at 300 K, and can complex with substitutional carbon to form C\(_i\)C\(_s\) [2, 6] or if there is sufficient oxygen present C\(_i\)O\(_i\) [5].

The isolated vacancy also becomes mobile and diffuses to form di-vacancy clusters (V\(_2\)) or defect complexes with impurity atoms that have trapped them. The temperature by which all the isolated vacancies have been trapped depends on the dopants and impurities present. The temperature at which isolated vacancies disappear after 15 minute anneals -as monitored with Electron Paramagnetic Resonance spectroscopy (EPR)- is 70 K in n-type, 150 K in p-type and 200 K in high resistivity silicon samples [7].

The type and concentration of dopants present also affects the Fermi level of the substrate which determines the vacancy’s dominant charge state. These are the V\(^{2-}\) for n-type, V\(^{2+}\) for p-type and V\(^0\) for high resistivity silicon; where the charge shown is that when occupied by an electron [3]. This seems to be correlated to the different trap energy levels associated with these charge states; V\(^{2-}\) is closest to the conduction band, V\(^{2+}\) close to the valance band and V\(^0\) lying in between. Each of these charge states is also believed to have different diffusivities, which also affects the annealling temperature of each charge state.
The forward momentum of interstitial host atoms created during high energy or heavy ion implantation (silicon recoils) also leads to a separation between the vacancy and interstitial profiles [6, 8, 9] which can enhance defect retention. Studies show vacancy-related defects in ion implanted silicon at depths less than the projected range of ions both for MeV Si implants [10, 11] and for keV F [12] and Si [13]. Although, these studies all involved implanted fluences above $1 \times 10^{13}$ cm$^{-2}$.

Most wafers used for device fabrication are not in fact thermally regulated during implantation, so the room temperature stable defects are of more interest to us than the Frenkel defects. Few isolated defects remain at room temperature, only 4-10% of the defects created during room-temperature implantation survive annihilation [2]. In the low fluence regime (< $10^9$ cm$^{-2}$) about 10-25% of the Frenkel defects that survive annihilation form a di-vacancy cluster [14] which is a characteristic defect for ion implanted silicon [1, 15]. Moreover, the di-vacancy and vacancy related complexes are important because they trap charge carriers in the substrate. The interstitial has also been reported to exist as a di-interstitial.

**Room Temperature Stable Defects**

The defects of prime importance for electrical devices are those that trap charge carriers in the device, these are said to be electrically active. Defects trap electrons mostly due to their dangling bonds (unpaired electrons), which rearrange in a certain way depending on the defect structure. EPR has played the major role in determining defect structures since it acts as an extremely sensitive probe of the local bonding environment surrounding the defect although not all defects produce an EPR signature.

On the other hand, interstitial silicon does not behave as an electrically active trap, although it can indirectly result in active traps such as interstitial carbon mentioned earlier [16]. Interstitial silicon does however play a key role in dopant diffusion processes by interacting with group III dopants, most notably boron, and can directly compensate them. It has also been implicated in compensating n-type dopants [17]. Since interstitials only have an indirect effect on the electrical properties of silicon, much of our knowledge regarding the interstitial has been obtained by studying their involvement in dopant diffusion and, as will be discussed in the next section, in the formation of secondary defects from annealing which consist of interstitials.

Active majority carrier traps can be described as unoccupied energy states in the band-gap with a level between the shallow dopant level and the mid band
gap. For electron traps in n-type silicon this roughly means defects between 0.01-0.55 eV below the conduction band. Of the many traps that can exist the most important of these are those that are closer to the middle of the band-gap since once charge is trapped it is difficult to empty, these are the Deep-Level traps.

Deep-level traps are often characterised by their activation energy ($E_t$). This is taken to be the energy of the trap with respect to the nearest band edge. So relative to the bottom of the conduction band ($E_c$) for electron traps and relative to the top of the valance band ($E_v$) for hole traps. The capture cross-section for the trap is also often quoted as $\sigma_c$.

The values reported for electron traps in ion-implanted silicon are found in Table 1.1. This table shows the average value for the trap energies found in the literature. Absolute errors in the last digit are shown in parentheses, no error is quoted for occasions where there is only one reference for the defect, nor is the error quoted for capture cross-sections that have an error that is over an order of magnitude difference. V indicates vacancy, other letters indicate elements, subscripts 2 & 3 indicate the number of vacancies in a cluster and superscripts indicate the charge state of the trap. Other subscripts indicate either substitutional or interstitial lattice positions in the crystal.

Note that the experimental studies presented in this thesis deal solely with n-type silicon and so discussion is restricted to electron traps relevant to n-type silicon devices.

The most common impurities in silicon wafers are dopants, oxygen and carbon and these therefore exist in the most common vacancy related (and therefore implantation related) defect complexes. The relative concentrations of defect species can, therefore vary with background concentrations of impurities. A typical example is the difference between a Float-Zone refined wafer (FZ-Si) and Czochralski grown wafer (Cz-Si). Here the background concentrations of oxygen can be several orders of magnitude less in the case of FZ-Si and therefore contain very few VO defects.

The surface is also known to act as a sink for defects, and in some cases also a source. Based on dopant diffusion experiments examining the effectiveness of the surface as a sink for vacancies a recombination length of up to 70 nm has been calculated by Rücker et al. [30]. Vacancy depth profiles have also shown that surface enhanced annihilation is more effective for shallow implants and that profiles are sharper than those predicted by Monte-Carlo simulations (that do not
<table>
<thead>
<tr>
<th>Defect type</th>
<th>Trap Energy (eV)</th>
<th>Capture cross-section (cm²)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C⁵⁻</td>
<td>0.10</td>
<td>-</td>
<td>[5]</td>
</tr>
<tr>
<td>H-related</td>
<td>0.10</td>
<td>-</td>
<td>[18]</td>
</tr>
<tr>
<td>H-related</td>
<td>0.13</td>
<td>-</td>
<td>[18]</td>
</tr>
<tr>
<td>HC</td>
<td>0.15(1)</td>
<td>-</td>
<td>[19, 20]</td>
</tr>
<tr>
<td>VO⁻</td>
<td>0.17(1)</td>
<td>7(4)×10⁻¹⁵</td>
<td>[15, 20, 21, 22, 23, 24]</td>
</tr>
<tr>
<td>C₇Cᵢ</td>
<td>0.17(0)</td>
<td>8×10⁻¹⁸</td>
<td>[2, 6]</td>
</tr>
<tr>
<td>V-related</td>
<td>0.19(1)</td>
<td>3.5×10⁻¹⁷</td>
<td>[21, 28]</td>
</tr>
<tr>
<td>V₂⁻</td>
<td>0.22(1)</td>
<td>5(4)×10⁻¹⁶</td>
<td>[15, 21, 22, 23, 24, 25]</td>
</tr>
<tr>
<td>V₂O</td>
<td>0.27</td>
<td>-</td>
<td>[2]</td>
</tr>
<tr>
<td>V₃O</td>
<td>0.30</td>
<td>-</td>
<td>[2]</td>
</tr>
<tr>
<td>VO-H, other H-related</td>
<td>0.30(2)</td>
<td>3×10⁻¹⁵</td>
<td>[15, 18, 20, 27, 22, 28]</td>
</tr>
<tr>
<td>V-related</td>
<td>0.35(1)</td>
<td>5×10⁻¹⁶</td>
<td>[22, 23]</td>
</tr>
<tr>
<td>H-related</td>
<td>0.39(1)</td>
<td>1×10⁻¹⁷</td>
<td>[21, 22]</td>
</tr>
<tr>
<td>H-related</td>
<td>0.41(1)</td>
<td>-</td>
<td>[18, 24]</td>
</tr>
<tr>
<td>VP⁺</td>
<td>0.42(2)</td>
<td>-</td>
<td>[2, 18, 21]</td>
</tr>
<tr>
<td>V₂⁺</td>
<td>0.42(1)</td>
<td>-</td>
<td>[21, 15, 23, 25, 2, 26]</td>
</tr>
<tr>
<td>H-related</td>
<td>0.45(1)</td>
<td>1×10⁻¹⁷</td>
<td>[15, 18, 21, 28, 29]</td>
</tr>
<tr>
<td>V₂-related</td>
<td>0.47</td>
<td>-</td>
<td>[21]</td>
</tr>
<tr>
<td>H-related</td>
<td>0.50(1)</td>
<td>-</td>
<td>[15, 20, 27]</td>
</tr>
</tbody>
</table>

Table 1.1: Defect characteristics as published in the literature for defects relevant to ion-implanted n-type silicon.
take defect annihilation/annealing into account) [14].

These primary defects anneal out by 400°C [3, 24]; the VP complex anneals at around 200°C, the V$_2$ cluster at around 300°C [5] and the VO complex anneals out at 360°C [5]. After these defects have annealed out, other secondary defects can form from their constituents. The V$_2$O is an example of this [2] or, as will be discussed in the next section, larger extended defects that consist of silicon interstitials can also form.

**Amorphisation**

If the implantation damage exceeds a certain amorphisation threshold a sufficient number of interstitial atoms or displaced (lattice) atoms are generated which renders the implanted layers amorphous. Although there is no long range order in amorphous silicon, there is still a degree of short range order with atoms maintaining a four fold coordination. The amorphous phase of silicon is also less dense than the crystalline phase [31] and has a different electronic structure [32]. An excellent review of implantation induced amorphisation is given by Pelaz et al. [33].

**1.1.2 Secondary Defect Structures - Extended Defects**

Although point defects almost completely anneal out by 400°C it has been observed with Transmission Electron Microscopy (TEM) that, after a critical damage concentration is reached [34], extended defect structures are formed that are stable up to higher temperatures and for longer times. These secondary defects that are created after annealing have been shown to be comprised of interstitial atoms and are not only common to implanted single crystal silicon but germanium as well [35]. The two main types of defects that have been observed are rod-like defects and loops. An understanding of these defects is important because they have been shown to enhance dopant diffusion during annealing [34, 36] as the interstitials trapped within them are released upon defect dissociation. These have been labelled as category-I defects [37] or secondary defects resulting from implantation at fluences below the amorphisation threshold.

Upon annealing of silicon that has been implanted beyond a certain implant threshold, secondary defects may be formed beyond the amorphous-crystalline interface (category-II secondary defects) and also, due to imperfect crystal regrowth, in the initially amorphous layer (category-III defects). If a buried amorphous layer was created, secondary defects can also remain where the two inter-
faces of the layer meet as the region is recrystallised (category-IV defects). If the impurity concentration exceeds the solid solubility limit in the substrate other defects associated with this impurity can also result (category-V defects).

The following sections will focus on defects created from pre-amorphisation implantation, i.e. category-I defects. However, although the formation characteristics may be different for each category of defects, the defects once formed seem to behave in a similar fashion with further annealing. Studies involving defects formed after amorphising implants will be duly noted in the text.

Structure & Orientation of Rod-like defects

When viewing a (100) Si sample prepared for plan-view TEM, rod-like defects have been observed to have an orientation along the [100] & [010] directions in samples amorphised by implantation[38]. These directions correspond to the projection of rods elongated along the set of (110) directions onto the (001) plane. Those oriented along [100] correspond to the projection of rods elongated along [101] & [101]. While those along [010] correspond to [011] & [011] (See Fig. 1.1). Therefore, for a (100) Si sample prepared for cross-sectional TEM (XTEM), rods will be seen to be elongated along [101] & [101] and [110] & [110] at 60° to each other.

![Diagram](image)

Figure 1.1: a) The six (110) growth directions for rod-like defects b) The projections of these onto the (001) plane [38].

Rod-like defects have been observed to be as small as 5 nm in length [39, 40],
to hundreds of nanometres long [41] and even as long as a micron [42]. They have been shown to be made up of hexagonal, 5-member and 7-member rings of interstitial Si monolayers [39]. The rod is actually rectangular, more like a tape worm or ribbon (See Fig. 1.2). This is revealed by careful analysis of high-resolution TEM (HRTEM) and is described in detail by Takeda [35]. Rod-like defects are also labelled as {311} defects owing to the habit plane of the defect. Although Claverie et al. [43] indicate that the planar {311} defect identified in HRTEM is in fact different to the longer rod-like defect most commonly identified in normal TEM [43]. A {111} habit plane and displacement vector of $\frac{\bar{a}}{10}(111)$ has also been reported for rod-like defects [42].

Figure 1.2: Schematic of the {311} defect viewed along a ⟨110⟩ direction, after Takeda et al. [35]. Numbered rings indicate the number of atoms in rings that are different from rings in a perfect crystal.

Structure & Orientation of Dislocation Loops

There are two types of dislocation loops observed: faulted (or Frank) dislocation loops (FDL), and perfect (or prismatic) dislocation loops (PDL), both of which have a {111} habit plane [44, 45]. Rectangular elongated defects have also been referred to in the literature [46], but are in fact perfect dislocation loops [43].

Both consist of two additional circular {111} planes of Si [43], but the difference between these types of loops is that Frank loops have a Burgers vector, $\mathbf{b}$ of $\frac{\bar{a}}{3}(111)$, while perfect loops have a Burgers vector of $\frac{\bar{a}}{2}(110)$ [44, 47].

There are four variants of loops, and when viewed along the [100] direction they appear as elliptical objects with major axes parallel to the [110] and [110] directions.

Loops are observed to have a range of sizes. Loops with diameters 10-40 nm are commonly observed as a band of defects in cross-sectional TEM [45], while Frank loops have been observed with up to a 100 nm diameter [41].
1.1.3 Implant Conditions for Extended Defect Formation

There have been many proposals over the years to determine the minimum implant requirements for extended defect formation. That is, the implantation conditions are such that after implantation there exists an annealing regime that will lead to the formation of extended defects. Some of these proposals have subsequently been experimentally falsified; the requirement of the presence of boron for the formation of extended defects for example. It has been shown that implantation of a variety of ions and in the complete absence of boron can lead to extended defect formation. Other proposals however, although in principle easy to test, have in reality proven to be rather difficult. For example, the determination of whether there is a threshold implanted ion concentration, or a threshold damage concentration which determines if extended defects will form, although seemingly easy to test in principle, in reality it has proven difficult to find a conclusive answer.

Jones et al. [37] and Eaglesham et al. [47] claim from their experiments that it is the implanted ion concentration that determines if secondary defects will form. Jones et al. suggested that there is a threshold peak concentration of implanted ions that is required for secondary defect formation, while Eaglesham et al. suggested a threshold ion fluence, which is tantamount to a threshold number of implanted ions. They found that independent of implant energy between 20 and 190 keV, either a fluence of $1.5 \times 10^{14}$ cm$^{-2}$ or a peak concentration of $1.6 \times 10^{19}$ ions/cm$^2$ was required before secondary defects were observed. These threshold implantation parameters were also found to be independent of implanted ion mass and ion flux over the implant energies examined.

These results led researchers to believe that the defect concentration created from implantation is irrelevant to secondary defect formation. The point defects created by implantation were said to completely annihilate during annealing, leaving behind an excess number of interstitial ions equal to the number of ions implanted. These excess interstitial ions then form the extended defects observed, this is the so called +1 model.

Ion Mass/Species Dependence

It has been subsequently shown however that the ion mass can affect the threshold fluence [34, 41], and that there are deviations from the +1 model depending on the ion mass [48, 36]. Heme et al. [36] showed that higher mass ion implants could result in more than one interstitial remaining per ion implanted after annealing, reporting +4.5 interstitial ions remaining after 200 keV $1 \times 10^{13}$ cm$^{-2}$ Pb implants.
Zhang et al. [49] found that higher implant fluences are required for rod-like defect formation when lower mass ions are implanted. However, this is in contrast to earlier work by Schreutelkamp et al. [50] who find that in fact higher fluences were required for high mass ions before secondary defects form. They suggest that higher fluences are required for higher mass implants because they create trapped interstitial silicon in amorphous zones which cannot migrate to form extended defects [51].

Wong-Leung et al. [41] and Fatima et al. [52] also found that whereas only rod-like defects are created in lower mass ion implants both loops and rod-like defects are created for higher mass ion implants. This effect was related to the higher and denser damage cascades created by higher mass ions and is consistent with the behaviour observed for increasing ion fluence.

**Implant Energy/Depth**

At higher energies the fluence required for secondary defect formation was shown to have a dependence on the implantation energy. Many authors have shown that as the ion energy is increased the threshold fluence required to yield secondary defects is decreased ([50] and references therein). This is related to the fact that more damage is created by higher energy ions [53].

This observation rules out there being a critical peak defect concentration that needs to be exceeded before secondary defect formation since the peak displaced atom concentration is already lower for higher energy implants [54]. In the case of MeV ions, a lower fluence was required for secondary defect formation compared to keV ions. This was found to hold true for ion species between boron and phosphorus for energies between 100 keV to 1 MeV. In the case of 100 keV compared to 1 MeV phosphorus implants, fluences of $2 \times 10^{14}$ cm$^{-2}$ and $5.6 \times 10^{13}$ cm$^{-2}$ respectively, were found to produce secondary defects [53].

To account for this observation Schreutelkamp et al. [34] argued that there is a critical amount of interstitial silicon rather than a threshold concentration that must be exceeded before secondary defects form. This is because interstitials are highly mobile, those created far from the peak defect range can still contribute to extended defect formation. This is in contrast to the postulate that it is the concentration or amount of implanted ions that is the key to extended defect formation. Indeed, they found that the critical amount of damage required increased with ion mass. For phosphorus the critical amount of displaced atoms was $5 \times 10^{16}$ cm$^{-2}$, whereas for boron it was $1.5 \times 10^{16}$ cm$^{-2}$ [55].

To corroborate the assertion that damage, rather than concentration of im-
implanted ions, controls secondary defect formation, Schreutelkamp et al. also argued that secondary defects are not formed at the projected range of implanted ions as Claverie et al. [43] and Jones et al. indicated [37] but in fact at the depth of peak damage [50]. However, this is often very close to the projected range and there is little evidence that clearly shows whether it is one or the other.

A stronger argument made by Schreutelkamp et al. is that secondary defect formation is not related to implanted ion fluence as ion channelling creates less damage and produces a smaller concentration of dislocation loops for the same fluence. There was no indication of the effect on rod-like defects in this paper and this is one of the subjects of study in Chapter 5.

It is generally accepted that compared to loops, rods form after lower fluence implants. When a higher concentration of defects are present, loops form instead [51]. This is also consistent with the annealing of amorphous layers where (category-III) loops are formed in the initially amorphous region, where the bulk of implantation damage lies, whereas (category-II) rods are formed beyond the end of range where there is less damage.

**Proximity of Surface**

An energy dependence was also observed by Zhang et al. [49]. They found that for rod-like defects, the formation threshold fluence is higher for lower energy implants. They suggest that this is due to the proximity to the surface rather than there being less damage being created. As discussed earlier it is expected that the surface will act as a sink for point defects such as interstitials. Interestingly, it has been shown with XTEM that rods closer to the surface, in a 50-150 nm deep layer, do not anneal out any faster than those deeper in the layer [56]. Zhang et al. [49] suggest that the proximity to the surface may limit rod-like defect formation although the proximity to the surface in their study involved ultra-low energy implantation (4 keV).

Other studies have surmounted this issue by polishing the surface down, to increase surface proximity, prior to annealing. It was found by Raman et al. [57] that when the distance from the surface is reduced, loops anneal out faster and are also larger with diameters ranging from 60-80 nm.

The effect of the surface on defect evolution has also been investigated in detail by Cristiano et al. [40]. They found that it is not the absolute distance between the surface and defects that determines its effect, but whether the relative distance between the defects compared to their distance from the surface is important. This is to say that the surface acts as a much stronger sink for
interstitials when the distance between defects is comparable to the distance to the surface.

**Implant Flux**

Eaglesham et al. [47] also claimed that there is no effect from changing the ion flux. However, Robertson et al. [58] have since shown that there is a flux dependence in the range $0.8 - 7 \times 10^{15}$ cm$^{-2}$s$^{-1}$ with less loops being created for a higher dose rate. This is consistent with dynamic annealing effects due to overlapping damage cascades from ions. Interestingly, the formation of rod-like defects was shown to not have such a dependence.

**Implant Temperature**

The effect of substrate temperature during implantation has been investigated by several authors. It has been shown that rods tend to form at elevated substrate temperatures (200-400°C) [59] and that loop formation is suppressed [60]. However, this may be dependent on other implantation parameters as it was previously shown that implants above 400°C suppresses rod formation [59]. It has also been found that at lower implant temperatures loops also tend to be smaller and there is a larger concentration of perfect loops.

These effects were related to the enhanced dynamic annealing when implanting at elevated substrate temperatures. This leaves less defects behind which limits loop growth and enables rod formation which, as indicated previously are more likely to form when there is a low concentration of defects. This is related to the formation energies of the defects and is discussed further below.

**Extended Defect Evolution**

Defect evolution as discussed in the literature can be misleading. In some cases, threshold fluences may in fact not be the true minimum because samples were either annealed at too low a temperature or annealing times were too short.

It is generally accepted that during annealing interstitials agglomerate first into di-intersitial clusters, then larger clusters with up to 10 atoms [61, 62, 63, 40] and provided the temperature and duration are sufficient, can then form larger extended defects that are visible with TEM ($10^3 - 10^4$ atoms) [64]. Although there are few direct experimental results indicating the presence of clusters in the intermediate range with $10 - 10^3$ atoms there is strong evidence from TED studies for their existence [40].
By considering formation energies it is argued that rod-like defects are formed before loops [65, 40] and in-situ annealing in the TEM provides strong evidence for this [48]. At lower annealing temperatures (750°C) they can grow up to 120 nm in length after 90 minutes upon which they dissociate [56]. During this growth phase rods also tend to reduce in number, a process known as Ostwald ripening [43]. At higher temperatures the rod evolution is faster and their ‘lifetimes’ are reduced [38, 66, 67, 40]. It is found that for 100 keV Si implanted samples annealed at 850°C, the maximum mean length is about 100 nm after only 150 seconds but they remain for up to 5 minutes of annealing [40]. At 900°C rods are observed to anneal out after only 90 seconds [38]. The length of the rods is also limited at higher annealing temperature [67].

It has been suggested for some time that at these higher annealing temperatures the rod-like defects dissociate to form perfect dislocation loops [39, 68] but was only recently directly observed with in-situ TEM experiments [48]. It has been argued that this only occurs if rods can grow large enough first [43].

If we consider that all loops are formed after rod-like defect formation, then the facts presented earlier regarding the implant conditions required before loop formation can be seen in a different light. Since experiments were conducted at a fixed annealing temperature for a fixed time, instead of indicating that a higher implant fluence or ion mass is required before loop formation it could be said that the evolution time is instead reduced by these factors. However, this is not to say that implants at lower fluences or with lower mass ions simply result in a longer evolution time as it has been observed that rod-like defects, which are formed after low fluence implantation can dissolve without loop formation [47].

It has been observed that depending on either the annealing conditions [43] or the implantation conditions [69] either Frank loops or perfect loops will dominate. In 150 keV Ge implanted samples Frank loops initially increase in concentration with annealing and are more stable than perfect loops which anneal out faster [69]. Conversely, in low energy 50 keV Si implanted samples it is found that the perfect loops were more stable, remaining after 900°C anneals of up to 2 hours.

This behaviour has been explained by examining the formation energies of both the perfect and Frank loops. When the concentration of interstitial atoms is high, there will be more perfect loops because their formation energy becomes lower than for Frank loops [69]. But when the initial concentration is low there will be more Frank loops as its formation energy is lower in this case.
1.2 Channelling Ion Implantation

Implantation for the fabrication of semiconductor devices often requires strict control on the depth of the implanted ions due to their planar design. This can be achieved if the ions are implanted into the substrate in such a direction that the ion sees an essentially random distribution of atoms (Fig. 1.4a). This results in the ions being quickly stopped and the depth profile of implanted ion concentration having a reasonably well defined distribution (see Fig. 1.3).

![Graph showing depth profile of implanted ion concentration](image)

Figure 1.3: A typical depth profile for the concentration of ions implanted in the random orientation as used by the semiconductor industry.

![Crystalline silicon lattices](image)

Figure 1.4: The lattice of crystalline silicon viewed in various orientations (a) random, (b) planar channeling, (c) axial channelling [70].

Due to the crystalline lattice structure of silicon the lattice planes or axial rows of atoms in it (Fig. 1.4b and c respectively) can guide or channel the ions in certain directions with a series of small angle collisions [70]. If the sample is aligned so that the ion beam is aligned with the plane normal of the crystal (as in Fig. 1.4c), this will result in axial channelling implantation. At lower energies
this tends to result in a broadened ‘channelling tail’ to the ion depth profile [71]. That is, there are more ions that travel deeper into the sample although the peak in ion concentration may be at the same depth as for random oriented implants. As ion energy is increased, a deeper projected range of ions may also result from channelling implants. This increased depth distribution or increased longitudinal straggle is at the expense of the lateral straggle which is smaller in comparison [72, 73, 74].

If the sample is tilted away from axial alignment along a planar direction then a planar channelling orientation shown in Fig. 1.4b is reached. Although less ions are channelled in this case compared to axial channelling there is never the less a significant fraction of channelled ions.

As the angle away from the axial channelling orientation is increased there is a continuous reduction in the channelled fraction until there are no longer any channelled ions. The range of angles in which channelling occurs is known as a channelling window which increases as ion energy decreases [75]. This approximately obeys an inverse square root relation. As ion beams generally have a finite divergence to them, smaller channelling windows can result in a channelling tail to the implant profile [76, 77]. This is relevant to modern device fabrication. As the trend towards fabrication of shallow donor junctions has led to the use of low energy ions, a larger channelling fraction leading to less defined doping profiles has become an issue.

As the implant fluence is increased however, damage builds up within the lattice and can lead to de-channeling [72, 78]. This is a result of the increased probability of collisions as more displaced atoms are created in the lattice. This prevents further ion channelling and the shape of the implant profile begins to change as more ions contribute to the random fraction of the profile, i.e. no more ions contribute to the channelling tail and a shallower peak begins to form. Thermal vibration of lattice atoms also affect profiles of channelled ions. Higher substrate temperatures are known to limit the range of channelled ions for example [79].

Channelling however is not necessarily a bad thing. It has been proposed that channelling be deliberately used to produce uniform doping profiles [72, 80]. Also, it has been known for some time that the resulting defect concentration from channelled implanted samples is less than in the case of random oriented implanted samples [81, 80].
1.2.1 Effect on Point defect Creation

Most studies of point defect profiles in channelled implanted samples have examined the displaced atom profiles [74, 81, 82, 83, 84, 85]. It is only recently that experimental studies of vacancies in channelled implanted samples have emerged [86, 87].

From early studies, it was established that channeling produces less defects than random implantation [81]. This is presumably due to the smaller angle collisions between host lattice atoms and the implanted ion resulting in less energy loss from the ion and therefore less damage created. These studies also showed that primary damage resulting from channeling implantation is deeper than that for implantation in the random orientation [81, 85]. Primary damage being in the form of displaced atoms and secondary damage in the form of extended defects that remain after annealing. The damage peak has also been shown to be shallower than the implanted ion peak in most cases [74, 88].

It has also been shown that the implantation angle can affect the relative concentrations of the electrically active defect species in samples [86]. This was observed in hydrogen implanted silicon, the ratio between the concentration of different defect species was observed to vary with the implant angle.

1.2.2 Effect on Secondary Defect Formation

There is relatively little in the literature regarding the effect of ion channeling on secondary defect formation. Only the group of Schreutekamp and Raineri have compared the secondary defects formed in samples implanted with channelled ions with samples implanted in the random orientation.

Since channeling has been shown to reduce the concentration of primary defects, it is natural to assume that there will be an effect on the formation of extended defects after annealing as well. Indeed, Schreutekamp et al. [88] and Raineri et al. [85] showed that channeling implantation reduces the concentration of extended defects formed. For 100 keV phosphorus implanted silicon annealed at 900°C for 15 minutes, a fluence between \(5 \times 10^{13} \text{ cm}^{-2}\) and \(2 \times 10^{14} \text{ cm}^{-2}\) was found to be required before dislocation loop formation. Furthermore, the band of loops formed from channelled implanted samples was 0.6 \(\mu\text{m}\) deeper and 1.5 times broader than those implanted in the random orientation [88]. This behaviour was also observed for 200 keV boron implants. However, in this case rod-like dislocations were observed and a fluence between \(1 \times 10^{14} \text{ cm}^{-2}\) and \(5 \times 10^{14} \text{ cm}^{-2}\) was required before dislocations were observed.
Secondary defects were also observed after annealing at 500°C for 1 hour. In this case a dense network of dislocations was reported, although these dislocations were not rod-like defects. The amount of damage was again less for channelled implanted samples [88].

Schreutelkamp et al. [89] and Raineri et al. [90] also claimed that the fluences required for secondary defect formation are higher for channeling implants. There does not appear to be sufficient evidence to show this. This conclusion seems to be based on the observation that channelled implanted samples produce less defects. However, their results seem to indicate that the same fluence is required for secondary defect formation. Namely $2 \times 10^{14}$ cm$^{-2}$ for loop formation in 100 keV phosphorus and $5 \times 10^{14}$ cm$^{-2}$ for dislocations in 200 keV boron implanted samples.

These studies although thorough, were not exhaustive. Only two annealing conditions were examined, 500°C for 1 hour and 900°C for 15 minutes. From the earlier discussions regarding defect evolution it may be possible that the defect evolution of channelled implanted samples is different to that of random oriented implanted samples. It has been claimed by Raineri et al. [91] that secondary defects begin to form in channelled implanted samples at a temperature 100°C lower than in random oriented samples. No experimental results to support this claim were shown in this paper. Also, although a fluence dependent study was conducted by Schreutelkamp et al. and Raineri et al. the fluences explored are reasonably far apart and samples may not represent minimum conditions required for defect formation. Thus, although they state that channelled implanted samples have a different threshold fluence before secondary defect formation, this remains to be experimentally verified.

### 1.2.3 Monte-Carlo Simulations

Monte-Carlo simulations of binary collisions are often used to simulated ion implantation to calculate the predicted ion range and initial Frenkel defect profiles. The most commonly used software package is the TRIM program [92] which simulates ion implantation into an amorphous target by considering an electronic screening potential developed by Ziegler, Biersack and Littmark [93], this is commonly referred to as the ZBL potential. This often gives a close approximation to implants into random oriented single crystal silicon. However, since it does not contain any crystallographic information it is not capable of simulating implants into single crystal silicon oriented in a channeling orientation. For such simulations, software packages such as MARLOWE [94] and Crystal-TRIM [95] have been developed.
Effects on channeling from thermal vibrations of lattice atoms can also be taken into account with these simulations and are characterised by the Debye temperature. Although previous calculations from X-ray studies suggested a Debye temperature of up to 530 K for the silicon lattice [96], Debye temperatures closer to 500 K have been shown to lead to better agreement between simulations and ion channeling profiles [79, 97]. The effect of damage accumulation on ion ranges has also been incorporated into both MARLOWE [98] and Crystal-TRIM [79] packages.

Comparisons of experimental data to Monte-Carlo code predictions for interstitial atom profiles have also been made for channelled implanted samples [91]. The major limitation of simulations is that many do not take into account defect annihilation and diffusion. There have been some attempts to modify them to calculate this. Jaraiz et al. [98] for example describe a model that requires only the determination of a recombination distance and have shown good agreement between simulations and experimental data. A comparison between simulations for vacancy profiles in planar channel implanted has also made [87]. However, no comparisons have been made between Monte-Carlo simulations and experimental results for vacancy profiles for axial channel implanted samples and this is addressed in Chapter 4.

1.3 Implantation Damage in Silicon Dioxide

Implantation through or into surface oxide layers will also create damage in the oxide. The structure of silicon dioxide consists of silicon bonded to four surrounding oxygen atoms with bond angles varying from less than 120° to 180° [99]. Although it is non-crystalline, a thermally grown oxide on silicon is not technically amorphous and instead has a degree of short range order, meaning that thermal oxides are better described as vitreous [99]. In the semiconductor community, defects within the oxide bulk are grouped into several categories: fixed oxide charge ($Q_f$), oxide trapped charge ($Q_{ot}$) and mobile ions ($Q_m$) [100]. The fixed oxide charge is located within 2nm of the oxide silicon interface, is predominantly positive and is not easily discharged. Oxide trapped charge in the bulk of the oxide on the other hand readily traps electrons and holes.

As with implantation damage in bulk silicon, atomic displacements and Frenkel defects constitute primary defects created in an oxide. As a result trapped and fixed charge concentrations are increased [100]. The trapped and fixed charge concentrations are usually measured using electrical techniques, however the lit-
erature on optical and electron paramagnetic resonance studies contain discussion of defect structures such as the Si-Si defect, E’ centres and peroxy radicals (POR).

The Si-Si defect is also known as a oxygen deficient centre (ODC) or simply an oxygen vacancy [101] and has an optical absorption peak at around 7.6 eV [101].

The E’ centre is related to the Si-Si defect and is also known as a bridging oxygen vacancy. The silicon ion facing the oxygen vacancy in this case has an unpaired electron and has a net positive charge [102], it can be represented as, \( \equiv \text{Si}^* \). The E’ is paramagnetic and has an EPR signature, and has a 5.8 eV absorption peak [101].

The POR can be described as an interstitial oxygen defect involving a O-O bond (\( \equiv \text{Si-O-O}^* \)) [101]. It is also paramagnetic with an EPR signature. The POR also contributes to the 7.6 eV absorption peak [103]. It has been suggested that it can be formed when interstitial oxygen forms molecules that then bind with the dangling bond in the E’ centre [101].

Depending on the oxide thickness and implantation energies oxygen recoils can also end up in the substrate silicon and may in fact increase the oxide thickness or result in SiO\(_x\) precipitates [104]. If the anneal is performed at low temperatures this will lead to a poor quality oxide & oxide interface [105]. Furthermore, if oxygen recoils into to the substrate this means that the oxygen vacancies in the oxide cannot be repaired or replaced unless annealing is performed in the presence of oxygen [106, 107].

These changes to the oxide will affect the electrical characteristics of any device fabricated on it. For example, it has been shown that changes to the stoichiometry of the oxide will affect the capacitance of a MOS capacitor [104].

### 1.3.1 Fluence Dependence

Implants of 30 keV N, 50 & 100 keV Ar with fluences from \( 1 \times 10^{12} \) to \( 1 \times 10^{14} \) cm\(^{-2} \) have been shown to produce roughly the same density of E’ centres [102]. If we make the approximation that there is a uniform distribution across the 300 to 350 nm thick films used this leads to a concentration of \( 3 \times 10^{16} \) to \( 3 \times 10^{17} \) cm\(^{-3} \). The concentration of E’ was found to saturate with fluence at \( 1 \times 10^{13} \) cm\(^{-2} \) [102].

Above fluences of \( 1 \times 10^{14} \) cm\(^{-2} \) however it has also been shown that E’ centre concentrations decrease [108]. This effect is related to E’ centre reactions with interstitial oxygen. On the other hand, in the case of oxygen implants a peak density of E’ centres was observed at \( 1 \times 10^{13} \) cm\(^{-2} \) whereupon higher implantation
fluences led to a decrease in E’ concentration [109].

After significant damage build up in the oxide a well known effect is oxide compaction \([110, 111, 112, 113]\). This has been known to be caused by many things besides implantation including neutron, electron and X-ray irradiation [114].

1.3.2 Role of Implanted Species

Unlike implantation damage in as-implanted silicon, the chemical effects from the implanted species cannot be neglected. The ion species being implanted in the oxide has been shown to affect the ratio of the types of defects observed due to chemical bonding between the ion and atoms in the oxide. Boron for example can form bonds with oxygen and therefore restrict the formation of POR and E’ centres. It has been shown that Si-Si defects dominate in boron implanted samples [101].

It has been shown that the electronegativity of the ion being implanted can be used to determine the predominant defect since this affects whether it will bond with oxygen [103]. Electropositive (low electronegativity) ions react with oxygen, whereas electronegative ions bond with silicon and any free oxygen ions can form molecular oxygen or POR.

Certain elements can exist in substitutional sites in the oxide. It has been shown that phosphorus and aluminium are two examples of this. Although the bond angles and lengths may be different for each of these [115]. It has been suggested that phosphorus and arsenic sit in substitutional oxygen sites in the oxide and they act as trapping sites [116]. Substitutional aluminium has also been tagged as a charge trap in oxides [117]. Experimental studies of as grown phosphosilicate glass indicates that phosphorus only bonds to oxygen [118]. Theoretical studies however have shown that phosphorus can bond to both silicon and oxygen atoms [115]. Whether the impurity bonds to silicon or oxygen may depend on if it is present during oxide growth or whether it is implanted.

1.3.3 Role of Electronic Energy Loss

Unlike implantation damage in bulk silicon, it has been suggested that the electronic energy loss from implanted ions can also play an important role in creating structural defects in the oxide [108, 111]. The electronic energy loss can break bonds in the oxide and lead to structural ‘re-ordering’. This damage created is also believed to be different from that created by nuclear stopping and collision
damage [111]. Electronic energy loss also creates electron-hole pairs which in bulk silicon would readily recombine [119]. However, in silicon dioxide the band gap is sufficiently large or the diffusion length is sufficiently small that they can remain for some time.

It has been suggested that E’ centres are preferentially created when the implanted ion loses more energy through electronic energy loss compared to nuclear energy loss [108]. This is most obviously the case when high energy light elements such as hydrogen and boron are implanted. Bogomolova et al. [108] examined the concentration of E’ centres in samples implanted with elements from boron to antimony using electron paramagnetic resonance spectroscopy (EPR). They found that the lighter the ion, the more E’ centres were formed. This effect was attributed to the larger fraction of electronic energy loss in lower mass implants. It is interesting that no chemical effects were observed as reported by other researchers. For example, Hosono et al. [101, 103] showed, in vacuum ultraviolet (V-UV) absorption and EPR studies, that there was no correlation found between the fraction of electronic energy loss and the concentrations of defects created. In contrast to Bogomolova et al. [108] they also found that in boron implanted samples there was a very low concentration of E’ centres created and they found that more Si-Si bonds are formed. Hosono et al. [101, 103] attribute these results to chemical effects as discussed above.

1.3.4 Oxide Damage Annealing

It has been shown that 1000°C anneals for up to 2 hours may not be enough to remove all oxide related carrier traps and that 1100°C is needed [120]. It is also said that primary defect damage (displacements) are annealed out at 600-650°C but secondary or residual damage remains [120, 111]. This has been related to different annealing behaviour for different types of damage created from electronic energy loss and nuclear energy loss [111]; although there is still some debate regarding whether there is any effect from electronic energy loss at all.

Annealing studies of the E’ centre have shown that 10 minute anneals up to 900°C of nitrogen and oxygen implants to fluences of $1 \times 10^{13}$ to $1 \times 10^{15}$ cm$^{-2}$ were not enough to completely anneal out the centre [121], although the concentration is dramatically reduced to a fraction of its as-implanted level.

In the case of through oxide implantation, rapid thermal annealing has been shown in some cases to increase oxide fixed charge levels [122] and lead to a fixed positive charge [105]. This again may be related to oxygen recoils and further growth of an oxide. Charge-to-Breakdown voltage measurements have
also shown that 1030°C, 20 second rapid thermal anneal can completely repair implantation damage in light ion (boron) implanted samples but not for heavier ions (phosphorus or arsenic) [123]. Secondary defect damage can also remain after annealing [124], an effect that was subsequently attributed to oxygen recoils in the substrate silicon [125, 126].

1.4 Oxide Interface Implant Damage

Interface traps are present in as-grown oxides and passivation anneals at around 400°C in the presence of hydrogen are used to reduce their concentration [100, 127]. They are also known as surface or fast states [128]. Studies have shown that implantation induced interface traps are not completely annealed out. It is suggested that the residual interface traps are due to oxygen knock-ons; oxygen in the oxygen rich regions then bonds with silicon and also creates P\textsubscript{b} centers (tri-valent silicon centers) [107].

Implantation either through the oxide or even prior to oxidation causes an increased interface trap density [105, 129]. These traps exist at the interface or up to 2 or 3 atomic layers into the silicon substrate [130]. They consist of dangling bonds so are paramagnetic and known as the P\textsubscript{b} centre to the EPR community.

It has been shown that interface traps increase with fluence for through-oxide implantation of 180 keV phosphorus (up to \(1 \times 10^{13} \text{ cm}^{-2}\)) into 40 nm thick thermal oxides [122].

Unlike carrier traps in bulk silicon, interface traps have a continuous energy distribution through the band gap. The distribution is not uniform and analysis of metal-oxide semiconductor (MOS) capacitors reveals a higher concentration of traps near the band edges [131]. Often a mid-gap concentration will be quoted for the interface trap density.

Depending on the electric field at the oxide interface, charge may be negative or positive. For an n-type substrate traps are taken to be negatively charged when populated and neutral when empty; for p-type substrates they are positively charged when empty [105].

Rapid thermal annealing at 1150°C for 10 seconds was also shown to reduce interface trap densities and was more effective than 900°C 30 minute conventional furnace anneals, although higher temperature anneals may in fact lead to more defects in the oxide [122].

Possible chemical effects must also be considered for interface trap densities. Oxygen implants for example create more interface states than silicon implants.
despite oxygen implants creating less vacancies [104].
References


Chapter 2

Experimental Techniques

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Several techniques were employed to examine ion implanted samples. The three main techniques utilised were Deep Level Transient Spectroscopy, Transmission Electron Microscopy and Kelvin-probe Force Microscopy. In addition to these Rutherford Backscattering Spectroscopy with Channelled ions was also used to examine displaced atom fractions and profiles in implanted silicon wafers.

2.1 Electrical Analysis of Semiconductors

Deep level transient spectroscopy (DLTS) was the principle technique used in this project to evaluate electrically active defect concentrations, trap energies and their capture cross-sections. By comparing these characteristics as well as the
annealing behavior of the defects, to the characteristics and annealing behavior of defects observed in the literature, it is possible to identify the species of defects present in the samples. Capacitance-Voltage measurements were also made to evaluate dopant concentrations.

Both of these techniques require fabrication of a semiconductor diode structure to facilitate electrical characterisation. For this project Schottky barrier diodes were fabricated, which are formed at a metal semiconductor interface.

2.1.1 Schottky Barrier Diodes

Schottky diodes are similar to p-n junction diodes except their characteristics only depend on majority carriers [1], whereas the p-n diode characteristics depend on both majority and minority carriers. The properties of the Schottky diode are a result of the Schottky barrier formed at the interface due to the difference between the work function of the metal (\( \phi_m \)) and semiconductor (\( \phi_s \)). This barrier is characterised by a barrier height (\( \phi_b \)), see Fig. 2.1.

![Figure 2.1: The bending of the energy bands for a n-type semiconductor Schottky barrier diode (After Schroder [2]).](image)

In general, the work function of a metal (\( \phi_m \)) is different to a semiconductor and when the two materials come into electrical contact with each other electrons will diffuse from the material with the larger Fermi level (or smaller work function).

The work function of a material describes the binding energy of the electrons and is related to the Fermi level (see Fig. 2.1). When the metal and semiconductor come into contact it becomes energetically favourable for electrons in the higher Fermi level material to diffuse across to the other material. In n-type silicon if the work function of the metal is larger than that for silicon, we get the situation shown in Fig. 2.1. The electrons in silicon drift across to the metal and the region left behind has a net positive charge. This is known as the depletion region since
it has been depleted of majority charge carriers. The width of the depletion region can be varied by an applied field \((V)\) and is temperature \((T)\) dependent. This is the depletion region characterised by a width \(\omega\) as seen in Fig. 2.1. The width of the depletion region can be expressed as:

\[
\omega = \sqrt{\frac{2\epsilon}{qn_D} (V_{bi} - \left( \frac{k_BT}{q} \right) - V)}
\]  

(2.1)

Where:
\(\epsilon\) is the dielectric constant of the semiconductor
\(n_D\) the concentration of dopants in the semiconductor
\(V_{bi}\) the built-in voltage

A thin oxide (10-20 Å) often exists between the metal and semiconductor and contributes a small amount to the barrier (see Fig. refigsd-oxide). Electrons readily tunnel through this thin oxide layer but there is still a small contribution [3]. Note that in a realistic diode this relation is not valid for all bias values \((V)\). If \(V\) is too positive there will be a forward bias leakage current, if it is too negative the diode will begin to breakdown and again a reverse bias leakage current will flow leading to erroneous capacitance measurements. This in essence limits the range of depletion widths.

The capacitance of the Schottky diode can be determined by considering the depletion region as a dielectric of width \((\omega)\) separating the metal contact of area \((A)\) parallel to the edge of the depletion region in the semiconductor:

\[
C = \frac{\epsilon A}{\omega}
\]  

(2.2)

Substituting equation 2.1 into 2.2 we have:

\[
C = A \sqrt{\frac{\epsilon q n_D}{2(V_{bi} - \left( \frac{k_BT}{q} \right) - V)}}
\]  

(2.3)

2.1.2 C-V Analysis –Dopant Profiling

By varying the applied voltage while measuring the capacitance we can determine the concentration of electrically active dopants in the semiconductor and the built-in voltage of the diode (which will be important for discussion of the DLTS results later). Equation 2.3 can be rearranged to read:
\[ \frac{1}{C^2} = \frac{2}{\epsilon q A^2 n_D} (V_{bi} - \frac{k_b T}{q} - V) \quad (2.4) \]

So if we plot \( \frac{1}{C^2} \) against applied voltage \( V \) we can obtain the doping concentration from the slope \( d(\frac{1}{C^2})/dV \):

\[ n_D(\omega) = \frac{-2}{q e A^2 \frac{d}{dV} \left( \frac{d(\frac{1}{C^2})}{dV} \right)} \]
\[ = \frac{-C^3}{q e A^2 \left( \frac{dC}{dV} \right)} \quad (2.5) \]

Where we assume that \( \frac{1}{n_D} \cdot \frac{dn_D}{dV} \ll 1 \). In practice, this assumption is easily met as doping levels are at least on the order of \( 10^{11} \) \( \text{cm}^{-3} \) and small voltage increments can also be taken.

The built-in voltage can also be determined from the intercept \( V_{int} \):

\[ V_{bi} = \frac{k_b T}{q} - V_{int} \quad (2.6) \]

The Schottky barrier height can then also be determined from the sum of the built-in voltage and the difference between the conduction band and Fermi energies [4]:

\[ \phi_b = V_{bi} + (E_c - E_f) \quad (2.7) \]

The calculated value for \( n \) at a given bias, \( V \) can be shown to be equal to the uncompensated donor concentration at the edge of the depletion region corresponding to the applied bias \( V \) [5]. Thus it is possible to calculate the uncompensated donor concentration \( n_D \) as a function of depth into the sample. It should be noted however that C-V dopant profiling with Schottky diodes is limited in the range that it can probe due to the zero bias depletion width and the maximum bias that can be applied before breakdown or too high a leakage current is produced. From equation 2.1, the zero bias depletion width can be seen to depend on both the temperature and the background doping of the substrate. It is therefore important to chose the resistivity of the substrate carefully to ensure that the range of depths of interest can be profiled. It can also be seen from equation 2.1 that as the bias is increased to larger negative values that the change in depletion width with each increment reduces.

It should also be noted that the equations above utilise what is known as the
depletion approximation where it is assumed that all donors within the depletion region are ionised and the depletion edge is sharp [6]. Due to carrier drift and diffusion however, the edge is not sharp and charge carriers are distributed over a length characterised by the Debye Length \( (L_D) \):

\[
L_D = \sqrt{\frac{ek_B T}{q^2(n_D)}}
\]  

(2.8)

This in essence sets a limit to the resolution of C-V profiling [7].

Also, according to Schroder [8], since dopant profiling using C-V measurements relies on mobile charge carriers it actually provides the free carrier concentration not the dopant concentration. Other authors simply consider the capacitance equations to depend on charge from uncompensated donors [4] in the depletion region and not mobile charge carriers since measurements are made under quasi-static conditions.

### 2.1.3 Deep Level Transient Spectroscopy (DLTS)

DLTS uses a changing bias to fill and empty charge traps to examine the traps over a given depth in the semiconductor. Fig. 2.2 shows an applied bias pulse cycle required for DLTS on a n-type substrate. The pulse cycle can be thought of as a reverse bias \((-V_b)\) that is periodically pulsed with a ‘filling’ pulse to some smaller bias \((-V_0)\). Fig. 2.3 shows the effect of changing the bias on the trap population in the sample, note also how the depletion region changes.

When the sample is initially at the smaller bias \((-V_0)\) the traps in region II and III are filled with electrons (Fig. 2.3a). Note that region I is the depletion region corresponding to the pulse voltage \((-V_0)\) which is often zero so region I, in this case, would be the zero bias depletion region.

Fig. 2.3b shows that upon reduction of the bias to some lower negative (reverse) bias \((-V_b)\), the traps in region II begin to empty as the band bending makes it energetically favourable for the electrons to spill over into the conduction band of the semiconductor.

When the bias voltage is pulsed to the higher \(V_0\) value for some filling pulse time \(t_f\) the traps in regions II and III are exponentially filled with electrons from the dopants or conduction band.

This emission is described by an exponential function that depends on the total concentration of filled traps in region II \([n_T(t = 0)]\) and an emission rate \( [\epsilon_n] \):
\[
n_T(t) = n_T(0)e^{-\alpha t}
\]  
(2.9)

The emission rate \( (e_n) \) depends on temperature \( (T) \), the trap energy level \( (E_T) \) and the capture cross section \( (\sigma_c) \) of the trap:

\[
e_n = \gamma_n \sigma_c T^2 e^{-\frac{E_T - E_F}{k_B T}}
\]  
(2.10)

\( \gamma_n \) is a set of constants [9] given by:

\[
\gamma_n = 2\sqrt{3}M_e (2\pi)^\frac{3}{2} \hbar^2 m^* e^{-3}
\]

where \( M_e \) is the number of minima in the conduction band of the semiconductor
and $m^*$ is the effective electron mass in it. Since the trap energy level and the capture cross section characterise different defects the emission rate may be different for each defect.

The capacitance transient and DLTS signal

The depletion width is affected by the trapped charge, and as the traps empty, the decrease in trapped charge causes a decrease in the depletion width [10]. The effect on the capacitance is shown in figure 2.4. In the depletion approximation this capacitance transient can be expressed as:

$$C(t) = C_0 \sqrt{1 - \frac{n_T(t)}{n_D}}$$  \hspace{1cm} (2.11)

![Capacitance transient](image)

Figure 2.4: The time variation of capacitance as traps empty (After Schroeder [2]).

If we now monitor the change in capacitance over some time interval (measurement window) ($t_1$, $t_2$) and define the change in capacitance over this window as:

$$\Delta C = C(t_2) - C(t_1)$$  \hspace{1cm} (2.12)

By dividing this by the final capacitance $C_0$ we form our DLTS signal ($S$) which can be written as:

$$S = \frac{\Delta C}{C_0} = \frac{n_T}{2n} \left[ e^{-\frac{T}{\tau_{11}}} - e^{-\frac{T}{\tau_{12}}} \right]$$  \hspace{1cm} (2.13)

Where the approximation for the case where $n_T << n_D$ is used so that
Eq. 2.11 now reads:

\[ C(t) \approx C_0 \left(1 - \frac{n_T(t)}{2n_D} \right) \quad (2.14) \]

This approximation is in fact required to determine the trap concentration from Eq. 2.13. This is one of the most significant limitations of DLTS for the study of defects in semiconductors; DLTS studies are limited to samples that have low defect densities relative to the background doping concentration. Typically, it is taken that the trap concentration should be no greater than 10% of the background doping concentration. Although the background doping concentration can be increased to compensate for this, this will in turn affect the zero bias depletion width and the range of depths that can be probed. Furthermore the assumption that emission follows an exponential behavior is not valid for large trap concentrations [11] and leads to erroneous DLTS signals.

If we take the transition depth into account then we have:

\[
S = \delta \frac{C}{C_0} = \left[ \frac{(\omega_b - \lambda)^2 - (\omega_p - \lambda)^2}{\omega_b^2} \right] \frac{n_1}{2n_d} \left[ e^{-\frac{t_1}{\tau_1}} - e^{-\frac{t_1}{\tau_2}} \right]
\]

where \(\omega_p\) and \(\omega_b\) are the depletion regions under pulse and reverse bias respectively [12].

The bias voltage is pulsed to the higher \(V_0\) value for the filling pulse time \(t_p\) to fill the traps again and the cycle is repeated. This allows many readings for the signal to be averaged over.

**Calculating trap energy levels and capture cross-sections**

By differentiating Eq. 2.13 with respect to \(T\) it is relatively simple to show that the emission rate at the peak DLTS signal temperature is given by the following equation:

\[
e_n(T_{\text{peak}}) = \frac{ln(t_2)}{t_2 - t_1} \quad (2.15)
\]

Eq. 2.15 shows that the measurement times \(t_1\) and \(t_2\) set what is known as a rate window for the emission rate. It can be shown that different rate windows cause the signal to peak at different temperatures, and by taking DLTS spectra at various rate windows we can obtain a range of peak temperatures associated with each emission rate. Using these values and noting that at the peak temperature the emission rate is given by Eq. 2.15, it is possible to calculate both the trap energy level and the capture cross-section.
Returning to equation 2.10 we can re-arrange it to give:

\[
\ln \left( \frac{e_n}{T^2} \right) = \ln (\gamma_n \sigma_e) - \left( \frac{E_n - E_T}{k_B T} \right)
\]

(2.16)

Since the temperature at which the DLTS signal peaks changes with the emission rate window we can generate an Arrhenius plot of \( \ln (\frac{e_n}{T^2}) \) for various temperatures and emission rates. The trap energy level can then be found from the slope and the capture cross section from the intercept of the line of best fit for this data. It should be noted that this is not a very accurate method for determining the activation energies and capture cross-sections of defects since the defect levels are not being directly probed but are inferred from carrier emission transients. Other optical techniques, such as photo-luminescence spectroscopy that directly probe the energy levels give much more accurate measures of defect levels.

Calculating trap concentrations

Fig. 2.5 shows how the signal changes as a function of temperature when a single trap is present. This occurs due to the temperature dependence of the emission rate and it is a plot of the DLTS signal as a function of temperature that forms a DLTS spectrum.

![Figure 2.5: The temperature dependence of the DLTS signal [2].](image)

Note that in Eq. 2.13, if the trap concentration \( n_T \) is zero then the signal is
also zero. This is to say that the magnitude of the DLTS signal is also proportional to the concentration of defects present, \( n_T \), and can be expressed as:

\[
\frac{\delta C}{C_0^{\text{max}}} = \frac{n_T}{2n_D} \frac{r - 1}{r^2 - 1}
\]

(2.17)

where \( r = \frac{t_2}{t_1} \). We can then write the trap concentration as:

\[
n_T = 2 \frac{\delta C}{C_0^{\text{max}}} n_D \frac{r^\frac{r}{r^2 - 1}}{r - 1}
\]

(2.18)

Note that it is also important to know the concentration of electrically active dopants in the same region that is being probed to determine the defect concentration in that region. Furthermore since the depletion approximation was used in determining this equation the calculated trap concentration \( n_T \) is at best only representative of the average trap concentration over the region that the depletion width changes during the filling pulse. Non-uniform trap and doping concentrations can lead to misleading results unless accounted for. These issues are addressed by performing defect depth profiling.

2.1.4 DLTS Depth Profiling

It is possible to use DLTS to probe the defect concentration level of a specific defect and determine how it changes with depth, hence producing a depth profile for the defect. This is achieved by fixing the temperature of the sample at the temperature at which the defect produces a peak DLTS signal, placing the sample under reverse bias (as in DLTS), and then running a series of filling pulses that vary in amplitude by some small amount. By doing this we probe a different slice of the sample with each voltage pulse. These slices are shown as light gray sections in Fig. 2.6.

Figure 2.6: DLTS filling pulses allows determination of defect concentration in a cross-sectional slice of the sample.
The defect concentration in the blue cross-sectional slice shown in Fig. 2.6 can be determined by calculating the change in defect concentration between the initial slice (small voltage pulse) and the final larger slice (larger voltage pulse). This is essentially calculating the change in concentration with depth since the two slices correspond to two different depths.

The defect concentration is given by Eq. 2.18 which depends on the DLTS signal. The depth depends on the reverse bias voltage and the filling pulse voltage expressed in Eq. 2.2 and 2.3. So, the defect concentration at the depletion edge can be expressed in terms of the change in DLTS signal with voltage:

\[
    n_t(\omega_p) = \frac{q\omega_h^2}{\epsilon} n_D(\omega_h)n_D(\omega_p) \frac{dS}{dV} \tag{2.19}
\]

Since we are mostly interested in deep traps, their energy levels will be less than the Fermi level. This means that traps are actually filled to a depth, \(\lambda\) less than the depletion width. This is known as the transition distance [13] and is given by:

\[
    \lambda = L_D \sqrt{\frac{2(E_f - E_t)}{k_BT}}
\]

Taking this into account equation 2.19 becomes [14]:

\[
    n_t(\omega_p - \lambda) = \frac{q\omega_h^2}{\epsilon} \left( \frac{\omega_p}{\omega_p - \lambda} \right) n_D(\omega_h)n_D(\omega_p) \frac{dS}{dV} \tag{2.20}
\]

where \(\omega_h\) is the width of the depletion region under reverse bias, \(\omega_p\) is the depletion width under the pulse voltage, \(n_D(\omega)\) is the doping concentration at depth \(\omega\), and \(\frac{dS}{dV}\) is the change in DLTS signal with voltage.

## 2.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) uses electron beams in place of light for imaging specimens. Typically electrons with energies in the range 100-400 keV are used, giving them deBroglie wavelengths of less than 4 pm [15]. This means the TEM has a much higher spatial resolution than optical microscopes.

The typical ray diagram for an electron microscope is shown in Fig. 2.7. The electrons are generated from a filament (typically W or LaB₆) and are then focussed with numerous condenser lenses (represented as convex lenses in the ray diagram) to produce either a convergent spot on the sample or a near-parallel
ray broad sample illumination. A condenser lens aperture is used to further limit beam divergence and increase beam coherence.

The most important optics lie below the specimen. The objective lens adjusts the magnification while the intermediate lens power is adjusted to either form a diffraction image or an image of the sample which the projector lens then projects and re-magnifies onto either a ZnS phosphorescent viewing screen or CCD camera (Fig. 2.7). To form a diffraction image the intermediate lens focuses rays that are diffracted from the same planes (from different parts of the sample) to the same spot (diffraction mode, Fig. 2.7a). To form an image of the sample the lens is adjusted to focus rays from the same part of the sample to the same spot to form an image of the sample (imaging mode, Fig. 2.7b).

![Ray diagram of Transmission Electron Microscope](image)

Figure 2.7: Ray diagram of Transmission Electron Microscope a) diffraction mode, b) imaging mode (After Williams & Carter [16])

There are two further apertures that play a key role in TEM imaging. The selective area aperture can be inserted at the first intermediate image plane to limit the rays that proceed to final image plane, to those that emerge from only a selective area of the sample. This is used to produce selective area diffraction (SAD) patterns. This enables a sharp diffraction image to be obtained from a small region of the sample while using near parallel illumination.
The diffraction patterns play a key role in determining the crystal structure of the sample and are explained by Bragg diffraction. A good description of electron diffraction and crystallography can be found in Williams & Carter [15] and Kittel [17].

The objective aperture is inserted below the objective lens and plays a key role in enhancing image contrast. It is inserted and positioned while viewing the diffraction pattern because it limits the diffracted beams that will subsequently be allowed through to form the image after returning to imaging mode. Without an objective aperture, all scattered and diffracted beams are allowed through and image contrast is due to inelastic scattering which attenuates the beam intensity. This occurs in regions with heavier atoms or where the specimen is thicker, known as mass-thickness contrast. This results in a bright image but with poor image contrast. By limiting the diffracted beams through however we can gain much better image contrast by selectively using light that is scattered in a specific direction or only light that is not scattered at all. This is discussed in the next section.

2.2.1 Image Contrast

Bright Field Imaging

In bright field imaging the objective aperture is adjusted to only allow the direct (un-scattered/non-diffracted) beam (0) through (Fig. 2.8a). This means that any object or region in the sample that scatters or diffracts the beam will now show up as a dark region in the image. Note that although a perfect crystal diffracts the beam it also allows the direct beam through so still shows up as a bright region. This is the most commonly used form of imaging and is essentially the same form of imaging used for optical microscopes.

Dark Field Imaging

To form a dark field image the objective aperture is placed in position that allows only a diffracted beam (e.g. G or -G) through (Fig. 2.8b). In this case, the regions of the sample which do not scatter the beam are dark in the image and only those regions that scatter or diffract the beam in the particular directly selected by the objective aperture show up as bright regions. It should be noted that, this is not the negative image of the bright field image, which would allow all beams other than the direct beam through.
Imaging with scattered beams however is not very practical. The image formed is difficult to focus because the image moves. Instead, the centred dark field (CDF) method is preferred where instead of using the objective to select the desired scattered beam, the beam is tilted by deflectors to bring the diffracted spot to the axial position where the direct beam was (Fig. 2.8c).

Two-beam Imaging

Dark field imaging is particularly useful for imaging crystalline defects and faults which tend to diffract the beam in specific directions. Since diffraction is related to the orientation of the planes we can gain information about the orientation of the object that is diffracting the beam by examining which directions it diffracts in. The most commonly used technique for examining this is under ‘two-beam conditions’. Here the specimen is tilted so that only the direct beam and one other diffraction spot are bright (strongly excited). In this case if a bright field image is made it is referred to as a two-beam bright field image.

For obtaining sharp strong contrast dark field images of extended defects the beam is tilted to bring the originally strongly diffracted spot (+G) on axis. This results in it becoming a weakly excited spot and this form of imaging is known as weak-beam (centred) dark field imaging.

The imaging of defects is only briefly presented here. For a detailed description of dislocations in crystals observed in TEM see Hull & Bacon [19] or Williams
& Carter [18].

The amplitude of the beams that emerge from the sample in the two-beam condition are most commonly described by the Howie-Whelan equations (see Goodhew et al. [20]). These equations take into account how the two beams (0 and G) interact with each other in the crystal. Most importantly, in the presence of a dislocation or defect, an extra phase term that depends on the dot product between $\mathbf{g}$ and $\mathbf{R}$ is added to the equation. This means that when different diffraction vectors (g) are used to form images the defect will appear with different intensities.

Under certain conditions the dot product will be zero so that there will be no difference between surrounding areas and the defect will therefore be invisible; this is known as the invisibility criterion. For screw dislocations the $\mathbf{R}$ is proportional to the Burger’s vector $\mathbf{b}$, and in general the defect is visible if the dot product $\mathbf{g} \cdot \mathbf{b}$ > $\frac{1}{2}$. By imaging with different diffraction vectors and noting the image contrast of defects, information about the defect structure to be obtained.

## 2.3 Kelvin-probe Force Microscopy

Kelvin-probe Force Microscopy (KFM) is a scanning-probe force microscopy based technique that exploits the electromagnetic force to obtain surface potential maps of a sample. It is related to the vibrating capacitor technique developed by Kelvin to determine surface potentials of metals except that one of the metals is replaced with a conducting scanning probe tip. It has been used in the past for many purposes such as: identifying different materials on a sample [21], for examining electric fields around electrical contacts [22], as well as for lateral dopant profiling of semiconductors [23, 24].

KFM has recently been used to examine as-grown defects in thin SiO$_2$ and at the SiO$_2$/Si interface [25]. It was shown that single charges could be identified. These were attributed to interface states. Defects created by irradiation of high energy, high mass ions into thick oxides have also been examined using KFM [26]. Dongmo et al. [27] have previously shown that KFM is sensitive enough to yield surface potential images of charge traps in oxides irradiated with MeV Kr ions; while Ludeke [28] has examined as-grown thermal oxides showing that interface trapped charge can be observed with KFM.

Experimental data regarding damage in thermally grown oxides on silicon formed by keV energy ion implantation using KFM has not previously been pub-
lished in the literature. This work intends to provide an in-depth study of the effect of implantation on thin oxides and the silicon substrate using KFM.

2.3.1 KFM - Theory of Operation

A schematic diagram for KFM is shown in Fig. 2.9. In conventional non-contact or semi-contact mode Atomic Force Microscopy (AFM) an oscillating voltage is applied to a bi-morph that physically oscillates the cantilever at resonance. The vibrational amplitude of the cantilever is electronically determined from the modulation effect on a reflected laser spot position on a heterodyne photo-detector with the aid of a Lock-in amplifier. The tip-sample separation affects the vibration frequency and hence the amplitude. Information regarding the vibrational amplitude is passed onto the feedback controller which adjusts the height of the cantilever to maintain a set-value for the amplitude and therefore set value for the tip-sample separation. The feedback therefore holds information regarding the topography of the sample.

![Diagram of Kelvin-probe Force Microscopy experimental setup.](image)

Figure 2.9: Schematic of Kelvin-probe Force Microscopy experimental setup.

In KFM the oscillatory voltage is instead applied to the conducting tip. When a potential \( V \) exists between an electrically conducting tip and sample an force \( (F) \) is created between them (Eq. 2.21), where \( \frac{dC}{dz} \) is the capacitance gradient between the tip and sample at the tip scanning height [29].

\[
F = \frac{1}{2} \frac{dC}{dz} V^2
\]

(2.21)
This tip sample potential \( V \) is the total potential difference between the tip and the sample and consists of the applied bias on the tip \( (V_b) \) and the surface potential \( (\phi_{surf}) \). The surface potential is made up of the contact potential difference between the tip and sample, as well as any net charge in the sample, this is further defined below. The surface potential is usually defined such that its contribution to the tip sample potential is given by \([30, 31]\):

\[
V = V_b + \phi_{surf}
\]

If we consider that the applied bias has both a DC component \( (V_{dc}) \) and an AC component \( (V_{ac} \sin(\Omega t)) \), then the tip sample potential can be written as:

\[
V = V_{dc} + V_{ac} \sin(\Omega t) + \phi_{surf} \tag{2.22}
\]

Substituting equation 2.22 into equation 2.21 we have:

\[
F = \frac{1}{2} \frac{dC}{dz} \left( V_{dc} + V_{ac} \sin(\Omega t) + \phi_{surf} \right)^2
\]

let \( V_0 = V_{dc} + \phi_{surf} \)

\[
\Rightarrow F = \frac{1}{2} \frac{dC}{dz} \left\{ V_0^2 + 2V_0 V_{ac} \sin(\Omega t) + V_{ac}^2 \sin^2(\Omega t) \right\}
\]

\[
= \frac{1}{2} \frac{dC}{dz} \left\{ V_0^2 + 2V_0 V_{ac} \sin(\Omega t) + \frac{1}{2} V_{ac}^2 \left[ 1 - \cos(2\Omega t) \right] \right\}
\]

\[
= \frac{1}{2} \frac{dC}{dz} \left\{ V_0^2 + \frac{1}{2} V_{ac}^2 + 2V_0 V_{ac} \sin(\Omega t) - \frac{1}{2} V_{ac}^2 \cos(2\Omega t) \right\} \tag{2.23}
\]

The force on the tip is detected courtesy of its effect on deflecting or vibrating the scanning probe cantilever. The deflection is filtered and analysed with Lock-In amplifiers that separate static and resonant vibrational modes. The mathematical expression of these modes can be seen in the terms shown in Eq. 2.23:

\[
F_{dc} = \frac{1}{2} \frac{dC}{dz} \left( V_0^2 + \frac{1}{2} V_{ac}^2 \right)
\]

\[
= \frac{1}{4} \frac{dC}{dz} \left( 2V_{dc}^2 + 2V_{dc} \phi_{surf} + 2\phi_{surf}^2 + V_{ac}^2 \right) \tag{2.24}
\]
\[ F_{\Omega} = \frac{dC}{dz} V_0 V_{ac} \sin(\Omega t) \]
\[ = \frac{dC}{dz} (V_{dc} + \phi_{surf}) V_{ac} \sin(\Omega t) \]  
\[ F_{2\Omega} = - \frac{1}{4} \frac{dC}{dz} V_{ac}^2 \cos(2\Omega t) \]

The \( F_{dc} \) term may be thought of as a static deflection of the cantilever. This is often difficult to detect \[32\] since the capacitance gradient is often quite small.

The last term \( F_{2\Omega} \) is the second harmonic term. Since the only sample dependent term is the capacitance gradient it is measured when performing scanning capacitance microscopy.

The \( F_{\Omega} \) term expressed in Eq. 2.25 is what is monitored in KFM. This term describes the cantilever oscillation modulated by a frequency \( \Omega \). To maximise sensitivity this frequency is set to the cantilever resonance frequency so as to maximise the amplitude of the cantilever oscillation. Although this term is also proportional to the capacitance gradient, since it is oscillatory it is possible to obtain accurate measurements by use of a lock-in amplifier. In KFM a feedback circuit is connected to the DC bias to reduce this term to zero. From Eq. 2.25 it can be seen that this condition is met if the feedback bias \( (V_{fb}) \) is equal and opposite to the surface potential:

\[ V_{fb} = V_{dc} = -\phi_{surf} \]

By maintaining this condition as the probe is scanned across the sample it is then possible to map the surface potential of the sample by recording the DC bias on the tip.

2.3.2 Charge Free sample

In the simple case where there is no net charge in the sample, the feedback voltage \( (V_{fb}) \) is simply equal to the tip sample contact potential or contact potential difference \( (\phi_{tc}) \), which is the difference between the work functions of the tip and
sample:

\[ V_{fb}^{\text{no charge}} = \phi_t \]
\[ = (\phi_t - \phi_s) \]
\[ = - \phi_{\text{sur}} \]  \hspace{1cm} (2.27)

So in this case, any variation of the surface potential is therefore a reflection of the changes in the sample work-function. This may vary for example due to doping concentration in a semiconductor or sample material. From Eq. 2.27, if the work-function of the sample \((\phi_s)\) is increased relative to a reference sample, then the feedback voltage will be decreased relative to this. However, the change in the surface potential will follow the sample work-function and also increase. This can be expressed mathematically as:

\[ \Delta V_{fb}^{\text{no charge}} = - \Delta \phi_s \]
\[ = - \Delta \phi_{\text{sur}} \]  \hspace{1cm} (2.28)

The feedback bias on the tip may also be thought of as bringing the tip-sample system into a flat-band voltage condition. This is illustrated schematically in Fig. 2.10. In this way the flat-band voltage will be proportional to the contact potential difference between the tip and sample as defined above. Note that the nomenclature for feedback voltage is (conveniently) just as suitable for denoting the flat-band voltage as well.

![Figure 2.10: Band diagram illustrating contact potential difference between tip and n-type semiconductor sample in an equilibrium condition, and the flat band condition after an applied bias \(V_{dc}\) is applied to the tip.](image-url)
To illustrate what we may expect to measure in a ion implanted sample let us consider the situation where there is a small n\textsuperscript{−} region created as a result of implantation damage, where the active doping concentration is lower, surrounded by an n-type region. The Fermi level in the the n\textsuperscript{−} region is closer to the mid-gap, therefore the work-function of this region is larger than that of the surrounding n-type region. This means that the feedback voltage (or flat-band voltage) when the tip is over the n\textsuperscript{−} region is reduced, relative to when the tip is over the n-type region (Fig. 2.11). Note that according to Eq. 2.28 this means that the change in the surface potential has increased over the n\textsuperscript{−} region. The n\textsuperscript{−} region is considered to have an increased surface potential, i.e. relative to the surrounding area, or a positive relative surface potential.

![Flat band condition diagram](image)

Figure 2.11: Band diagram illustrating contact potential difference between tip and a n-type region in a semiconductor sample under the flat band condition after an applied bias \( V_{dc} \) is applied to the tip, and for a n\textsuperscript{−} region under flat band conditions where a smaller \( V'_{dc} \) is applied.

To gain a feel for the magnitude of changes one might expect to observe we can examine the contact potential differences for aluminium MOS capacitors (\( \phi_{mos} \)) shown in Table 2.1. Since the metal does not change here, the change in the contact potential difference can be attributed to the change in the semiconductor work-function. N.B. From Eq. 2.27 the change in the contact potential is equal and opposite to the change in the semiconductor work-function.

We can see that if there is an n-type doped region to \( 1 \times 10^{18} \text{ cm}^{-3} \), in a substrate with a background doping level of \( 1 \times 10^{15} \text{ cm}^{-3} \), it will have a larger contact potential by 0.15 V. This is to say that the flat band voltage is increased over the higher doped region although the surface potential is decreased by this amount. On the other hand a similarly doped p-type region with \( 1 \times \)
Table 2.1: The metal semiconductor contact potential differences ($\phi_{ms}$) for aluminium contact MOS capacitors on substrates of various doping levels (After Sze [30]).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\phi_{ms}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Si ($1 \times 10^{18}$ cm$^{-2}$)</td>
<td>-1.00</td>
</tr>
<tr>
<td>intrinsic Si</td>
<td>-0.50</td>
</tr>
<tr>
<td>n-Si ($1 \times 10^{15}$ cm$^{-3}$)</td>
<td>-0.20</td>
</tr>
<tr>
<td>n-Si ($1 \times 10^{18}$ cm$^{-3}$)</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

$10^{18}$ cm$^{-3}$ doping will lead to a decreased flat band voltage by 0.8 V, or an increased surface potential.

Henning et al. [23] examined through oxide ion implanted samples after performing an oxide etch and regrowth anneal at 900°C to leave only a doped substrate and good quality oxide. Their implants of boron into an n-type substrate revealed an increased ‘electrochemical potential difference’ (contact potential) over implanted areas. Since boron doping is expected to increase the work-function of the substrate however, from Eq. 2.28 we would expect a decrease in the contact potential. Furthermore, equations published along with their work indicate that the contact potential should decrease. Interestingly, their numerical simulations predict an increase in the contact potential difference in line with their experimental results. It would appear that there is a reversal in the sign of the potentials they consider through the paper since they later quote Eq. 2.37 without the associated minus sign. They also label their later plots as surface potential which according to Eq. 2.27 is of the opposite sign to the contact potential.

Furthermore, their theoretical models do not accurately predict the magnitude of the change in contact potential difference and tend to over estimate the measured value. This was attributed to several factors including the effect of the tip sample geometries on electrostatic forces and also contributions from surface charges and contaminants.

2.3.3 Effect of Net charge in the sample

In the case where there is a net charge in the sample there will be an additional Coulomb force ($F_C$) that must be considered. If we consider, for simplicity a point charge, $Q$, in the sample, this will induce a charge $-Q$, in the tip in addition to the applied bias which adds a charge $CV_b$. The total charge in the tip $Q_t$ is then
given by [33, 34]:

\[ Q_t = CV_b - Q_s \]

N.B. If the sample is biased and the tip earthed then the sign of \( V_b \) must be reversed.

The Coulomb force, which must be added to equation 2.23, can then be written as [33, 34]:

\[
F_C = \frac{1}{4\pi \epsilon} \frac{Q_s Q_t}{z^2} = \frac{1}{4\pi \epsilon} \frac{Q_s}{z^2} (CV_b - Q_s)
\]

\[
= \frac{1}{4\pi \epsilon} \frac{Q_s}{z^2} C [V_{dc} + V_{ac} \sin(\Omega t)] - \frac{1}{4\pi \epsilon} \frac{Q_s^2}{z^2}
\]

\[
= E_s (CV_{dc} - Q_s) + E_s CV_{ac} \sin(\Omega t)
\]

(2.29)

where \( E_s \) is the electric field at the tip, due to a charge \( Q_s \) in the sample.

The static (Eq. 2.24) and first harmonic (Eq. 2.25) components of the force are now given by:

\[
F_{dc}' = \frac{1}{4} \frac{dC}{dz} (2V_{dc}^2 + 2V_{dc}\phi_{surf} + 2\phi_{surf}^2 + V_{ac}^2) + E_s (CV_{dc} - Q_s)
\]

(2.30)

\[
F_{\Omega} = \frac{dC}{dz} (V_{dc} - \phi_{ts}) V_{ac} \sin(\Omega t) + E_s CV_{ac} \sin(\Omega t)
\]

\[
= \left[ \frac{dC}{dz} (V_{dc} - \phi_{ts}) + E_s C \right] V_{ac} \sin(\Omega t)
\]

(2.31)

From Eq. 2.31, the DC voltage due to the feedback bias in KFM mode is now given by:

\[
V_{fb} = V_{dc} = \phi_{ts} - \left( \frac{dC}{dz} \right)^{-1} E_s C
\]

\[
= \phi_{ts} - \left( \frac{1}{C} \frac{dC}{dz} \right)^{-1} E_s
\]

(2.32)

As noted before, the capacitance gradient is often small. Looking at Eq. 2.32 this is now beneficial to measurement sensitivity, although the capacitance is often on the order of an atto-Farad (\( \sim 10^{-18} \) F). In addition, since the working distances are relatively small (order of tens or hundreds of nanometres) the electric field strength is reasonable large for even a small amount of charge. It has
been demonstrated that it is in fact possible to detect the presence of a single charge [25].

2.3.4 Analytical Models for Capacitance Gradient

The accuracy of the analytical equations that model the electrostatic forces relevant to scanning probe microscopy were examined by Belaidi et al. [35]. From Eq. 2.21 we see that the electrostatic force is directly proportional to the capacitance gradient and the capacitance gradient can be determined by dividing the equations presented by $\frac{1}{2}V^2$.

It has been shown that the scanning probe can be modelled as consisting of three parts: the tip point, tip cone and the cantilever. Belaidi et al. [35] showed that certain models are more accurate depending on the tip sample separation. For small separations where the separation is less than the hemispherical tip radius, the hemispherical tip dominates the behaviour of the force. At larger separations the conical tip begins to contribute, and finally at distances much larger than the tip length the cantilever begins to contribute. The equations for the capacitance gradient for each of these sections is shown below.

Curiously, most papers seem to discuss the magnitude of the electrostatic force or indicate that it has a positive value. The capacitance gradient however is assumed to exclusively have negative values since we expect an increasing tip sample separation to lead to a decreasing capacitance.

Model for tip point

At small distances where the tip sample separation ($z$) is less than the tip radius ($R$) the capacitance gradient is given by the simplified sphere model as:

$$\left. \frac{dC}{dz} \right|_{z<R} = -2\pi\varepsilon_0 R \frac{1}{z}$$

(2.33)

The complete (full) sphere model, valid for larger separations, considers the capacitance of a conducting sphere above an infinite conducting plane. The expression for the capacitance gradient calculated from the equation presented by Belaidi et al. [35] is given by:
\[ \left. \frac{dC}{dz} \right|_{\text{sphere-plane}} = 4\pi \varepsilon_0 \sum_{n=1}^{\infty} \left( \frac{\text{Coth}(\alpha) - n \text{Coth}(n\alpha)}{\text{Sinh}(n\alpha)} \right) \quad (2.34) \]

where
\[ \alpha = \text{ArcCosh}(1 + \frac{z}{R}) \]

These capacitance gradients have been calculated for the tips used in our experiments. The resulting curves are shown in Fig. 2.12 in comparison to the simplified sphere model. As can be seen the capacitance gradient as calculated with the simplified sphere model diverges from the complete sphere model at larger separations. In our tips this occurs at only 3 nm.

![Figure 2.12: Plot of the capacitance gradient calculated from analytical models of tip sample geometries as a function of tip sample separation. Data for numerical simulations (TCAD) are also shown here although discussed in Chapter 6.](image)

**Model for tip cone**

The contribution of the conical part of the tip can be modelled by the ‘Uniformly charged line model’. For tip sample separations much smaller than the tip length and small cone angles, the capacitance gradient from this model is given by:

\[ \left. \frac{dC}{dz} \right|_{R<z<L} = -\frac{2\pi \varepsilon_0}{\text{ArcSin}^2(\text{Cot}(\theta))} \log \left( \frac{L}{4z} \right) \quad (2.35) \]
The full equation without approximations is given by:

$$\left| \frac{dC}{dz} \right|_{\text{charged line}} = \frac{-\lambda^2}{2\pi \epsilon_0} \log \left[ \frac{(2d + L)^2}{4d(d + L)} \right]$$

(2.36)

where

$$\lambda = \frac{2\pi \epsilon_0 \text{ArcSinh}(C \delta(\theta))}{d} = z\sqrt{1 + \tan^2(\theta)}$$

2.3.5 Flat-Band Voltage Shift

An alternative method for determining how charge in the sample can affect the feedback voltage is to consider how the flat band voltage is shifted as a result of the charge. This is exactly equivalent to what is described in texts regarding metal-oxide-semiconductor structures and the effect of oxide charges. The general expression for the shift in flat band voltages due to fixed oxide charge ($Q_f$), mobile ions ($Q_m$), oxide trapped charge ($Q_{ot}$) and interface charge ($Q_{it}$) and interface charge ($Q_{it}$) is given by:

$$\Delta V_{fb}^{\text{charge}} = -\frac{(Q_f + Q_m + Q_{ot}) + Q_{it}}{C_o}$$

(2.37)

Where ($C_o$) is the capacitance of the oxide layer.

So we see from Eq. 2.37 that positive charges result in a reduction in the flat-band voltage, i.e. more negative. As an example, the flat-band voltage shift for a 5 nm oxide (where the oxide capacitance is $6.9 \times 10^{-7}$ F/cm²) with a charge concentration of $Q/e = +1 \times 10^{11}$ cm⁻² is:

$$\Delta V_{fb} = -\frac{Q}{C_o} = -\frac{1.602 \times 10^{-19} \times 10^{11}}{6.9 \times 10^{-7}} = -0.023V$$

It should be noted however that Eq. 2.37 was intended to describe a MOS capacitor system where there is a flat electrical contact. It is not expected to precisely describe the case where the flat contact is replaced with a conical scanning probe tip. Indeed it has been shown that the tip geometry plays an important role in determining the potentials measured [35].
2.4 Rutherford Backscattering Spectroscopy

Channelled ions can also be used to determine the depth profile of lattice damage. This is a well established technique, there are standard texts that cover it in detail and only a brief account of it is given here. The classic text on Rutherford Backscattering Spectroscopy (RBS) is given by Chu et al. [36] while an excellent treatise of materials analysis using RBS of channelled ions (RBS-C) is given by Feldman et al. [37]

In standard RBS light ions with MeV energies irradiate a sample and are scattered with a certain energy distribution depending on the constituents and structure of the sample. This is well described by elastic collisions between a fast moving light ion and a heavy stationary nucleus. When the detector is placed at a small angle with respect to the surface normal of the sample good elemental resolution is obtained. When the detector is placed close to the plane of the sample surface, optimum depth resolution is obtained.

If ions are incident in the channelling direction there will be a reduced yield of backscattered ions. If there is damage in the crystalline sample such as stacking faults or interstitial atoms then the channels will not be empty as in a perfect crystal (c.f. Fig. 1.4c). These atoms can then scatter any channelled ions and thereby increase the scattered yield and show up in the RBS-C spectrum as a peak in scattered ion yield. This typically occurs if the atoms are displaced greater than 0.15 Å from a substitutional site [36].

When the incident ion collides with an atom in the sample it loses energy. This is characterised by the kinematic factor (K) so that the energy (E) after collision is related to the initial energy (E₀) by:

\[ E_1 = K E_0 \]

The kinematic factor depends only on the angle of the detector and the masses of the particles involved.

The ion will also lose energy on the inward and outward path principally due to inelastic interactions with the electrons in the target. Hence the deeper into the target the atom that the ion scatters off the more energy will have been lost. The final energy can now be written as [38]:

\[ E_1 (x_0) = E_2 - x_0 S \]

Where \( x_0 \) represents the depth of the scattering atom, \( S \) is the energy loss.
factor which encapsulates the attenuation of energy on inward and outward paths, and \( E_2 \) the energy of the ion had it scattered from an atom at the surface.

For a known initial energy of the ion it is possible to determine the depth of the target atom responsible for scattering the ion. So if this atom is in an interstitial location we have a mechanism for probing the depth of damage. With the increased yield giving information on the amount of damage and the energy range that this extends over indicating the range in depth the damage extends over.

The displaced atom fraction can also be calculated if along with the RBS spectrum from the sample a spectrum is obtained from a virgin (un-implanted) sample under the channelling condition and also under a random oriented condition. The yield from the un-implanted sample is representative of no displaced atoms whereas a random spectrum represents a totally disordered lattice or a displaced atom fraction of 1. The displaced atom fraction from other samples can then be calculated by subtracting the virgin spectrum from the sample spectrum and dividing by the difference between the random spectrum and the virgin spectrum.
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Chapter 3

Primary Experimental Equipment

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Major pieces of equipment used for this project are described here.

3.1 NEC Ion Implanters

Implantation requiring ion energies above 50 keV were performed on the 1.7 MV National Electrostatics Corp. (NEC) tandem accelerator at the Australian National University (Figure 3.1). The ion source on the implanter was a ‘Source of Negative Ions by Cesium Sputtering’ (SNICS), which provides a source for a wide range of ions from solid cathode materials. The created ions are accelerated by electrostatic potentials and ion species selected by passing the beam through a 90° magnet. The ion is then further accelerated by the terminal potential of the Tandem accelerator. To extract a positive beam the ion is stripped of an electron or electrons by N₂ gas bled into the centre of the terminal. For ion energies less than 100 keV however, the ion is not stripped of electrons and the accelerator is simply used to transport the ions through. An additional 15° magnet is also present after the tandem accelerator to select between any ions with different charge states (therefore velocity) created.

Whilst moving along the beam line the ion beam passes through various
sets of collimating slits that help confine the beam and limit divergence. This is important for the purposes of ion channelling since tight constraints are required for the angle of implantation.

To irradiate a sizable sample the beam is raster scanned over an aperture by X-Y scanners. This will add an error to the angle which can be calculated.

In the ion implanter the surface normal had to be determined, once again using a reflected laser beam concentric with the ion beam. In this case, a second laser was also reflected from the implantation stage and projected on to a wall at some distance from the implant chamber to allow precise tilting of the stage (see Fig. 4.1).

The implant chamber is evacuated using a combination of a rotary roughing pump, sorption pump and cryo-pump which leads to a base pressure of about \(1 \times 10^{-7}\) Torr. There is a copper cold shield that surrounds the sample stage that is cooled with a liquid nitrogen reservoir to trap any organic molecules that remain in the system and limits the amount of carbon stitching to the surface of samples during implantation. The cold shield is additionally biased to up to -300 V to suppress the secondary electron emission from the sample during implantation and to ensure the correct beam current (and hence fluence) is measured. The sample stage is made of nickel so it can be heated with an internal heater or cooled by filling an internal reservoir with liquid nitrogen. The sample stage is also positively biased to about +180 V to suppress secondary electron emission.

### 3.2 KTH-ANU DLTS Spectroscope

The DLTS system at the Australian National University (ANU) at the time experiments were conducted was developed along with control and data acquisition software at the Royal Institute of Technology (KTH), Stockholm. The system consisted of a computer controlled Hewlett-Packard C-V meter and pulse generator. The control software and data acquisition system was initially written in Basic, a LabView based program was later written and commissioned along with a Agilent pulse generator. The system digitises the capacitance transient and collects the full transient which is then analysed to determine DLTS signals over numerous rate windows. Often 6 to 7 rate windows with time windows between 40 ms and 1.28 sec were used for analysing silicon samples.

Temperature control at the time was a free run style system that consisted of immersing the sample stage in a liquid nitrogen bath.
Figure 3.1: 1.7 MV NEC Ion Implanter
3.3 SULA DLTS Spectroscope

The DLTS system at the University of Melbourne was a commercially available system purchased from SULA Technologies, USA. It consists of a hardware controlled C-V meter and pulse generator. The system also included four electronic correlators to measure the DLTS signal over separate rate windows. Rate windows were often kept short, since for these windows peak temperatures for defects appear at higher temperatures allowing a larger range of energy levels to be examined with the temperature span of the DLTS system. Time windows less than 1 ms in width were achievable with this system.

Data acquisition was based on LabView software and purchased along with the equipment from SULA technologies. The sample chamber was an Air Liquide cryostat that was evacuated with a rotary pump to a base pressure of 380 mTorr. The copper stage was cooled by syphoning liquid nitrogen through it while the temperature was software controlled with the aid of a heater within the copper stage and a Lakeshore temperature controller.

3.4 JEOL 4000EX Transmission Electron Microscope

The JEOL TEM at the University of Melbourne consisted of an electron accelerator capable of up producing 400 keV electrons although only 250 keV electrons were used for these studies. This was to limit the amount of damage created by the electron beam during imaging. The microscope consisted of a top entry holder with a double angle tilt sample stage with a range of 40° tilt on each axis. The microscope column was evacuated with a combination of rotary pumps, diffusion pumps and sputtered ion pumps. A cold trap was also present within the microscope but was typically not used during imaging.

The microscope did not possess a system to correct for image rotation and this was determined from images and diffraction patterns of cross-sectional (001) Si samples. Due to the lens design this was constant for the small range of magnifications used for imaging.

Although the microscope consisted of traditional film imaging a 2x3 mega-pixel CCD was later added. The CCD has a very high dynamic range and images often had a sizable gradient to them. The MaximDL software package was used for data acquisition and image processing. Typically the brightness and contrast was adjusted along with image flattening. Some images were also passed through
a FFT low-pass filter to remove noise from images as well.

### 3.5 NT-MDT SMENA Scanning Probe

Topographical and surface potential maps were obtained with a NT-MDT SMENA scanning probe microscope at the University of Melbourne using a two pass technique. Non-contact mode Atomic Force Microscopy was performed in the first pass to measure sample topography with no applied biases to the tip. KFM imaging was performed in the second pass following the same path as the first pass, with some height offset, so as to eliminate topographical contributions to the Kelvin-probe image.

Non-contact AFM/KFM scans of 512×512 pixels over 42×42 μm² with a 50 μm/sec scan speed were made with the University of Melbourne NT-MDT SMENA SPM. Tip sample separations of 200 nm were used for all KFM scans unless otherwise specified. Either TiN or Pt coated Si cantilevers with typical resonant frequencies of 300 kHz were used. Tip radii were quoted to typically be 35 nm with a 10° half angle. They were between 10-20 μm high and on cantilevers that were typically 35×130 μm² in dimension.

According to the NT-MDT manual and software to perform KFM scanning the output recorded is the feedback bias applied to the probe. In the case of a electrically grounded sample the value of this should be exactly equivalent to the flat-band. However, for reasons that will be discussed later in section 6.5.4, it appears as though the output data is in fact the opposite sign to the flat-band voltage and is therefore referred to as the surface potential instead.

KFM data was analysed using the NT-MDT Nova software package. First and second order curvature correction was applied and the average surface potential calculated over a 2×2 μm² regions in KFM scans. For each sample the average difference between the average surface potentials of implanted and un-implanted regions was calculated from up to 9 different regions. This is what will be referred to as the relative surface potential, i.e. the measured surface potential of an implanted area relative to the surface potential of the un-implanted area.
Part II

Experimental Studies
Chapter 4

Channelling & Primary Defects

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As the trend towards smaller device dimensions continues, so does the use of lower energy ion implantation as part of the fabrication process. These lower energy ions however have a larger probability of channelling. Although ion channelling has been extensively studied in terms of the effect on implanted ion range, the effect on damage has only been studied to a limited extent. It has been known for some time that channelling results in less implantation damage but experimental studies have mostly focussed on displaced atom profiles rather than vacancy profiles. Since vacancies form the main constituent of electrically active defects, it is important to study the vacancy profile in ion implanted silicon. There has however only been a handful of experimental studies of ion channelling on vacancy profiles. It is also unclear if Monte-Carlo ion implantation simulations accurately predict the concentration and profile of vacancies (relative to random oriented implantation) as a result of ion channelling.

This chapter discusses an investigation into the effect of ion channelling on the profile of residual vacancies in n-type Cz-grown (100) Si using defect depth profiling with Deep Level Transient Spectroscopy. Experimental difficulties encountered during this study, involving sample contamination, are also discussed.
To better understand the dynamic annealing of Frenkel defects the residual vacancy concentration profiles were also compared to predicted profiles obtained using the Monte-Carlo implantation simulation program Crystal-TRIM.

### 4.1 Experimental Setup

Phosphorus doped 0.7-1.1 Ω.cm Cz-grown n-type (100) silicon was implanted at room temperature with the 1.7 MV NEC Tandem implanter at the Australian National University. Wafers were cleaved into 1.5×1.5 cm² chips, cleaned with acetone then isopropanol and finally dried with compressed nitrogen. Samples were mounted with Ta clips on the implant stage and centred on the beam axis; to minimise the level of planar channelling when implanting at small tilt angles the [110] edged were oriented with a twist of 10° from tilt axis of the stage. Samples were implanted with tilt angles (θ) ranging from 0° to 1° from the surface normal with fluences in the range 2×10⁸–5×10⁸ cm⁻². To enable implantation with such low fluences the implant area was maximised by scanning the beam through a 2×4 cm² aperture, upstream collimation slits were wound in and the ioniser power reduced at the ion source. This resulted in an ion flux of ≈3.3×10⁷ cm⁻²s⁻¹. The ion beam spot had a 2 mm diameter, corresponding to a beam divergence of 0.02°. Since the range that is probed with C-V and DLTS measurements is governed by the range of the depletion width of the Schottky diode, an implant energy of either 450 keV or 600 keV was selected to place ion and damage depths within the range for the wafer type used.

The [100] direction of the wafers used was determined to be within 0.05° of the surface normal by channelling 2 MeV He ions. This was conducted on a separate chip from the same wafer as used for implantation with the Pelletron accelerator at the University of Melbourne. The surface normal was aligned with the beam line axis by passing a laser beam down the beam line and through a small aperture to reflect off the sample surface. The sample was then oriented until the reflected beam spot returned directly back through the aperture.

For implantation, the sample normal was aligned with the ion beam axis with an accuracy better than 0.1° again by using an incident laser coaxial with the beam axis. A laser was also used to determine the tilt angle by reflecting a separate laser from an implant stage face 90° to the implant face (Fig. 4.1).

After implantation chips roughly 4×5 mm² in size were cleaved from the centre of the samples. By using only the central region of the implanted sample the error in the implant angle is reduced to a total error in beam angle no greater than 0.3°. Prior to deposition of electrical contacts samples were cleaned
by immersing in warm trichloroethylene for 3 minutes, then rinsed in isopropyl alcohol for a further 3 minutes, followed by a 2 minute etch in 5% hydrofluoric acid to remove the native oxide. They were then rinsed with de-ionised water, dried with compressed nitrogen and promptly transferred to a thermal evaporator (base pressure $< 5 \times 10^{-6}$ Torr). An aluminium shadow mask with $\approx 0.8$ mm diameter circular apertures was used to deposit 200 nm thick gold electrical contacts to form Schottky diodes. Ohmic contact was made to the abraded back surface with In-Ga eutectic after gold contact deposition. Given that the calculation of depletion width (therefore probe depth) is directly dependent on the diode area, the diode dimensions were subsequently measured with a step-profiler at the Australian National University.

C-V measurements were performed on all samples to determine the doping profile and ascertain the quality of the diodes produced. Analysis of the data reveals a relatively uniform doping profile with less than 10% carrier compensation towards the surface. This was not always the case and as will be discussed later, and a strict cleaning regime was required.
4.2 Crystal-TRIM Simulations

Version 98f of Crystal-TRIM [1] which calculates full ion cascades (Crystal-TCAS) was used to simulate implantation of 600 keV P into (100) Si at several substrate temperatures under the same alignment conditions as used for actual implants. A displacement-energy of 13 eV and Debye temperature of 500 K was used for simulations and ions were considered to be at rest when ion energy reached 1 eV. As noted in Section 1.2.3 this value for the Debye temperature results in good agreement between simulations and experimental profiles. With regard to the rest energy, it was found that the recommendation that it be set equal to the displacement energy resulted in a much shallower ion ranges compared to results from MARLOWE, another Monte-Carlo simulation program previously used. To limit computation time only $10^4$ ion impacts were simulated, results were then smoothed with the fast fourier transform function in the genplot plotting program. It was found that simulating more ion impacts did not greatly improve statistics or curve shape. The Crystal-TRIM package used limits simulations to 100 data points, this in turn limits the depth resolution or bin size. For these simulations a bin size of 50 nm was determined to be required to cover the depth range of channelled ions.

From simulations it is expected that the majority of ions are channelled for implants aligned with the [100] direction (solid line, Fig. 4.2a.) and that the random fraction of implanted ions increases with implant angle. Note that the peak position of the channelled ions is more than twice that of the non-channelled ions (dotted line) and the end of range is predicted to be up to 2.7 $\mu$m into the sample. An implant angle of 0.4° away from the crystalline axis is predicted to produce a intermediate implant profile where the projected range is between that of an axially channelled and a random oriented implant. It can be seen that the channellling window for 600 keV phosphorus is expected to be quite small and that an implant angle 1° away from the crystalline axis is enough to create a profile equivalent to a random orientation.

Results for simulations of created vacancies (Fig. 4.2b.) demonstrate that the concentration of created vacancies increases with the implant angle, an effect known for some time [2], however the peak concentration depth is not predicted to vary much from 0.7 $\mu$m. This is a rather significant prediction as it implies that channelling implantation leads to the peak damage region being shallower than the projected range of ions.
The vacancy profiles also exhibit a channelling tail that extends further into the substrate as the beam angle approaches perfect channelling alignment. It should be noted that the concentrations predicted by Crystal-TCAS are for total created vacancies. Since simulations do not take defect annihilation into account only some 4-10 % of these are expected to remain in stable defects after implantation at room temperature [3].

![Graph](image1.png)

(a) Implanted P concentration profiles

![Graph](image2.png)

(b) Created vacancy concentration profiles

Figure 4.2: Crystal-TRIM simulations of (100) Si implanted with $5 \times 10^8 \text{ cm}^{-2}$ 600 keV P.
4.3 DLTS Spectra

DLTS scans were performed with a reverse bias of -6 V and a 6 V 50 ms filling pulses. Experiments with longer pulses up to 3.8 s show little change from the 50 ms pulse, and hence the 50 ms pulse is considered to have effectively filled all the traps in implantation damaged silicon. A typical DLTS spectrum using the SULA DLTS system is shown in Fig. 4.3. As can be seen there are three predominant peaks, these have been analysed by producing a linear fit to the Arrhenius plot and were found to correspond to trap levels 0.17, 0.22, and 0.42 eV below $E_c$. Based on previous annealing studies of 450 keV P implanted samples these levels were attributed to the vacancy-oxygen centre (VO), the double negative charge state of the divacancy centre ($V_2^{2-}$), and the superposition of the vacancy-phosphorus center with the single negative charge state of the divacancy centre ($V_2^{-}/VP$) respectively.

![DLTS Spectra](image_url)

Figure 4.3: DLTS Spectra for n-type 0.7-1.1 W.cm Cz-grown (100) Si implanted with 600 keV P at 0° & 1° tilts to a fluence of 2x10^8 P/cm².

The same types of defects were observed independent of implantation angle. This is in contrast to previously published work by Deenapanray et al. [4] involving helium ion implantation. Here it was observed that as the implantation angle of helium implanted silicon was varied, the ratio between the concentration of DLTS signals from different species also varied. It is possible that this is an effect that is only apparent for implants from low mass ions, where there is a
significantly smaller damage cascade, or that it is a helium related effect. There is insufficient evidence at this stage, to indicate the reason for this discrepancy.

The 0.4° implants were also performed, however the large experimental error in implant angle meant that they could not be reliably distinguished from the 0° or 1° implants and results from these have been omitted. Also, the ratio between the defect peaks was not found to significantly change with angle or implantation fluence up to the maximum fluence implanted in this work. The defect concentrations however were not calculated from the peak values obtained from DLTS signals since this only provides an average defect concentration. Given the variation in defect profiles expected between random oriented and channelled implanted samples this may lead to erroneous conclusions. Defect concentrations are much better examined by performing defect depth profiling and is presented in the next section.

4.4 Vacancy Profiles

The $E_c$-0.42 eV level in samples was chosen to be profiled since it has the largest DLTS signal. This is due to the concern that the signal to noise ratio from other defects would be too small for defect depth profiling in some samples since smaller regions are probed compared to DLTS. Profiling of samples implanted with fluences of either $2 \times 10^8$, $5 \times 10^8$ or $1 \times 10^9$ cm$^{-2}$ were performed isothermally at 188 K with a $(1.28 \text{s})^{-1}$ rate window on the KTH-ANU DLTS system. A reverse bias of -15 V was used which enabled depth profiling over the range 0.3-1.7 $\mu$m.

The Debye length during measurements was calculated to be $\approx 40$ nm for these measurements. This essentially sets the depth resolution for depth profiles. However, achieving such a resolution is not practical since the corresponding voltage increments and thus the change in depletion region, would be so small that very few traps would be probed with each pulse. This yields only a small signal which in practise would not be much higher than the noise from the electronics. Voltage increments of 0.5 V were used for profiling which resulted in a range of depth increments between 25 nm at greater depths and 115 nm near the surface. This range of intervals is due to the fact that the depletion width is not linearly dependent on the bias applied (c.f. Eq. 2.1 in Chapter 2). Given that the depth increments are smaller than the Debye length at greater depths any features in the profiles are likely to be due to noise or a computational artefact.

The measured profiles of the $V_7^-$/VP centre are shown in Fig. 4.4 along with results from Crystal-TRIM simulations for comparison. The 0° channelled
implanted sample (solid triangles) shows a broad profile peaked at approximately 0.9 \( \mu m \) below the surface, while the sample implanted with a 1\degree tilt shows a narrower profile peaked at \( \approx 0.75 \mu m \), both of which are more than one Debye length deeper than the predicted peak depth of \( \approx 0.68 \mu m \). Most significantly, in both cases there are much fewer defects than predicted towards the surface but the profiles remain within the depth range of the tail of the predicted profile. Indeed the simulations provide a good match to results deeper in the sample. This is indicative of the surface enhanced annihilation of migrating defects reported in the literature [5, 6]. The defect profile is therefore not considered to have been created deeper or shifted deeper, but that surface enhanced annihilation has lead to more defect annihilating near the surface.

![Graph](image)

Figure 4.4: Crystal-TRIM simulations for created vacancies in (100) Si implanted with 600 keV P to a fluence of 5\times10^8 cm\(^{-2}\) (lines) are shown with experimental DLTS depth profiles for implants at 0\degree & 1\degree tilts.

Although only one defect species has been profiled here previous work has shown little difference between the peak concentration depths of different vacancy related defects [5]. These studies over a similar depth range with higher dose random oriented implanted silicon also showed a similar reduction in concentration of V\(_2^-\)/VP centres towards the surface. Profiles were observed to be narrower near the surface than simulated TRIM profiles, as observed here. There was no indication of the peak being shifted however.

Interestingly the only other published work by Kortegaard-Nielsen et al. [7] involving planar channelling implantation over similar depth ranges, did not show any evidence of surface enhanced annihilation. This work however involved im-
plantation into an $n^+\text{-}p$ diode where the $n^+$ layer was MBE grown which suggests that surface enhanced annihilation is highly dependent on the substrate materials or fabrication conditions.

Note that the peak concentration of $V_2^-/VP$ centres is several orders of magnitude less than the vacancy concentrations predicted by Crystal-TRIM. This is much less than the fraction expected to remain after Frenkel pair annihilation. Since the di-vacancy consists of two vacancies and - as DLTS spectra show - there are other vacancy related defects that must be considered when determining the total vacancy concentration. If we simply consider the sum of the peak concentrations present rather than integrating over the depth profile, we find that we can approximately account for 1.5% of the predicted peak concentration. This percentage is smaller than that quoted in the literature and either suggests that there is a more efficient defect annihilation process present in these samples, or that simulations over predict the concentration of vacancies created. It is possible that a determination of the total vacancy concentration by integrating over the depth profiles of all defect species present may lead to a different percentage. It should also be noted that DLTS only probes electrical traps and is not sensitive to defects such as higher order vacancy clusters. Surface enhanced annihilation may also be playing a role in reducing the total vacancy population in addition to affecting the shape of the profile. In addition, some of the created vacancies may have formed higher order clusters towards the surface rather than annihilate, although formation of these are not expected due to the low fluence used. The fluence dependence of the defect concentrations presented below also confirms this.

### 4.4.1 Fluence Dependence

The sample implanted to a fluence of $1 \times 10^9$ cm$^{-2}$ was also profiled on the KTH-ANU system with the same parameters as the sample implanted to a fluence of $5 \times 10^8$ cm$^{-2}$. The sample implanted with $2 \times 10^8$ cm$^{-2}$ however was examined on the SULA system where the maximum reverse bias was limited to -10 V. This only allowed for a profiling depth range of 0.3-1.3 $\mu$m to be examined. While other parameters remained the same a rate window of $(8.6 \text{ ms})^{-1}$ was used for depth profiling. The resulting peak signal temperature at which measurements were made was 221 K. This leads to a slightly longer Debye length of $\approx$44 nm. Repeat measurements of the same sample have shown little difference in results obtained from the two systems. The SULA system does produce much cleaner
spectra for small rate windows though. The depth intervals for profiles now range between 30-170 nm for samples implanted to a fluence of \(2 \times 10^8\) cm\(^{-2}\) while samples implanted to a fluence of \(1 \times 10^9\) cm\(^{-2}\) have a range of 50-130 nm.

![Graph](image)

Figure 4.5: Crystal-TRIM simulation for created vacancies in (100) Si implanted with 600 keV P \((1 \times 10^9\) cm\(^{-2}\)) at 1° tilt (dotted line) are shown with experimental DLTS depth profiles at various fluences. A line through the data is also shown to guide the eye.

The depth profiles of the \(V^*_2/VP\) peak after implantation to various fluences are shown in Fig. 4.5 for 1° tilt implants, while Fig. 4.6 shows profiles obtained from channelled implanted samples. Interestingly there seems to be a small shift in the peak defect depth as the fluence is increased. The sample implanted at a 1° tilt to a fluence of \(1 \times 10^9\) cm\(^{-2}\) shows a defect peak that is now \(\approx 0.1\) \(\mu m\) deeper than predicted. The peak depths for the samples implanted with a lower fluence of \(2 \times 10^8\) cm\(^{-2}\) on the other hand appear to be closer to the surface and in closer agreement with the predicted peak depth. It is difficult to say if this is a clear fluence dependence however due to the limited range of fluences examined. If there is a fluence dependence the results suggest that as fluence is increased there is a more efficient annihilation of defects in the peak region where the concentration is predicted to be higher. This however contradicts the earlier suggestion that there is a smaller shift in the peak depth of the sample implanted to a fluence of \(5 \times 10^8\) cm\(^{-2}\) with a tilt of 1° because the damage concentration is higher. This perhaps suggests that the shape of the defect profile as well as the defect concentration plays a role given that channelled implanted samples have much broader profiles than random oriented implanted samples. It is also
Figure 4.6: Crystal-TRIM simulation for created vacancies in (100) Si implanted with 600 keV P (1×10^9 cm^{-2}) at 0° tilt (solid line) are shown with experimental DLTS depth profiles at various fluences. A line through the data is also shown to guide the eye.

possible that this effect is related to gettering of impurities from the surface. The DLTS spectra do not show any additional impurity related peaks and the free carrier profiles obtained from C-V measurements show no sign that this is the case.

Note that the peak defect concentrations scale almost linearly with fluence (c.f. Fig. 4.7), indicating that there is little or no vacancy clustering. This agrees with the work of Svensson et al. [5] who showed this to be the case for implant fluences less than 3×10^9 cm^{-2}. Fig. 4.7 also indicates that not only do channelling implants result in a lower peak concentration of vacancies but that the rate of production of vacancies is also lower for channelled implanted samples.

4.5 Sample Contamination

4.5.1 Dopant Compensation

During fabrication of samples for these DLTS studies it was often difficult to find processing conditions that limited dopant compensation to a level acceptable for DLTS analysis. This section outlines some of the processing effects observed.
Figure 4.7: The peak concentration of $V_{2}^-$/VP as determined by DLTS depth profiling in (100) Si implanted with 600 keV P as a function of fluence is shown for implants at $0^\circ$ & $1^\circ$ tilt angles.

Originally, 20% HF was used to remove the native oxide and instead of etching for a specific time, each sample was visually examined for signs of hydrophobic behaviour. This can normally be used to indicate that any oxide (which is hydrophilic) has been removed, and that a hydrogen terminated silicon surface is instead present [8]. However, since sample sizes used in this case were on average 4×5 mm², surface tension of water was often enough to produce a bead of water between the tips of the tweezers used to handle the sample and often lead to the erroneous decision that the oxide was still present. This in turn lead to relatively long etch times, sometimes up to 15 minutes. The combination of concentrated HF and long etch times lead to samples where dopants within the first 0.5 μm were compensated by up to 30% even in un-implanted virgin samples. This resulted in defect profiles that were skewed. It should also be noted that the energy of implantation was initially 450 keV and only later increased to 600 keV in an attempt to push the region of interest further away from the surface where the compensation was higher.

Although DLTS is not considered to be applicable if the defect concentration is more than 10% of the doping concentration. It was not immediately clear if in this case the defects which compensate the dopants, as apparent in Fig.4.8 contribute to the DLTS signal and if they render DLTS analysis invalid. Nevertheless, although compensated dopants may not lead to erroneous DLTS spectra, they can still lead to erroneous defect profiles. This is because as seen in Eq.2.20,
the defect concentration is dependent on the doping concentration. Therefore, if the doping concentration is reduced towards the surface, then the defect concentration will also be reduced and the profile skewed towards deeper depths. In some cases the signal even resulted in negative values being calculated for the defect concentration towards the surface. These negative values are taken to be an artefact from the calculations because DLTS spectra taken only over the near surface region did not yield any negative signals in the spectra, which might be indicative of minority carrier traps.

Reducing the HF concentration to 5% and etch time to 2 minutes was not enough to eliminate dopant compensation. It was observed that the amount of compensation was often correlated with the implant fluence (see Fig. 4.8). The level of compensation however was not consistent and varied from sample to sample, even for samples implanted in the same way. Fig. 4.8 is therefore only intended to indicate the maximum compensation observed at each fluence.

![Graph showing doping profiles obtained from C-V measurements of (100) Si implanted with 600 keV P (1° tilt) are shown for implants at various fluences.](image)

**Figure 4.8:** Doping profiles obtained from C-V measurements of (100) Si implanted with 600 keV P (1° tilt) are shown for implants at various fluences.

Due to this variability, the compensation is not believed to be directly due to implantation damage, such as higher order vacancy clusters, interstitial silicon or direct collisions producing interstitial dopants. Instead it is suspected that the implantation damage is gettering impurities from the surface, perhaps hydrogen from the HF solution although no hydrogen related defect peaks appeared in the DLTS spectra.

A fluence of up to $5 \times 10^8$ cm$^{-2}$ was found to most consistently provide sam-
samples with less than 10% dopant compensation. It should be noted that although $1 \times 10^9 \text{cm}^{-2}$ lead to acceptable channelled implanted samples, random implanted samples still showed appreciable compensation due to the higher defect concentrations in these samples.

### 4.5.2 Metal Impurity peak

In several cases, a spurious peak appeared in DLTS spectra that seemed to be related to an impurity introduced from the thermal evaporator used (Fig. 4.9). Analysis of this peak yields a trap level of $E_c - 0.36 \pm 0.02 \text{ eV}$. It did not seem to be eliminated by different chemical cleaning and sample preparation. Only by performing ‘dummy’ evaporations with no sample in place, to coat the evaporator surfaces and clean the boat and source material, did the peak disappear. Cleaning the evaporator surfaces with abrasive SiC paper however seemed to reveal the source of the contaminant and bring back the peak. Note that the contaminant peak does not significantly reduce di-vacancy peaks. This suggests that it is not a copper-vacancy complex as has been previously identified [9]. This defect has also been discussed in the literature [5]. Furthermore implantation with copper into the back face and annealing for an extended period of time at high temperatures prior to implantation into the front face did not reproduce the contaminant peak.

![Figure 4.9: DLTS spectra from (100) Si implanted with 600 keV P (0° tilt) shown for a contaminated and uncontaminated sample. Spectra have been scaled by the average doping concentration to take variations into account.](image-url)
4.6 Conclusion

In summary we have implanted n-type Cz-grown (100) silicon wafers under channelling and random orientations with 600 keV P to fluences up to $1 \times 10^9$ cm$^{-2}$. Crystal-TRIM simulations predicted a channeling window of 1° for these implant parameters and interestingly predicted that the peak damage depth does not vary much with implant angle although the ion range and width of the vacancy profile do exhibit a marked variation. This implies that channeling implantation results in the ion range and peak defect depth being separated.

DLTS spectra show three main peaks identified as the VO, $V_2^{2-}$, and $V_2^-$/VP. The ratio between the concentration of defects was not observed to significantly change with implant angle. Interestingly there was no dependence of types of defect species present on implant angle in contrast to the work of Deenapanray et al. [4]. It is unclear if this is unique to helium implantation of their work or whether it is an ion mass dependent variation.

Experimental results for vacancy depth profiles from axial channeling implanted samples had not previously been published and this was performed for the first time. The $V_2^-$/VP defect was depth profiled with DLTS and compared to simulated vacancy profiles obtained from a version of Crystal-TRIM that calculated full ion cascades. The most striking feature of the defect depth profiles is that both implants at 0° & 1° show profiles that have a much lower concentration of defects near the surface than predicted. This is attributed to surface enhanced annihilation of migrating defects and is consistent with the published literature [5, 6].

Surface enhanced annihilation is also believed to lead to an offset between the measured peak damage depth and predicted peak depth of $\approx 0.68 \mu m$. Depth profiles of channelled implanted samples show a maximum concentration at a depth of 0.8 $\mu m$ for samples implanted to a fluence of $2 \times 10^8$ cm$^{-2}$, up to a depth of 0.9 $\mu m$ for samples implanted to fluences of $5 \times 10^8$ cm$^{-2}$ and above. Samples implanted at an angle of 1° from the channeling axis showed profiles with a peak defect depth ranging from 0.75 $\mu m$ for samples implanted to fluences of $2 \times 10^8$ & $5 \times 10^8$ cm$^{-2}$, to a depth of 0.8 $\mu m$ for an implant to a fluence of $1 \times 10^9$ cm$^{-2}$.

It is unclear why the peak depths of samples implanted at 1° tilts show a smaller apparent shift. If this shift is related to enhanced annihilation it may suggest that only a fixed amount of defect annihilation is enhanced, given that the concentration of defects is higher in samples implanted at a 1° tilt this would result in less of an effect on the profile.

Regarding the measured change in peak defect concentration depth with
implant fluence, with only three fluences examined it is difficult to say with certainty if there truly is any fluence dependence to the level of surface enhanced annihilation. It is plausible however that as the fluence is increased there is a more efficient annihilation of defects in the peak region where the concentration is higher which leads to the peak depth appearing to shift deeper into the sample. It is also possible that the reduction in defect concentrations towards the surface are not the result of enhanced annihilation but gettering of impurities from the surface. This effect would also be expected to increase with fluence. However, based on DLTS spectra and free carriers profiles there is no indication that this is the case.

The measured profiles all lie within the tail of the predicted profiles and simulations show a good agreement with results deeper within the sample. It is proposed that simulations do indeed accurately predict the created damage profiles but the effect of the surface plays a key role in determining the resulting profile of vacancy-related defects. Results also suggest that the effect of surface enhanced annihilation extends up to 0.8 \( \mu m \).

Although not all defects were profiled, results shown in the literature indicate that there is not a large variation between the profiles of vacancy related defects. The \( V_2^-/\text{VP} \) profile is therefore taken to represent the residual vacancy profile. Based on the measured peak concentration of the \( V_2^-/\text{VP} \) and the ratio between the different defect species present the total vacancy concentration was calculated to be only 1.5\% of that predicted by Crystal-TRIM to be created during implantation. This is much less than the range of 4-10\% reported in the literature, however it is unclear if this is simply a poor approximation of the true vacancy concentrations or if Crystal-TRIM over predicts the level of damage created.

It was also experimentally demonstrated that defect concentrations scale linearly with fluence in accordance with the expectation that no defect clustering should occur for low fluence implants. However, results also show that the rate at which the residual peak vacancy concentration increases with fluence is lower for channelled implanted samples. It is unclear if this is due to a more efficient defect annihilation in channelled implanted samples or if channelling implantation is less efficient at producing defects.

Finally, sample contamination was a major hindrance in this work and was attributed to the chemical cleaning process and the metal contact fabrication. These introduced significant dopant compensation and an impurity defect peak respectively. To combat these issues the hydrofluoric acid concentration and etch times were reduced and dummy evaporations were performed to coat exposed surfaced of the thermal evaporator prior to contact fabrication.
References


Chapter 5

Channelling & Secondary Defects

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As device dimensions are reduced higher implant fluences are also required. This increases the dopant concentration so that a large number of carriers can be maintained, but also increases the concentration of defects created. In particular, interstitial atoms can form extended defects such as rod-like defects and dislocation loops after annealing. Further annealing of these defects has shown that their dissociation and subsequent release of interstitial enhances dopant diffusion. This essentially affects accuracy with which devices can be fabricated and to control this a better understanding of the defect formation and evolution is required.

As discussed in Chapter 1 there is some controversy regarding the exact mechanisms that govern whether extended defects will form after annealing. It has been shown that there is often a threshold fluence that must be crossed before extended defect formation. However, it is unclear if it is the fluence of ions that directly determines whether extended defects form or if it is the amount of damage created by these ions. The published work by others has indicated that the number of interstitials contained within the defects was equal to the number of ions implanted, and so was born the +1 model. Departures from this
have been observed though; for example, it has been shown that implanted ion mass and substrate temperature both affect the threshold fluence for extended defect formation and the number of excess interstitials remaining. This suggests that it is not the amount of ions being implanted that governs extended defect formation but rather the amount of damage created or specifically the number of interstitials present.

To investigate the defect formation mechanisms the effect of ion channelling on extended defect formation was studied. Channelling provides an interesting framework to study extended defect formation as it is known to produce a broader implanted ion profile and also result in less damage. Some work on this has previously been conducted by Schreutelkamp et al. [1]. They found that there was no difference in the formation threshold for dislocation loops, but that channelling implantation resulted in a lower concentration of loops. Their work however, did not examine rod-like defect formation and utilised either low temperature (500°C) long anneals (1 hour), or high temperature (900°C) intermediate duration (15 min.) anneals. The annealing time and temperature is important as it controls not only the formation of defects but also their evolution. It is generally accepted that clusters form first, which then form rod-like defects upon further annealing. Rod-like defects are not stable and annealing for a longer duration results in their dissociation and the formation of dislocation loops.

The work presented in this chapter will examine the effect of ion channelling on rod-like defect formation using intermediate temperature and intermediate duration anneals. In addition to exploring the effect of ion channelling, the effect of implantation fluence and annealing duration on extended defect formation is also examined.

5.1 Experimental Setup

Phosphorus doped 5-10 Ω.cm n-type (100) Cz-grown silicon wafers were used for this study. Samples were implanted at room temperature with 75 keV $^{31}$P ions using the 1.7 MV NEC Tandem implanter at the Australian National University. Wafers were cleaved into 1.5×1.5 mm$^2$ chips with edges parallel to (111) directions, they were cleaned with acetone, then isopropanol and dried with compressed nitrogen prior to being mounted on the implant stage. Tantalum clips were used to secure samples on the implant stage and chips were mounted with a twist of 10° from the rotation axis of the implant stage to minimise planar channelling when implanting at small tilt angles.

Samples were implanted with tilt angles ($\theta$) of either 0° or 8° from the sur-
face normal to produce channelled and random oriented implanted samples. An ion flux of \(2.1 \times 10^{11} \text{ cm}^{-2} \text{s}^{-1}\) was used for implantation to fluences in the range \(0.5 - 4.5 \times 10^{14} \text{ cm}^{-2}\). Implants were performed at room temperature for extended defect and RBS-C studies but implants were performed at 400°C, for SIMS measurements. Implants were also performed at -190°C for RBS-C studies. The rationale for implanting at different temperatures will be discussed in the relevant sections.

Sample alignment was performed as described in Section 4.1; the sample normal was aligned with the ion beam axis with an accuracy better than 0.1°, again by using an incident laser coaxial with the beam axis. Another laser was used to determine the tilt angle by reflecting off the implant stage face 90° to the implant face (Fig. 4.1). The beam spot obtained for 75 keV phosphorus ions was \(\approx 5 \text{ mm}\) in diameter, corresponding to a divergence of 0.05°. Scanning the beam across a \(1.5 \times 1.5 \text{ cm}^2\) aperture contributes a further 0.1° to the error in the implantation angle and leads to a maximum error in angle of 0.3°. This is well within the channelling window of \(\approx 4°\) for 75 keV phosphorus ions.

Following implantation, samples were cleaved into smaller chips and cleaned with de-ionised water, acetone, isopropanol and dried with compressed air prior to being annealed in a conventional quartz tube furnace at 750°C. It should be noted that the furnace was initially believed to be set for 800°C, however subsequent calibration showed the temperature to be closer to 750°C. Based on the work by Li et al. [2] who examined the evolution of extended defects at 800°C for similar implants to ours, a 10 minute anneal was chosen as they showed that a similar number of rod-like defects and loops were formed after such an anneal.

Plan view samples were then fabricated by cutting 3 mm diameter disks using an ultrasonic drill with 400 grade SiC grit and water. The back surfaces of samples were then mechanically polished back to 100 \(\mu\text{m}\) with increasingly finer grades of SiC paper (600–4000 divisions/inch). Finally, samples were mounted face down on plastic paddles and the edges masked with Lacmit varnish for etching in a 48% hydrofluoric acid, nitric and acetic acid (HNA) mixture in a ratio of 1:5:1. This produced an etch rate of about 20 \(\mu\text{m}/\text{min}\). The etch pit formed has a crater like shape and etching was performed until a small hole is formed in the centre of the pit. The sample is therefore thinnest near the hole and is thicker away from it.
5.2 Depth Profiles

5.2.1 Crystal-TRIM Simulations

Crystal-TRIM [3] version 98f which calculates full ion cascades (Crystal-TCAS) was used to simulate implantation of 75 keV P into (100) Si at several substrate temperatures under the same alignment conditions as used for actual implants. A displacement-energy of 13 eV and Debye temperature of 500 K was used for simulations. It was found that the recommendation that the rest energy be set equal to the displacement energy resulted in much shallower channelling profiles compared to results from MARLOWE [4], another Monte-Carlo simulation program previously used; instead, ions were considered to be at rest when ion energy reached 1 eV. To limit the computation time for simulations, only $10^4$ ion impacts were simulated, results were then smoothed with the fast fourier transform function in the Genplot plotting program [5]. It was found that simulating more ion impacts did not greatly improve statistics or curve shape. The Crystal-TRIM package used also limits simulations to 100 depth intervals which limited the depth resolution. For these simulations an interval of 10 nm was determined to be required to cover the depth range of channelled ions which was more than adequate as profiles were relatively broad.

Results for the simulated implanted ion concentration profile are shown in Fig. 5.1. They show that for room temperature (300 K) implantation aligned with the [100] direction ($\theta = 0$, dashed line) the majority of ions are expected to be channelled, resulting in a broad implant profile extending between the range of 100 nm up 900 nm. The simulated implant at an angle of 8° from the [100] direction (solid red line) shows a relatively sharp peak at a depth of 90 nm, corresponding to a random oriented implant and ions only extend up to 400 nm. Simulations at implant angles of 2° and 4° reveal that the channelling window has a half angle of approximately 4°, i.e. implant angles larger than 4° from the channelling axis will result in an implant profile that closely matches a random-oriented implant.

Since the version of Crystal-TRIM used does not take into account damage accumulation (which leads to de-channelling of ions) it was felt that it is unfair to compare simulations to room temperature implantation at relatively high fluences (where damage accumulation will affect ion depth profiles). SIMS measurements were, as mentioned earlier, performed on samples implanted at an elevated temperature of 400°C to limit damage accumulation by promoting Frenkel pair annihilation. However, elevated substrate temperatures also lead
to de-channelling due to increased lattice vibrations. Fortunately the version of Crystal-TRIM used can take this into account.

Fig. 5.1 shows a simulation for channelling implantation into a sample at 400°C (dotted blue line). The simulation predicts that a considerable number of the ions are de-channelled and stop at shallower distances into the substrate. This is due to the increased thermal lattice vibrations. Note that the peak concentration of ions is at a depth of 120 nm and is only slightly deeper than the case of random oriented implant. There is still however a significant fraction of the ions that are predicted to be channelled and reach depths of up to 700 nm. Note that since thermal vibrations only affect channelling there is no effect on the random oriented implant profile.

![Graph showing phosphorus concentration vs depth](image)

Figure 5.1: Crystal-TRIM simulations of implanted phosphorus concentrations in 75 keV P channelled and random oriented implanted (100) Si.

Results for simulations of created recoiled lattice atoms are shown in Fig. 5.2. Since recoiled atoms are most likely to reside in interstitial lattice positions they are synonymous with interstitial atoms. It should be noted however that the predicted concentrations are far higher than what is expected to be found in experimental samples because simulations do not take Frenkel pair annihilation into account. The simulations can however give us some comparison between different implant conditions, as well as an insight into what discrepancies we may find between simulations and experimental results.

The simulated channelled implant (dashed line) can be seen to have a peak
concentration roughly a factor of 5 times less than that predicted for the random orientation (solid red line). This reduction is, as explained in section 1.2, expected and has been known for some time [6]. The region over which damage is predicted to extend in the channelling case however is, as for the implanted ion range, much broader and deeper than the random case; extending from the surface up to a depth of 1 μm into the sample. This is more than twice the depth range of the random case which extends up to 0.4 μm. The peak interstitial concentration depth for channelled implanted samples however is predicted to be at 90 nm only some 30 nm deeper than the peak interstitial depth for random oriented implants.

We can also consider the total amount of damage created in each case. This is to say that by integrating the simulated data we can determine the concentration of interstitials per unit area. For the channelled implanted simulations a total created interstitial concentration of $5.5 \times 10^{11}$ cm$^{-2}$ is predicted. Whereas in the random orientation case we find that a total created interstitial concentration of $9.8 \times 10^{11}$ cm$^{-2}$ is predicted. So although simulations show that the channelled implanted samples are still predicted to have less damage, the total number of recoiled atoms for the channelled implant is slightly less than half that for the random implant, while the peak concentration is less by a factor of five.
5.2.2 Secondary Ion Mass Spectroscopy

SIMS measurements were performed in order to verify the accuracy of Crystal-TRIM. They were conducted by Dr. Mladen Petravic using a Riber MIQ256 SIMS at the Research School of Physical Sciences, Australian National University. A Cs beam was used and the depth of the sputtered pit was measured using a Tencor step profiler.

Results from samples implanted at a temperature of 400°C to a fluence of $3 \times 10^{14}$ cm$^{-2}$ are shown in Fig. 5.3. Results show that for the random oriented implant ($\theta = 8^\circ$), simulations accurately predict the peak concentration, peak depth and shape of the profile. Although, there appears to be slightly more channelled ions in the SIMS profile (open circles, ○) in the depth range between 200 nm and 300 nm. The divergence of the SIMS data away from simulations at greater depths is however the sensitivity limit of the SIMS being reached. This sensitivity limit is due to background noise and/or contamination in the system and from the data appears to be $6 \times 10^{17}$ P/cm$^3$.

![Figure 5.3: SIMS results and Crystal-TRIM simulations of phosphorus concentration in 75 keV P channelled and random oriented implanted (100) Si.](image)

SIMS results from the channelled implanted sample at 400°C are also quite good. There does seem to be slightly more de-channelling than predicted by Crystal-TRIM however. This may be due to several reasons: the sample substrate could have in fact being at a higher temperature than intended, leading to more de-channelling; there may be some damage accumulation leading to de-channelling, even at the elevated implant temperature. Having said this, the
results as they are only show a difference, between the predicted peak concentration depth and the measured depth, of some 20 nm. Only slightly more significant however is the measured peak of $1.3 \times 10^{18}$ P/cm$^3$ compared to the predicted peak of $1.0 \times 10^{18}$ P/cm$^3$.

The measurements of real importance however are those of room-temperature implanted samples since they match the implantation conditions used for TEM samples. Without these measurements however it is difficult to determine the likely effect of damage build up on implanted ion profiles and at what fluence the damage is great enough to cause this.

Unfortunately, there was not the opportunity to profile room temperature implanted samples but an idea of what we might expect can be gained by examining SIMS results published by Schreutelkamp et al. [7, 8]. They show that for channelled 100 keV phosphorus room temperature implanted samples, as the fluence is increased beyond $5 \times 10^{13}$ cm$^{-2}$ to $2 \times 10^{14}$ cm$^{-2}$, the number of ions that are channelled saturates and only the peak corresponding to the random fraction is observed to increase. This effect is attributed to the increased de-channeling probability due to the increased damage. They also calculated the number of displaced silicon atoms from RBS-C measurements to be $1.7 \times 10^{16}$ cm$^{-2}$ in the case of an implant to the fluence of $5 \times 10^{13}$ cm$^{-2}$ and $1.1 \times 10^{17}$ cm$^{-2}$ in the case of samples implanted to a fluence of $2 \times 10^{14}$ cm$^{-2}$.

5.2.3 Rutherford Backscattering Spectroscopy

Rutherford Backscattering Spectroscopy with channelled ions (RBS-C) was used to determine the displaced atom profiles in samples. The majority of displaced atoms are expected to be as a result of recoiled atoms and interstitial in nature so results can be compared to simulation results. Analysis was performed with a 2 MeV α particle beam and the sample chamber had a base pressure of $1 \times 10^{-6}$ Torr. A copper cold shield cooled with liquid nitrogen was used to trap hydro-carbons in the chamber and limit the amount of carbon stitching on the surface of samples during analysis. Results for implants under channelling and random orientation conditions to various fluences are shown in Fig. 5.4. Also shown with these results are channelling spectra from an un-implanted sample and spectra collected at a random orientation.

The RBS-C spectra show that implanted samples have an increased backscat-
Figure 5.4: RBS-C of 75 keV P implanted (100) Si at at room temperature to various fluences and under random or channelling orientations.
tering yield (compared to an un-implanted/virgin sample) near the surface peaked at a depth of approximately 80 nm. This increased backscattering, as explained in Section 2.4 is due to displaced or interstitial atoms in the substrate created as a result of ion implantation damage. Spectra clearly show that the samples are not amorphised by implantation with any of the fluences used. This would result in a backscattering yield in the near surface region matching the yield obtained at a random orientation condition.

Results also show for samples implanted to a given fluence that those implanted under channelling conditions exhibit a damage peak which is lower in yield and deeper into the sample compared to those implanted at a random orientation. For channelled implants, the damage also extends deeper into the sample. This is completely consistent with Crystal-TRIM simulations shown in Fig. 5.2.

![Graph showing peak displaced atom fraction vs. fluence for different implant angles](image)

Figure 5.5: Calculated displaced atom fractions from 75 keV P implanted (100) Si at room temperature to various fluences under random or channelling orientations.

Fig. 5.5 shows the calculated peak displaced atom fraction from RBSC spectra as a function of fluence for both random oriented and channelled implanted samples. Directly comparing channelled and Random oriented implanted samples we find that at the relatively low fluence of $1.5 \times 10^{14} \text{ cm}^{-2}$ random oriented samples show a peak damage that is a factor of $\approx 2.8 \times$ higher than channelled implanted samples to the same fluence. Comparing spectra from Random oriented implanted samples to a fluence of $2.8 \times 10^{14} \text{ cm}^{-2}$ to channelled implanted samples to a similar fluence of $3 \times 10^{14} \text{ cm}^{-2}$ however, the random oriented implanted sample only has a higher damage level by a factor of $\approx 2.2 \text{ now}$. If we now look at
how the measured amount of damage increases with fluence we find that in the
case of the channelled implants, as the fluence is doubled from $1.5 \times 10^{14}$ cm$^{-2}$ to
$3 \times 10^{14}$ cm$^{-2}$ there is an increase in the damage by a factor of $\approx 5.6$. In random
oriented implants however where the fluence is increased from $1.5 \times 10^{14}$ cm$^{-2}$ to
$3.0 \times 10^{14}$ cm$^{-2}$ there is only an increase in damage by a factor of $\approx 4.2$.

This is most likely due to there being sufficient damage being accumulated
during channelled implantation after implantation to a fluence of $3.0 \times 10^{14}$ cm$^{-2}$. Damage leads to de-channelled and with more ions being de-channelled there
is even more damage created. Note however that the depth of peak damage
concentration is still deeper than in random oriented implanted samples. This
indicates that there is still a reasonable channelled fraction contributing to the
damage profile.

Note also that if the displaced atom fraction is multiplied by the density of
silicon then the peak displaced atom concentration can be calculated. The concen-
trations obtained for the random implanted sample are surprisingly close to
the predicted concentrations, e.g. a peak concentration of $7 \times 10^{21}$ cm$^{-3}$ is calcu-
lated for the random oriented sample implanted to a fluence of $1.5 \times 10^{14}$ cm$^{-2}$,
compared to the predicted value of $9 \times 10^{21}$ cm$^{-3}$ (c.f Fig. 5.2). The calculated
peak concentration of damage in the channelled implanted sample implanted to
a fluence of $1.5 \times 10^{14}$ cm$^{-2}$ also shows a surprisingly good agreement with simu-
lations. However, the channelled implanted sample implanted to a fluence of
$3 \times 10^{14}$ cm$^{-2}$ has a concentration higher than predicted and as noted earlier is
indicative of de-channelled. The agreement between experiment and simul-
ation in these samples was greater than might be initially expected. Earlier work
(Chapter 4) along with the literature indicated that only a small fraction of the
created defects survive room temperature implants. However, the samples exam-
ined in this chapter were implanted to a much higher fluence than those studied
in Chapter 4. It is possible that when the fluence is high enough, recoiled atoms
or interstitial silicon form stable defect structures that inhibit Frenkel pair an-
nihilation. It should also be noted that RBSC provides a measure of displaced
atoms and that these may not necessarily be interstitial in nature, the actual
concentration of interstitial silicon may be lower than the displaced atom concen-
tration.

**Low Temperature Implants**

There was initially some concern that the equipment was not sensitive enough
to measure the amount of damage left from room-temperature implants. Al-
though (as discussed in section 1.1.1) interstitials are mobile down to 4 K it is also known that implantation at lower temperatures does limit defect annihilation. 75 keV phosphorus implants were therefore performed at -190°C to a fluence of $5 \times 10^{13}$ cm$^{-2}$. Spectra obtained for samples implanted to a fluence of $5 \times 10^{13}$ cm$^{-2}$ at liquid nitrogen temperatures are shown in Fig. 5.6.

![Figure 5.6: RBS-C 75 keV P implanted (100) Si at various implant angles.](image)

The RBS-C spectra show that implanted samples exhibit an increased backscattering yield (compared to an un-implanted/virgin sample) near the surface at a depth of approximately 100 nm. At this low fluence however, the samples are not any where near the amorphisation threshold. This is despite the low temperature implant limiting defect annihilation.

The spectra show similar results for both the sample with the surface normal aligned with the beam axis ($\theta = 0^\circ$, open circles •) and that implanted with a tilt of $1^\circ$ from the beam axis (blue ×, filled triangle ▲). This indicates the channelling window was large enough, and our alignment good enough during implantation, that implants are still channelled with tilts of up to $1^\circ$ from the surface normal. When the tilt or implant angle is increased to $4^\circ$ and above however there is an increased displaced atom fraction as ions begin to de-channel. As expected from the simulations they are also slightly shallower.

Spectra were analysed with the Nd program [9] to determine the depth profile of the displaced atom fraction. Results from this are shown in Fig. 5.7. Here we
can see that the displaced atom fraction reaches 0.3. We can now clearly see that the displaced atom profile for the random oriented samples peaks at 60 nm while the channelled sample shows a peak at 90 nm. This is exactly as predicted by Crystal-TRIM simulations.

Interestingly however, only a very slight channelling tail is observed for low angle implants. This is presumably due to damage build up at the surface leading to de-channelling of ions. The ratio between the displaced atom fraction for a channelled implanted sample and a random oriented implanted sample is also only 1:1.5, not 1:5 as predicted from simulations. This is another indication that there is damage accumulation in the channelled implanted samples that leads to de-channelling of ions and more damage near the surface.

So under certain conditions de-channelling becomes prevalent as a result of damage accumulation. These effects are not simulated in the version of Crystal-TRIM used, although there are other versions available that attempt to do so. In this case, simulations under-estimate the amount of damage and over-estimate the range of damage created in samples implanted in the channelling orientation. In the absence of damage accumulation and de-channelling the concentrations of recoiled atoms predicted very closely match the displaced atom concentrations measured with RBSC. It is unclear what fraction of the displaced atoms are in fact interstitial in nature though.
5.3 Transmission Electron Microscopy

A 250 keV electron beam was used for imaging; two beam conditions were obtained by tilting approx 10° from the [100] zone axis. This was achieved by moving to a region of the sample thick enough that Kikuchi lines were visible in the Condensed Beam Electron Diffraction (CBED) condition, then tilting the sample so that the deviation parameter (s) was in excess, indicated by the Kikuchi line being just on the outside of one of the 022 diffraction spots. A typical zone axis CBED image revealing the Kikuchi lines is shown in Fig. 5.8. Weak beam dark field images were then constructed using diffraction vectors in ⟨022⟩ directions.

![CBED Image](image)

Figure 5.8: A typical condensed beam electron diffraction (CBED) image. Image has been deliberately saturated so that Kikuchi lines are visible.

5.3.1 Fluence dependence

Random Oriented Implants

Samples implanted in the random orientation to fluences up to $1.5 \times 10^{14}$ cm$^{-2}$ and annealed for 10 mins did not show any evidence of extended defects. Although the bright field image (Fig. 5.9) shows small dark dots of less than 10 nm diameter,
these features do not show any contrast in the dark field images (Fig. 5.10 & 5.11). The contrast observed from the bright field images is attributed to mass-thickness contrast from particles on the surface. Note that since there were no identifiable features in dark field images however it was almost impossible to select an image of the same region as observed in bright field images.

![Image](image_url)

Figure 5.9: $1 \times 10^{14}$ cm$^{-2}$ 75 keV P random oriented implanted (100) Si annealed at 750°C for 10 minutes under an argon ambient. Bright field image.

When the fluence reaches $2 \times 10^{14}$ cm$^{-2}$ however the threshold for creating extended defects has been crossed in this annealing regime. Weak beam dark field images of samples implanted to a fluence of $2 \times 10^{14}$ cm$^{-2}$ (Fig. 5.12 & 5.13) show mostly dislocation loops but also rod-like defects. Rod-like defects were observed to have lengths in the range of 10–60 nm long with a typical length of about 40 nm. Loops on the other hand had major axis 10–20 nm in diameter. Note that rod-like defects have the strongest contrast when elongated perpendicular to the diffraction vector $\vec{g}$, and that none appear parallel to the diffraction vector. There are also smaller elliptical spots of 10 nm diameter and less. They are in fact loops that appear as spots due to the imaging conditions (specifically the orientation angle between the Burger’s and diffraction vector, see next section for an example of this). Note that some loops also show evidence of faceting and look hexagonal, others appear rectangular and elongated. Although generally the appearance of faceting is not enough to distinguish between perfect and Frank loops as both
Figure 5.10: $1 \times 10^{14}$ cm$^{-2}$ 75 keV P random oriented implanted (100) Si annealed at 750$^\circ$C for 10 minutes under an argon ambient. Weak beam dark field image, $\bar{g}=(022)$.

Figure 5.11: $1.5 \times 10^{14}$ cm$^{-2}$ 75 keV P random oriented implanted (100) Si annealed at 750$^\circ$C for 10 minutes under an argon ambient. Weak beam dark field image, $\bar{g}=(022)$. 

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may exhibit faceting [10], the rectangular elongated defects would however seem to be perfect loops based on their distinct appearance in previous papers [11]. To correctly determine the nature of the defects requires a full invisibility criterion analysis to determine the habit planes and Burger’s vectors.

Note that due to the habit plane of loops, they are not expected to be viewed edge on from the [100] direction. The elongated or rectangular loops are therefore what have been referred to in the past as rectangular elongated defects or prismatic loops. Note that they seem to be elongated along the \( \langle 010 \rangle \) and \( \langle 001 \rangle \) directions, while rods are found to be elongated also along the \( \langle 01 \bar{1} \rangle \) directions as expected (c.f. section 1.1.1). Curiously a few of the rectangular loops also appear to be elongated along the \( \langle 01 \bar{1} \rangle \) directions.

Based on the discussion regarding defect evolution in section 1.1.3 the dominance of loops and the length of rod-like defects seen in these images suggest that rod-like defects are in a latter stage of evolution. This is to say that rods have Ostwald ripened (to longer lengths and begun reducing in number) while loops have only just begun to form.

![Image](image.png)

Figure 5.12: \( 2 \times 10^{14} \) cm\(^{-2} \) 75 keV P random oriented implanted \((100)\) Si annealed for 10 minutes under an argon ambient. Weak beam dark field image, \( \mathbf{g} = (022) \).

The threshold fluence for extended defect formation for 75 keV phosphorus and a 10 minute 750°C anneal is thus in the range \( 1.5 - 2 \times 10^{14} \) cm\(^{-2} \) in agreement
with threshold fluences reported by Jones et al. [12] & Eaglesham et al. [13] for dislocation loops. For loops to be the dominant species after only 10 minutes of annealing is also consistent with the studies of Li et al. [2] where, for a similarly implanted sample annealed at 800°C, loops were shown to form after only 5 minutes and began to dominate after 10 minutes.

It is interesting to note that both rod-like defects and loops were observed on the outset of extended defect formation. Other papers [14] note that rods are preferentially formed at lower fluences while loops only appear at higher fluences or after further annealing. For example, Eaglesham et al. [13] indicate that rod-like defects should be formed (for a similar anneal) at fluences down to $5 \times 10^{12}$ cm$^{-2}$. It may be that in the small range of fluences between $1.5 - 2 \times 10^{14}$ cm$^{-2}$ there is a fluence at which only rod-like defects have formed after annealing at 750°C for 10 minutes.

Channelled Implants

Defect formation as a result of channelling implantation seems to result in a similar behaviour to random implanted samples. Again small dots of less than 10 nm diameter are observed in images however they are now present in both dark
and bright field images (Fig. 5.14 & 5.15). Larger features are present in the bright field images but they do not produce a strong contrast in dark field images. These are attributed to surface particles that do not have any structure and therefore do not result in strong diffraction contrast. The smaller features may be due to defect clusters that are referred to in the literature [15] as precursors to rod-like defects. Note that there are also more features that show high contrast in the dark field image than in the bright field images, it is unclear what this means.

![Image](image_url)

**Figure 5.14:** $1 \times 10^{14}$ cm$^{-2}$ 75 keV P channelled implanted (100) Si annealed at 750°C for 10 minutes under an argon ambient. Weak beam dark field image, $\mathbf{g}=(022)$.

As the fluence was increased to $3 \times 10^{14}$ cm$^{-2}$ the threshold for the creation of extended defects was crossed. Images shown in Fig. 5.16, 5.17 & 5.18 reveal dislocation loops but few rod-like defects. Given that RBS-C results (Fig. 5.4a) show that a similar amount of damage is created by a random oriented implant of $2 \times 10^{14}$ cm$^{-2}$, where extended defects are first observed to form, it is not surprising that defects are observed to also form in this case.

Loops are 10-15 nm in diameter while rod-like defects are only $\sim$10 nm long, elongated along the (011), (01\overline{1}) and (010) directions. Small spots of diameter less than 10 nm appear to be smaller loops which depending on the diffraction vector used for imaging appear as spots rather than loops. This is illustrated in Fig. 5.16 & 5.17 which show the same region under different imaging conditions.
Figure 5.15: $1 \times 10^{14} \text{ cm}^{-2}$ 75 keV P channelled implanted (100) Si annealed at 750°C for 10 minutes under an argon ambient. Two beam bright field image. Same region as previous image.

This is discussed in detail in the paper by Wong-Leung et al. [14].

So the threshold fluence for extended defect formation for channelled 75 keV phosphorus implanted samples annealed for 10 minutes at 750°C is within the range $1.5 - 3 \times 10^{14} \text{ cm}^{-2}$. The finding that the threshold fluence for extended defect formation due to channelled ion implantation is comparable to that for random oriented implants, is consistent with the findings of Schreutelkamp et al. [1, 8]. Although a sample with a channelled implant to a fluence of $2 \times 10^{14} \text{ cm}^{-2}$ was not examined, in light of the afore mentioned work, it would not be surprising to find that extended defects are also present in such a sample.

Unfortunately, since RBS-C showed that the peak implantation damage, where secondary defects are first observed to form, is similar for both random and channelled implants it is not possible to verify the claim by Schreutelkamp et al. that it does not play a role in extended defect formation. Given that both channelled and random oriented implanted samples to a fluence of $1.5 \times 10^{14} \text{ cm}^{-2}$ do not result in secondary defects and that they both have a much lower implanted defect concentration suggests that there may still be some peak threshold that must be exceeded. Examining whether a channelled implanted sample implanted to a fluence of $2 \times 10^{14} \text{ cm}^{-2}$ and annealed in the same way contains extended
Figure 5.16: $3 \times 10^{14}$ cm$^{-2}$ 75 keV P channelled implanted (100) Si annealed at 750°C for 10 minutes under an argon ambient. Weak beam dark field image, $\mathbf{g}=(0\overline{2}2)$.

Figure 5.17: $3 \times 10^{14}$ cm$^{-2}$ 75 keV P channelled implanted (100) Si annealed at 750°C for 10 minutes under an argon ambient. Weak beam dark field image of the same region as the previous two images, $\mathbf{g}=(02\overline{2})$. 

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defects may shed some light on this however. Furthermore, since there has been no opportunity to perform SIMS analysis on these samples it is difficult to show that the peak concentration of implanted ions also does not play a role.

Note also that the total amount of damage in the channelled implanted sample implanted to a fluence of $3 \times 10^{14}$ cm$^{-2}$ is similar to that found in the random-oriented implanted sample implanted to a fluence of $2 \times 10^{14}$ cm$^{-2}$ since it is broader and has a lower peak concentration. This is the alternative criterion for extended defect formation championed by Schreutelkamp et al. [1]. Without ruling out whether peak defect concentration plays a role it is difficult to confirm that results support this theory.

The defect sizes and concentrations however are drastically different between channelled implanted samples and those implanted in the random orientation. It may be that due to the higher fluence in the channelled implanted $3 \times 10^{14}$ cm$^{-2}$ sample compared to the random oriented implanted sample to a fluence of $2 \times 10^{14}$ cm$^{-2}$ and consequently larger total number of interstitials created, but not higher peak concentration, that the evolution of rod-like defects is accelerated and they have already begun to dissociate. Or perhaps due to the concentration of interstitials they do not reach large lengths because it is energetically favourable for the interstitials to form dislocation loops instead. This is
in line with the work of Raineri et al. [16] who found that channelled implanted samples produce less extended defects.

Regarding the dislocation loops however, it would seem that the lower peak concentration of interstitials in the channelled implanted sample results in smaller loop sizes a factor of $1.5 \times$ smaller than loops observed in random-oriented implanted samples.

Increasing the fluence further still to $4.5 \times 10^{14}$ cm$^{-2}$ does result in larger loop sizes, with 20 nm diameter loops appearing in images (Fig. 5.19 & 5.20). Images may not be of high enough quality to discern if rod-like defects are present however as small rod-like features that are present seem slightly elliptical or curved. These may in fact be prismatic loops. Although loops also appear to be more numerous or more concentrated, this may be due to imaging a thicker film since film thicknesses were not measured. It should be noted that although the as-implanted sample implanted to this fluence was not examined with RBS-C the fluence is not expected to amorphise the silicon.

![Image](image.png)

Figure 5.19: $4.5 \times 10^{14}$ cm$^{-2}$ annealed for 10 minutes under an argon ambient. 75 keV P channelled implanted (100) Si. Weak beam dark field image, $g=(022)$. 

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5.3.2 Annealing duration dependence

Random Oriented Implants

As shown before, the threshold fluence for extended defect creation was found to be $\approx 2 \times 10^{14}$ cm$^{-2}$ for 75 keV phosphorus implants and annealing at 750°C for 10 minutes. The evolution of the rod-like defects and loops observed for an implant at this threshold fluence was briefly examined by performing an anneal for only 5 minutes. A weak beam image of this sample is shown in Fig. 5.21.

Although not a particularly good image, Fig. 5.21 seems to show the presence of small clusters and elongated defects smaller than 10 nm. As discussed in section 1.1.1, this is consistent with the evolution of defects observed by Pan and Tu [17], where clusters are first formed, then short rod-like defects. Although the time scales they observed for evolution were much shorter, this is most likely due to the higher annealing temperatures they used as well as the higher fluence and lower energy ions leading to an amorphous surface layer.

To further investigate the interplay between implantation fluence and extended defect evolution, the sample implanted to a fluence of $1.5\times10^{14}$ cm$^{-2}$ was an-
nealed for 15 mins. The corresponding TEM images are shown in Fig. 5.22–5.24.

Images show the presence of spots with $\approx 5$ nm diameters and short elongated defects of lengths up to 10 nm. Note that elongated defects show a stronger contrast when elongated along a direction perpendicular to the diffraction vector ($g$). Since they show different contrast conditions depending on the diffraction vector they are clearly not the result of preferential image blurring in one direction as a result of a misaligned electron microscope. These spots may be residual interstitial clusters that have still not evolved to another form of extended defect.

With the increased annealing time images also begin to show the presence of loops, albeit small loops 10-15 nm in diameter. It is also possible that the small spots observed are in fact loops that are too small to be distinguished. Given that all images are plan-view TEM images and sample thicknesses are at least 80 nm thick (the projected range of the ions) and most likely more it is difficult to obtain better contrast of these features. To truly examine the nature of these spots, cross-sectional TEM samples would need to be prepared where the film thickness may be as low as 20 nm and even high-resolution TEM becomes possible. So although the threshold fluence for extended defect formation for random oriented 10 minute anneals at 750°C was previously found to be in the
Figure 5.22: $1.5 \times 10^{14}$ cm$^{-2}$ 75 keV P random oriented implanted (100) Si annealed at 750°C for 15 minutes under an argon ambient. Weak beam dark field image, $\mathbf{g} = (022)$.

Figure 5.23: $1.5 \times 10^{14}$ cm$^{-2}$ 75 keV P random oriented implanted (100) Si at 750°C for 15 minutes under an argon ambient. Weak beam dark field image, $\mathbf{g} = (022)$. 

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range $1.5 - 2 \times 10^{14} \text{ cm}^{-2}$, we now find that the upper limit for the threshold for 15 minute anneals is reduced to $1.5 \times 10^{14} \text{ cm}^{-2}$. If one accepts that there is an absolute fluence or amount of damage that needs to be created before any extended defects are created, regardless of annealing regime, this would imply that the threshold is in fact $1.5 \times 10^{14} \text{ cm}^{-2}$ or less. This is exactly the fluence previously determined by Jones et al. [12] & Eaglesham et al. [13].

That extended defects take longer to form at lower fluences would suggest that due to the lower concentration of defects it takes longer for them to accumulate or coalesce to form extended defects. This work does not agree with Eaglesham’s extended defect formation diagram that suggests that at lower implantation fluences, rod-like defects begin to form after the same annealing time as those at higher fluences. In contrast, it appears that for extended defects to form in samples implanted at a lower fluence, a longer annealing time is required compared to samples implanted to a higher fluence. This perhaps suggests that at higher fluences the evolution is faster due to the higher concentration of defects.
Channelled Implants

In the case of a 75 keV phosphorus channelled implanted sample and a fluence of 1.5e14 cm\(^{-2}\) and annealed for 15 minutes there are also small spots and some elongated defects observed. Cluster sizes are again less than about 5 nm while rod-like defects are again 10-15 nm in length. Dark field images are shown in Fig. 5.25 & 5.26. No dislocation loops however were identified in this sample.

![Image showing channelled implanted sample with a fluence of 1.5e14 cm\(^{-2}\) and an anneal of 15 minutes. The image shows small spots and elongated defects.](image)

Figure 5.25: 1.5×10\(^{14}\) cm\(^{-2}\) 75 keV P channelled implanted (100) Si at 750°C for 15 minutes under an argon ambient. Weak beam dark field image, \(\mathbf{g}=(0\overline{2}2)\).

Again the rod-like defects show a stronger contrast when elongated perpendicular to the diffraction vector (\(\mathbf{g}\)).

The threshold fluence or damage level seems to be the same for the formation of these elongated defects and spots. The apparent reduction in the concentration of extended defects with channelling implantation is also in line with what was observed earlier for 10 minute anneals and also the work of Schreutelkamp et al. [1] for dislocation loops.

The fact that no dislocation loops are observed here however is in contrast with the work of Schreutelkamp et al. [1] because there appears to be a difference in the threshold fluence for dislocation loop formation. It would appear that for a 75 keV channelled phosphorus implanted sample annealed for 15 at 750°C the fluence required before loop formation is more than 1.5×10\(^{14}\) cm\(^{-2}\).
Figure 5.26: $1.5 \times 10^{14}$ cm$^{-2}$ 75 keV P channelled implanted (100) Si at 750°C for 15 minutes under an argon ambient. Weak beam dark field image, \( g = (022) \).

Returning to the RBS-C results, the peak concentration of damage for random implanted samples was found to be higher than for channelled implanted samples. This may suggest that the peak concentration does affect dislocation loop formation. Although as discussed previously, the small spots observed may indeed actually be small loops that simply cannot be distinguished in these samples. Given that it was also previously noted that channelled implanted samples result in smaller sized defects it would not be surprising if any loops present are simply too small to be distinguished as loops. It is not a result of the imaging conditions that loops appear as spots however since this depends on the orientation or habit plane of the loops. Given that this is randomly distributed there must be some that are oriented in a way to produce a contrast condition in which they do appear as loops (c.f. Fig. 5.17).

5.4 Conclusion

We have examined the effect of ion channelling on rod-like defect formation using intermediate temperature (750°C) and intermediate duration anneals. In addition to exploring the effect of ion channelling, the effect of implantation fluence and annealing duration on extended defect formation was also examined.
Rutherford Backscattering Spectroscopy with channelled ions (RBSC) revealed that under certain conditions de-channelling becomes prevalent as a result of damage accumulation. These effects are not simulated in the version of Crystal-TRIM used and simulations under-estimate the amount of damage and over-estimate the range of damage created in samples implanted in the channeling orientation. In the absence of damage accumulation and de-channelling however the concentrations of recoiled atoms predicted very closely match the displaced atom concentrations measured with RBSC. It is however unclear what fraction of the displaced atoms are in fact interstitial in nature though.

The effect of ion channeling on extended defect formation was found to agree with the work of Schreutelkamp et al. [1] although different annealing conditions were examined. For samples annealed at the same temperature for the same duration it was found that there was a similar threshold fluence for extended defect formation although channelled implanted samples had a lower peak concentration of displaced atoms. Defects in channelled implanted samples were also smaller in size. Results also seem to indicate that the formation threshold of loops is in fact slightly higher for channelled implanted samples given that none were observed in samples implanted to a fluence of $1.5 \times 10^{14}$ cm$^{-2}$ and annealed for 15 minutes at 750°C. However, even random implanted samples only showed the presence of a few dislocation loops and a sample annealed for up to 20 minutes could also be examined to determine if there really is a difference in the loop formation threshold.

Channeling provides an interesting framework to study extended defect formation as it is known to produce a broader implanted ion profile and also result in less damage. Crystal-TRIM simulations predicted a peak damage concentration 5 times less; however, RBS-C experiments show that this is not necessarily the case, and that it varies with the implant fluence. For a lower fluence of $1.5 \times 10^{14}$ cm$^{-2}$ it was found that the peak displaced atom fraction in channelled implanted samples was a factor of 10 lower, however samples implanted to a fluence of $\approx 3 \times 10^{14}$ cm$^{-2}$ indicate that there is only a factor of 2.5 less damage. This is attributed to damage accumulation which was able to be simulated with the version of Crystal-TRIM used. Damage accumulation leads to de-channelling of ions which in turn leads to more damage created. This implies that simulations that do not take damage accumulation into account cannot be used to identify the fluences where channelling and random-oriented implants result in the same peak damage concentrations. With more time available samples could be analysed with RBS-C to determine these fluences. It would seem for example, that a channelled implanted sample to a fluence of $2 \times 10^{14}$ cm$^{-2}$ may have a similar peak damage concentration to a random-oriented sample implanted to a fluence.
of $1.5 \times 10^{14}$ cm$^{-2}$. Perhaps a random-oriented sample implanted to a fluence of $1.7 \times 10^{14}$ cm$^{-2}$ could also be examined as RBS-C results would suggest that this has a similar peak defect concentration to a channelled sample implanted to a fluence of $3 \times 10^{14}$ cm$^{-2}$.

It was also found that although the literature suggests that there is a fixed threshold fluence and annealing duration at which extended defects will form, our results show that the threshold fluence depends on the annealing duration. Specifically it was found that extended defects can be shown to form at lower fluences if the annealing duration is increased from 10 to 15 minutes. This is in contrast with the findings of Eaglesham et al. [13] who claimed that the threshold fluence is the same regardless of annealing duration. This is believed to be due to the effect of defect concentration on the evolution time of defects, with higher concentrations leading to a faster evolution. It is however also possible that extended defects have formed after only 10 minute anneals but are simply too small to be imaged in plan-view samples. Further high-resolution cross-sectional TEM however is beyond the scope of this work.

Unfortunately, based on the RBS-C results it is difficult to say if peak concentrations really do matter for extended defect formation. Although the peak damage concentration of samples annealed for 10 minutes at 750°C, is similar for both random oriented implants to a fluence of $2 \times 10^{14}$ cm$^{-2}$ and channelled implants to a fluence of $3 \times 10^{14}$ cm$^{-2}$, it is possible that both of these exceed a supposed threshold peak concentration. This peak concentration must be more than that measured for a random oriented implant to a fluence of $1.5 \times 10^{14}$ cm$^{-2}$ since these samples did not show extended defect formation. The only true falsification of whether there is a peak damage concentration threshold is if a random oriented implant and channelling implant result in the same peak defect concentration, and one of them does not show extended defect formation.

Note also that the total amount of damage in the channelled implanted sample implanted to a fluence of $3 \times 10^{14}$ cm$^{-2}$ is very similar to that for the random-oriented sample implanted to a fluence of $2 \times 10^{14}$ cm$^{-2}$ since it is broader and has a lower peak concentration. This is the criterion for extended defect formation championed by Schreutelkamp et al. [1], however it is difficult to say that our results confirm this theory without first disproving whether the peak defect concentration is important. It may also be possible to examine if samples implanted to a lower fluence match this theory by examining the random-oriented sample implanted to a fluence of $1 \times 10^{14}$ cm$^{-2}$ since RBS-C shows that this has a similar level of damage to the channelled sample implanted to a fluence of $1.5 \times 10^{14}$ cm$^{-2}$ which produced extended defects.
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Chapter 6

Implantation effects on Surface Potential

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6.8 Conclusion

The ability to which we can create well defined dopant structures in silicon with ion implantation is limited by the level of dopant diffusion after subsequent thermal processing. Thermal processing is required for both annealing of implantation related defects and for activation of dopants in silicon. In recent years this has been accomplished by the use of rapid thermal annealing at high temperatures for short periods of time. Another important thermal process involved is the growth of the thin surface oxide. Thermal oxide growth however involves high temperatures for longer periods of time which may lead to excessive dopant diffusion. Thermal oxidation after implantation is for example incompatible with implantation of single ion arrays for the fabrication of a solid state quantum computer. Through oxide implants may be a way to combat this problem and there has been a limited amount of research into its use (c.f Section 1.3).

Although damage in oxide on silicon structures has been well studied due to their technological importance to the semiconductor industry, the majority of these studies do not utilise techniques that are able to spatially resolve damaged regions. Furthermore, few techniques can examine as-implanted oxide on silicon structures implanted to fluences in the range $10^{12}$–$10^{14}$ cm$^{-2}$.

Scanning probe techniques are ideally suited to this, but there has been little research into their use for the study of ion implantation damage. Kelvin-probe Force Microscopy (KFM) for example is extremely sensitive to changes to the surface potential and has previously been used to examine native oxide traps by Ludeke [1]. There has however only been one study that has used it to examine implantation damage [2].

What is presented here is a semi-quantitative study of the effect of ion implantation on the surface potential of thin oxides on silicon using KFM. Specifically the effect of: the implant fluence, different implanted ion species, and thermal annealing. An issue with scanning probe based studies however is the lack of depth information. By performing oxide etching it was hoped that oxide and oxide interface damage removal would allow the effect of damage and dopant activation in the silicon substrate to be isolated.
6.1 Experimental Details

The oxides used for this study were thermally grown on 2 inch diameter 3–5 Ω.cm phosphorus doped n-type silicon wafers. Oxide growth was performed in a triple wall quartz tube furnace under a dry oxygen ambient at the University of New South Wales and oxides were grown to either 5, 15 or 50 nm thicknesses. The 15 nm oxides were the first to be available for experiments and also had a n+ diffusion doped region with an aluminium back contact fabricated. For the 5 and 50 nm oxides, it was decided that it was sufficient for the back surface to be abraded to obtain an Ohmic contact. The 5 and 50 nm oxides were also subjected to a 400°C 15 minute passivation anneal in a 4% hydrogen in nitrogen (forming gas) ambient to reduce interface trap densities.

In order to directly compare ion implanted areas to un-implanted areas, an implantation mask with microscopic apertures was required. This eliminates any difficulties that may arise from comparing results from two broad area implanted samples such as a non-constant tip work function.

Originally, holey carbon ‘quantifoil’ films with a thin gold film evaporated on them (supported by a copper TEM grid) was used as implant mask. These films had 1 μm diameter holes and were considered to be ideal for an implantation mask. However, it was found that the grids were not uniformly flat and that reproducibility between implanted samples was difficult to obtain.

An improved implantation mask was produced by spin coating a UV sensitive polymer photo-resist (AZ-5214E) on wafers at the Australian National University. This was performed at 4000 rpm for 30 seconds to produce a 1 μm thick layer. A standard adhesion promoting polymer (hexa-methyl-di-silazane, HMDS) was also found to be required for 5 and 50 nm thick oxides and was spun on prior to photo-resist spinning. Without the HMDS on the 5 and 50 nm oxides it was found that the photo-resist would peel off during either the developing step or de-ionised water rinsing. Curiously this was not found to be required for the un-passivated 15 nm thick oxide samples. This may be a result of the passivation anneal changing the surface properties of the oxide. Samples were then baked at 85°C for 15 minutes in a standard laboratory oven to harden the photo-resist. 8×8 arrays of 3 μm diameter circular apertures were patterned using UV photolithography (Fig. 6.1). Implantation through this mask will (ideally) result in pancake shaped buried dopant islands in the substrate.

Although photolithography produced a more reproducible reliable pattern there were additional concerns regarding its use as an implantation mask. Topo-
Figure 6.1: Optical image of photo-resist aperture array used as an implantation mask for experiments.

Figure 6.2: Non-contact AFM topological map of a photo-resist aperture used as an implantation mask for experiments.

graphical maps (Fig. 6.2) obtained with non-contact Atomic Force Microscopy, show that there is unfortunately some variability in the photolithography. Fig. 6.2 shows that the sidewalls of the apertures are not perfectly sharp and may have up to a 30° angle from the surface normal. This means that implanted ions incident on the very edge of the aperture may still penetrate into the sample albeit with a lower energy, having imparted this into the photo-resist, and therefore implant at a shallower depth than ions that pass directly through the aperture. This results in implanted regions that are not completely uniform, and up to half a micron around the implanted spot may contain implanted ions that are closer to the surface compared to the central regions of the spot.

It is also difficult to say with certainty if apertures had completely developed, although aluminium deposition by thermal evaporation through the masks with
subsequent photo-resist lift-off indicates that the developing procedure led to fully developed openings (Fig. 6.3). It is possible however, that a thin photo-resist layer could remain at the bottom of the aperture between the aluminium and sample surface. This is a concern because if a thick enough photo-resist layer is present during implantation it will prevent any ions from being implanted into the sample. However, if it is thin enough the photo-resist will only attenuate the ion beam and result in an implantation that is much shallower than intended. This in turn will lead to an erroneous interpretation of results, this is discussed later along with the data obtained. Monte-carlo simulations with the TRIM package indicate that 15 keV phosphorus ions may be stopped by as little as 30 nm of photo-resist. This however is based on the density and composition of AZ-111 photo-resist built into the TRIM package [3] as the density of the baked photo-resist used is not known.

![Image of aluminium evaporated through photo-resist aperture array](image)

Figure 6.3: Optical image of aluminium evaporated through photo-resist aperture array used as an implantation mask for experiments.

To verify that the ion beam was not attenuated in any way by residual photo-resist, implants were also performed through nickel TEM grids with an array of $2 \times 2 \, \mu m^2$ apertures with a 15 $\mu m$ spacing. These were not used for all implants as the total grid area was relatively small, producing a circular total implanted region with only a 3 mm diameter. This not only made the implanted area on the sample difficult to locate but also lead to less implanted real-estate for further
studies such as annealing and oxide etching studies.

All wafers were mounted with adhesive carbon tape on the implant stage faces of the Australian National University’s Low-Energy Implanter. The chamber was pumped to a base pressure of $5 \times 10^{-7}$ Torr and the cold trap in the chamber was cooled with liquid nitrogen after the pressure fell below $\approx 5 \times 10^{-6}$ Torr.

Samples were implanted with the surface normal parallel to the beam axis, with either 10 keV or 15 keV ions of $^{10}$B, $^{28}$Si, $^{29}$Si or $^{31}$P. The beam was raster scanned over a 2.56 cm$^2$ aperture with a scanned beam current of $\approx 85$ nA corresponding to an ion flux of $\approx 2.1 \times 10^{11}$ cm$^{-2}$s$^{-1}$. The fluences of implants ranged between $1 \times 10^{12}$ cm$^{-2}$ and $1 \times 10^{14}$ cm$^{-2}$.

The photo-resist mask was chemically removed after implantation. Initially, samples were immersed into an acetone ultrasonic bath, followed by an isopropyl alcohol ultrasonic bath for 5 minutes each. It was found from AFM topographic maps that a ring of photo-resist between 5 and 20 nm in thickness where the apertures were often remained. Since the ions may penetrate up to 30 nm of photo-resist, it is postulated that the side walls of apertures are cross-stitched to the sample. In an attempt to remove the photo-resist both chloroform and warm AZ-100 resist stripper were used with limited success. It was found that by far the most effective method for complete photo-resist removal was by using a ‘Piranha’ solution; a 3:1 mixture of 95% sulfuric acid and 42% hydrogen peroxide. This was then followed by two de-ionised water rinses, an isopropyl alcohol rinse, and finally dried with compressed nitrogen. It should be noted that it is quite easy to spot residual photo-resist in KFM maps since it has a different work-function to silicon and silicon dioxide. Residual resist down to a 5 nm thickness was quite easily identified in scans.

Wafers were then cleaved into quarters and treated in various ways. Some were subjected to a rapid thermal anneal under argon flow at 1000°C for 5 seconds, some were subjected to a 5% hydrofluoric acid etch to remove the thermal oxide, while other samples were annealed then also oxide etched. Etch times used were slightly longer than required based on a published etch rate of 23 nm/min [4], a minimum of 15 seconds was used for 5 nm oxides and at least 45 seconds for 15 nm oxides.

Rapid thermal annealing was performed using a Modular Process Technologies RTP-600 furnace in a clean-room environment at the University of Melbourne. Temperature was moderated using a pyrometer situated below a 3-inch silicon support wafer that samples were placed on. In addition, a thermocouple
in thermal contact with the support wafer was used to monitor the temperature below 400°C. The cycle began with the sample chamber being purged with argon for 30 seconds with a 8 l/min flow, the flow was then dropped to 2 l/min prior to temperature ramp up and anneal. To allow for a prompt stabilisation at the desired annealing temperature of 1000°C the furnace was first ramped up to 600°C at a rate of 50°C/s before being ramped up to 1000°C at 100°C/s; the temperature varied by no more than 25°C during the annealling period. Upon the end of the 5 second anneal the argon flow is increased to 8 l/min to aid in the cooling of the sample.

The back face of 5 and 50 nm thick oxide samples were then abraded with 800 grade silicon carbide paper. This was not required for 15 nm samples as they had an aluminium ohmic contact fabricated on the back face prior to implantation. Samples were then mounted with adhesive carbon tape to copper plates for scanning probe analysis with a NT-MDT SMENA system.

Electrically conducting scanning probe tips coated with either tungsten carbide (W2C) or platinum were used. These had a typical cantilever resonant frequency of either 170±10 kHz or 315±15 kHz; studies indicated that neither the tip coating or the cantilever resonance frequency affected the relative surface potentials measured in KFM scans. The height offset of the sample was adjusted in the second pass to maintain a second pass working tip sample separation of 200 nm for KFM unless otherwise stated. To calibrate this the cantilever amplitude was monitored while reducing the tip sample separation, when the amplitude was reduced to zero the change in height from the original position was taken to be the working height and an appropriate offset selected to maintain the desired tip sample separation. Scans were all 512×512 pixels over the maximum scan range of 45×45 μm² and scanned at a speed of 50 μm/s. KFM scans were made once over each area only as subsequent scans show that the scanned area had a modified surface potential as a result of the feedback biases applied during scanning. This appears to be due to charging of the oxide and/or as-grown oxide traps.

6.1.1 Image Analysis

The NT-MDT Nova software was used to analyse KFM results. Typically, images also required slope subtraction although the two pass technique is meant to remove any contributions from the topology to the surface potential. Scan line artifacts were also often present due to particles on the surface of the sample.
or tip wear. Since they were typically a pixel wide it was possible to remove them with the Nova software which smooths or averages these lines out based on surrounding pixel values.

Line profiles taken were exported for plotting in an external plotting program while selective area average surface potential statistics were obtained directly from the Nova software. To determine relative surface potentials only the central region of implanted areas was analysed to determine the average surface potential. The difference between this and the average surface potential of an adjacent un-implanted area was then calculated to be the relative surface potential. Each selected area contained several hundred data points. This was typically repeated over six or more different implanted areas, the average of these was calculated and taken to be the (average) relative surface potential. By selecting specific areas of the data, contaminated regions of the sample could also be avoided. Furthermore, by calculating the relative potentials, issues involving the tip work-function changing from sample to sample and leading to different absolute values for the surface potential was avoided.

6.2 Ion Range and Damage Profiles

Before examining the experimental results, there needs to be some understanding of the structures that are expected to be created however. Prior to the annealing of samples, the ions implanted into the silicon substrate are not expected to contribute to the surface potential since they are yet to be activated as dopants, i.e. they sit on interstitial sites in the lattice and do not donate or accept charge carriers. There will be some small fraction of the implanted ions that will occupy substitutional sites in the as-implanted state which may make a small contribution to the surface potential. It is unclear however if the un-activated implanted ions exist -or indeed whether they can exist- in an ionised charge state. If they are ionised, they will then contribute to the surface potential. It is also unclear what state the ions implanted into the oxide are in, and whether they may also be ionised. In considering this, it is important to know where the implanted ions lie, the ion range profiles were therefore calculated with the Monte-Carlo code TRIM-2003 [3].

The dominant effect we expect from as-implanted samples will be due to damage created by the implanted ions. This may be in the form of: oxide trapped charges ($Q_{ot}$), fixed oxide charges, interface trapped charge, or damage in the
substrate that either directly compensates bulk dopants in the silicon substrate or traps the donor electrons. According to the literature, fixed oxide charges are positively charged, so if present, the surface potential be higher. Since oxide trapped charge and interface charge may take the form of either positive or negative charge, this may either increase or decrease the surface potential respectively. In the case of donor electron trapping we expect the work-function will be larger and therefore the surface potential also will be larger. Since the majority of electron traps in n-type silicon are vacancy related, we expect that the electrons traps should more closely follow the profile of created vacancies and the expected vacancy profiles were calculated with TRIM.

Dopant compensation however, is not expected to be due to direct knock-on of substrate dopants into interstitial positions. If it were a significant contribution, the compensated dopant profile would be expected to follow the profile of the recoiled ions. The concentration of recoiled substrate ions may be up to the order of $10^{21}$ cm$^{-3}$ however only perhaps 10% of these survive Frenkel pair annihilation as noted in Chapter 1. If we then consider that the background dopant concentration is lower than the silicon density by approximately an order of $10^6$ then of the surviving recoiled atoms only a very small fraction of these will be a background dopant.

After annealing however, most of the substrate damage is expected to be annealed away and phosphorus implanted regions in the silicon substrate are expected to produce a region with a smaller work-function, therefore a smaller surface potential. Any boron implanted regions in the silicon substrate are expected to produce a region with a larger work-function and therefore a larger surface potential. As noted in Chapter 1 it is possible that some oxide damage remains after annealing.

Although predictions for the concentrations of implanted ions are expected to be a close match to the actual concentrations generated, it should be noted that the predicted concentrations of created vacancies and recoiled ions from simulations are not expected to match the actual concentration remaining since they do not take defect recombination into account. Only the profiles, trends and relative values are expected to be reflected in experimental results.

### 6.2.1 Species Dependence (5 nm Oxides)

Of all the samples examined in this study, the 5 nm thick oxides are of the most importance for the fabrication of a silicon quantum computer as this is the oxide
thickness in prototype devices. The range profiles for \(1\times10^{14} \text{ cm}^{-2}\) ions implanted through a 5 nm oxide are shown in Fig. 6.4(a). We see that the projected range is well beyond the interface in both cases, 32 nm into the substrate for 10 keV B and 20 nm for 15 keV P representing a true through oxide implant. Although, there is a small fraction of the ions that are implanted into the oxide. The concentration of these however is predicted to increase towards the interface where it reaches \(8 \times 10^{18} \text{ P.cm}^{-3}\) in the case of 15 keV P implants, and \(5 \times 10^{18} \text{ B.cm}^{-3}\) in the case of 10 keV B implants. These are sizable concentrations of ions and if the implanted ions remain ionised will make a significant contribution to the surface potential.

Since many of the electronic defects in the silicon substrate are vacancy related only the predicted vacancy profile will be examined and discussed here. In terms of the damage created, Fig. 6.4(b) shows that, for the implants used, the peak concentration of vacancies is predicted to lie between 15 nm and 25 nm into the sample. Most significantly however is the prediction that the peak concentration created by boron implantation is about a quarter of that for phosphorus and silicon implants. Note that since phosphorus and silicon have a very similar mass, they are expected to produce a similar amount of damage. This implies that any observed difference between implants of the two species must be directly related to the species of ion. Since the majority of damage is located within the silicon substrate one might expect that the effect of implantation on the surface potential to be dominated by changes to the substrate. Also note that the created damage concentration is not enough to amorphise the silicon substrate. This is confirmed by TEM measurements made by other researchers within the research group.

It is possible that if Frenkel pair annihilation in the substrate is far more efficient than defect annihilation in the oxide (due to higher interstitial atom and vacancy diffusion), then more damage may actually remain in the oxide. Furthermore, oxygen recoils that penetrate the silicon substrate will not diffuse back into the oxide and are said to instead form SiO\(_2\) precipitates that cannot be annealed out [5]. The profile of oxygen recoils is discussed later.

### 6.2.2 Variation with Oxide Thickness

Since the density of the oxide (2.21 g.cm\(^{-3}\)) is not far removed from that of the silicon substrate (2.32 g.cm\(^{-3}\)) the range profiles were not found to change significantly with oxide thickness (Fig. 6.5). The effect on implanted ion concentrations
Figure 6.4: TRIM simulations for implants of $1 \times 10^{14}$ ions/cm$^2$ through 5 nm thermal oxide on a silicon substrate. In each case the interface depth is indicated by a vertical line.
in the oxide and in the interface however do vary significantly however. In the case of the 15 nm oxide we now find up to $3.2 \times 10^{19}$ P/cm$^3$ at the interface, while for the 50 nm oxide we have a peak concentration of $3.8 \times 10^{19}$ P/cm$^3$ in the oxide and an interface concentration of only $2 \times 10^{18}$ P/cm$^3$. This is roughly a factor of 4 increase in concentration at the interface in the case of the 15 nm oxide sample and a factor of 4 decrease in the case of the 50 nm oxide sample compared to the 5 nm oxide.

![Graph showing TRIM simulations of ion range for implants of 15 keV P (1 x 10^14 cm^-2) through thermal oxides of various thicknesses on a silicon substrate.](image)

Figure 6.5: TRIM simulations of ion range for implants of 15 keV P (1 x 10^14 cm^-2) through thermal oxides of various thicknesses on a silicon substrate.

For the 50 nm oxide (Fig. 6.6, dash-dotted line) the majority of vacancies are created in the oxide with a concentration of only $2 \times 10^{20}$ vacancies/cm$^3$ at interface. This is two orders of magnitude less damage predicted as compared to the 15 nm sample. So any changes to surface potential of the sample should be related to the bulk oxide and not any interface or silicon substrate related phenomena.

In the case of the 15 nm oxide however there is a significant number of vacancies created in the oxide and at the interface. Fig. 6.6 shows that for phosphorus implants up to $1.2 \times 10^{22}$ vacancies/cm$^3$ are created. This sample is seen as being intermediate between the 5 and 50 nm thick oxide samples where there is a dominance of either substrate or oxide damage respectively, in the case of the 15 nm sample however there is a maximal level of interface damage.
Figure 6.6: TRIM simulations of produced vacancies for implants of 15 keV P (1×10^{14} cm^{-2}) through thermal oxides of various thicknesses on a silicon substrate.

### 6.2.3 Oxygen Recoils

The collisions of the implanted ion with lattice atoms in the oxide can also produce recoiled lattice atoms with enough energy to penetrate into the silicon substrate. Fig. 6.7 shows that a fraction of the oxygen recoils are predicted to penetrate up to 6 nm into the substrate. Although the fraction of the total oxygen recoils created that are predicted to remain in the oxide is much larger, there is never the less a large concentration of oxygen ions that are predicted to stop in the underlying silicon. For the 5 and 15 nm oxide this concentration is on the order of 10^{21} cm^{-3} at the interface but rapidly drops off away from the interface into the sample though a significant amount of oxygen extends up to 6 nm or more into the silicon substrate. It has been shown in the past that the incorporation of large amounts of oxygen in silicon can lead to strain in the lattice and result in SiO_{2} precipitates [5], upon annealing there may even be further growth of a poor quality oxide [6].
Figure 6.7: TRIM simulations for recoiled oxygen atoms due to implants of 15 keV P ($1 \times 10^{14}$ cm$^{-2}$) through thermal oxides of various thicknesses on a silicon substrate.

6.3 Implanted 15 nm Oxides

6.3.1 Species Dependence

The first set of experiments involved 15 keV implants of $^{28}$Si and $^{31}$P into thermally grown 15 nm oxides. These samples were cleaned either in an ultra-sonic chloroform bath or with warm AZ-100 resist stripper (heated to 85°C) in place of a Piranha etch. This was not always effective in removing all the photo-resist around the apertures and sample surfaces were often cleaned with the aid of gentle brushing with cotton cue tips soaked in the solvent used.

Depressions were observed up to 0.5 nm deep over implanted areas (Fig. 6.8a). Given that TRIM simulations show that a large portion of the damage created lies within the oxide this is believed to be due to implantation induced compaction of the oxide [7, 8, 9]. This is not believed to be due to sputtering due to the low sputter yield of approximately 2 atoms per implanted ion predicted by TRIM simulations. Based on the density of the oxide this results in less than an Angstrom of material being sputtered for the highest fluence.

A typical surface potential map obtained with KFM for a 15 keV phosphorus
implanted sample is shown in Fig. 6.8b. Samples implanted with phosphorus ions to a fluence of $1 \times 10^{14}$ cm$^{-2}$ showed an increased average surface potential of 210 mV with a standard deviation of 10 mV. Implanted areas are seen as circular regions of roughly 4 μm diameter where the surface potential is increased with respect to the surrounding un-implanted background. This is larger than the expected aperture size and it is unclear if this effect is due to a reduced contrast and resolution of KFM or due to low aspect ratio photo-resist masks resulting in larger implanted areas. Given the variability of the photolithographic developing process the latter explanation seems more likely.

There are also several explanations for the increased surface potential. Based on the equations in Section 2.3.3 a net positive charge can lead to an increased surface potential. This is plausible since oxide fixed charge is known to be positive; the implanted ions may also be ionised. Interface trapped charge may also be positively charge. It should also be noted that the charge is not expected to be directly due to the implanted ions since they were negatively charged by the ion source. Implantation results in a net negative charge being deposited into the sample which is collected to determine the total dose.

In principle the presence of a net charge should be detectable with Electrostatic Force Microscopy, depending on the sensitivity required. The increased surface potential is also consistent with implantation damage compensating background dopants in the substrate however. Following Eq. 2.32 and Fig. 2.11 a reduction of background n-type dopants leads to an increased semiconductor work-function and increased surface potential. Also, as indicated in TRIM simulations a fraction of the created oxygen recoils are knocked into the silicon substrate and as noted by Zaumseil et al. [5] may form SiO$_2$ precipitates. It is unclear how this
may affect the surface potential however. KFM scans of oxide etched samples, leaving only substrate damage, may shed some light on this.

![Topography and Relative Surface Potential](image)

Figure 6.9: KFM scan of 15 nm thermal oxide on silicon implanted with 15 keV $^{28}$Si ($1 \times 10^{14}$ cm$^{-2}$).

The surface potential map for a silicon implanted sample is shown in Fig. 6.9. An average increased surface potential of 70 mV ($\sigma = 30$ mV) is found for this sample. The profile of the surface potential relative to the un-implanted surroundings of a typical implanted area is shown in Fig. 6.10 along with that for a phosphorus implanted sample.

Although the measured signal from phosphorus implanted samples is a factor of 3 times larger than for silicon implanted samples, the predicted amount of damage for phosphorus implantation is not a factor of 3 times larger. In fact TRIM simulations predict a very similar damage level for the two species (c.f. Fig. 6.4). It is possible that the presence of phosphorus leads to a greater increase in surface potential. This is plausible since phosphorus is more easily ionised than silicon. It should also be noted that measurements of silicon implanted samples were conducted over 3 months after implants were made and there may be some time-dependent effect that reduces the surface potential. This is investigated in the next section.

### 6.3.2 Degradation over time

After a period of over one year a phosphorus implanted sample was cleaned with iso-propanol, dried with compressed nitrogen and scanned with KFM.
Curiously the implanted areas of these samples also now show an increased height in the topography. Since there is no applied bias to the tip it is not expected for the change in height observed in topographic scans to be due to electrostatic effects. It may be possible that the compacted oxide has annealed over time and that the swelling is now due to substrate damage. There have indeed been reports of room temperature annealing affects over periods as short as three months \cite{10}, and this is also consistent with the effects of thermal annealing on oxides \cite{11}.

Furthermore, the increase in height is unlikely to be due to any organic substance on the surface since samples that were subjected to a Piranha solution clean reveal the same features (See Fig. 6.12).

The surface potential of the sample can also be seen in Fig. 6.11b to now show a reduced surface potential of \(\approx 60\, \text{mV}\). It is unclear why the surface potential has changed over time. For reasons that will become apparent in the next section it is not believed to be due to the annealing of damage in the oxide. However, since samples were not stored, cleaned or measured in a clean-room environment, it is possible that implanted areas have gettered negative ions such chlorine. It should be noted that many of the initial measurements of samples were performed over a period of 6 months after implantation yet still showed an increased surface potential. The photo-resist apertures in those cases were not stripped until immediately prior to measurements suggesting that the photo-resist protects samples
Figure 6.11: Kelvin-probe scans of 15 nm thermal oxide on silicon implanted with 15 keV P ($1 \times 10^{14}$ cm$^{-2}$) repeated one year after original scans.
Figure 6.12: Kelvin-probe scans of 15 nm thermal oxide on silicon implanted with 15 keV P (1 × 10^{14} cm^{-2}) cleaned with Piranha solution one year after implantation.

from contamination.

6.3.3 Effect of Photo-resist Mask

As discussed earlier, there was some concern that if photo-resist masks were not fully developed the ion ranges would be attenuated leading to shallower implants. To address this issue both phosphorus and silicon implants were repeated through nickel grid apertures to determine if the photo-resist apertures had affected the implantation in any way. Silicon implants were now performed with silicon-29 ions and the beam was raster scanned over a 2.56 cm² grid metallic holder that held four grids and was in direct contact with the sample surface. The scanned beam current used for silicon implants was $\approx 100$ nA corresponding to an ion flux of $2.4 \times 10^{11}$ cm$^{-2}$s$^{-1}$, while only a 70–75 nA scanned beam current was obtained for phosphorus implants, this corresponded to an ion flux of $\approx 1.8 \times 10^{11}$ cm$^{-2}$s$^{-1}$. Since there was no photo-resist to remove samples were only cleaned with acetone and iso-propanol prior to KFM scanning.

Results shown in Fig. 6.13 & 6.14 reveal that there is still an increased surface potential over implanted areas as previously observed. Phosphorus implanted samples to a fluence of $1 \times 10^{14}$ cm$^{-2}$ show an increase of $\approx 60$ mV, however the silicon implanted sample implanted to the same fluence curiously shows a much larger increase in surface potential of $\approx 110$ mV. This perhaps suggests a flux dependence. Given that these implant areas and shapes are different these values are not expected to match those previously obtained from implants through photo-resist apertures however.
The silicon implanted sample also shows an increase in the topography of the implanted area of $\approx$1-2 nm while the phosphorus implanted sample shows increase in topography of up to 1 nm. It is unclear why there is a difference between the two samples. This difference in the amount of swelling would not appear to be related to ion damage given that TRIM simulations predict that both ions lead to very similar damage levels. Although TRIM simulations do not take any flux dependence into account, damage to the silicon substrate is expected to be reduced as the flux is increased. This means that the silicon implanted samples, which were implanted at a higher flux, should show less substrate silicon damage. It is however unclear how the flux affects the oxide damage levels.

![Topography](image1.png)

(a) Topography

![Relative Surface Potential](image2.png)

(b) Relative Surface Potential

Figure 6.13: Kelvin-probe scans of 15 nm thermal oxide on silicon implanted with 15 keV $^{29}$Si ($1 \times 10^{14}$ cm$^{-2}$) implanted through a Ni-grid mask.

It is unclear why there is now swelling observed over the implanted area rather than depressions as observed with photo-resist masked samples. Perhaps the fact that the apertures are smaller and further apart has some effect. It is not completely surprising for an irradiated oxide to undergo swelling rather than compaction as this effect has been known for some time [12]. These results however, may suggest that the level of oxide swelling has a flux dependence. A
comprehensive study of this effect is beyond the scope of this work.

It is also possible that the increase in height is not due to swelling of the sample at all, but due to greater carbon stitching as a result of the implantation. Although, it is unclear why this was not also observed in the original set of samples, nor is it clear why there should be more in the case of a silicon implant. Furthermore, the amount of carbon stitching should be very low since the chamber is pumped down to a base pressure of $5 \times 10^{-7}$ Torr and a copper cold trap is used in the implant chamber. If this is the case however, the presence of cross-stitched carbon will affect the surface potential. A complementary technique such as X-ray induced Photo-electron Spectroscopy would be required to examine the surface of as-implanted samples to test this hypothesis.

![image](image.png)

Figure 6.14: Kelvin-probe scans of 15 nm thermal oxide on silicon implanted with 15 keV P ($1 \times 10^{14}$ cm$^{-2}$) implanted through a Ni-grid mask.

Since piranha solution cleaning can also remove any carbon that has been stitched to the surface, samples were therefore examined after Piranha solution cleaning was performed. It should be noted that it was not known at the time that surface potentials of samples changed over time and this experiment was performed 3 months after original measurements. Results for phosphorus implanted samples (Fig. 6.15) now show a decrease of $\approx 25$ mV in surface potential. However, silicon implanted samples still show an increased surface potential over implanted areas of $\approx 25$ mV. Note that there is now no change observed in the topography of the implanted areas however.

It would seem that the surface potential is reduced by a fixed amount of 80 mV. It is unclear however, if it is the period of time or the Piranha solution that is the cause of this effect. These results are completely consistent with what was found in photo-resist masked samples examined one year after implantation
without Piranha solution cleaning. It is possible that over the period of just 3 months implanted areas have gettered negative ions which reduce the surface potential. It is again also possible that there has been some room temperature annealing of the oxide that has reduced sample swelling. Alternatively it may be that there was carbon stitching to the surface of the sample and that this is now removed by the Piranha solution.

Unfortunately, these samples were not examined prior to Piranha solution cleaning three months after initial scanning to verify this. To resolve this issue either Piranha solution cleaning would need to be performed immediately after implantation or samples would need to be re-examined 3 months after implantation without Piranha cleaning.

![Image](image_url)

(a) Topography

![Image](image_url)

(b) Relative Surface Potential

Figure 6.15: Kelvin-probe scans of 15 nm thermal oxide on silicon implanted with 15 keV P\((1 \times 10^{14} \text{ cm}^{-2})\) implanted through a Ni-grid mask then cleaned in a Piranha solution.

### 6.3.4 Oxide Removal

A HF etching experiment of the photo-resist masked samples was conducted on a sample implanted with 15 keV silicon to a fluence of \(1 \times 10^{12} \text{ cm}^{-2}\) which, like samples implanted to \(1 \times 10^{14} \text{ cm}^{-2}\), showed an increased surface potential. After oxide etching the sample now shows a reduced surface potential (Fig. 6.17). The
Figure 6.16: Kelvin-probe scans of 15 nm thermal oxide on silicon implanted with 15 keV $^{28}$Si ($1 \times 10^{14}$ cm$^{-2}$) implanted through a Ni-grid mask then cleaned in a Piranha solution.
average relative surface potential of implanted areas was found to be -53 mV with a standard deviation of 2 mV. Note also that there is no change in the topography of the substrate for implants of such low fluence. This is contradictory to the expectation of the implanted areas having compensated donors which would result in an increased surface potential.

Unfortunately, this experiment was performed six months after implantation and there is a question mark over whether this is a true representation of the surface potential of the substrate directly after implantation. If indeed the reduction is due to the gettering of impurities into implanted areas as suggested before, these measurements suggest that they are in fact gettering into the substrate. If this is not the case then this result suggests that implantation damage to the substrate results in a reduced surface potential. This is further examined in Section 6.5 by examining implants into 5 nm oxides. Furthermore, if changes to the surface potentials add linearly, then it also suggests that the increased surface potential observed before oxide removal is due to something other than the silicon substrate. Namely, the oxide, oxide interface or the oxide surface.

6.3.5 Effect of Annealing

Phosphorus implanted samples were annealed in argon at 1000°C for 5 seconds, again some 6 months after initial scans were made. Silicon implanted samples however were annealed within a week of initial scanning. These samples were not oxide etched or cleaned in a Piranha solution.

Results for phosphorus implanted samples show that there is a reduction in the surface potential of implanted areas but that there is still a net increase. Annealed P implanted samples, to a fluence of $10^{14}$ cm$^{-2}$, still show an average increase in surface potential over implanted areas of 80 mV with a standard deviation of 15 mV (Fig. 6.18). The 1000°C anneal is expected to activate the majority of implanted P resulting in a decreased substrate work-function, which according to Eq. 2.28 will result in a reduced surface potential over the implanted area. This is again at odds with our observations, but it should be noted that since the oxide is still present, it may be affecting the surface potential.

To determine if there is a contribution to the surface potential due to residual damage after annealing, silicon implanted samples were also annealed and examined. If indeed the implanted phosphorus has been activated in the substrate and its effect of decreasing the surface potential is a linear superposition with something else that increases the surface potential, then an annealed silicon
Figure 6.17: Kelvin-probe scans of 15 nm thermal oxide on silicon implanted with 15 keV $^{28}$Si ($1 \times 10^{12}$ cm$^{-2}$) after the oxide has been stripped off, examined six months after original scans.
implanted sample should reveal areas that have an even greater increase in the surface potential since there is no n-type doping to reduce it. However, areas implanted with silicon also show an increased relative surface potential after annealing (Fig. 6.19), but the change in surface potential is less than in the case of phosphorus implanted samples.

This may suggest that either separate influences on the surface potential do not add linearly or that phosphorus in the oxide may be involved in some chemical effect that increases the surface potential.

That there is still an increase in the surface potential indicates that implantation damage is not completely annealed out whether there is phosphorus present or not. This may be related to the amount of oxygen recoiled into the substrate and the formation of SiO₂ precipitates or perhaps the oxygen deficient oxide. Oxygen can also act as an acceptor in silicon which would lead to an increased surface potential. The concentration of oxygen predicted by TRIM in Fig. 6.7 is certainly high enough to compensate and perhaps even produce a very thin p-type region if this were the case. It is also possible that if any impurities were gettered into the sample that these could have been thermally activated.
Figure 6.19: Plot of the relative surface potential for 1000°C 5 sec annealed and un-annealed 15 nm oxides on silicon implanted with 15 keV $^{28}$Si to a fluence of $1 \times 10^{14}$ cm$^{-2}$. A FFT smoothed fit of the data is shown as a line to guide the eye.

6.3.6 Fluence dependence

The fluence dependence of the effect of implantation on 15 nm thick oxides on silicon was also briefly examined. Topographical maps of samples implanted with 15 keV phosphorus show a highly uniform surface up to a fluence of $1 \times 10^{13}$ cm$^{-2}$. It is only an implant fluence of $1 \times 10^{14}$ cm$^{-2}$ that resulted in depressions in the surface (see Fig. 6.8).

Typical profiles of the relative surface potential for samples implanted with 15 keV phosphorus with fluences in the range $1 \times 10^{12} - 1 \times 10^{14}$ cm$^{-2}$ are shown in Fig. 6.20. We see that the surface potential increases between $1 \times 10^{12} - 1 \times 10^{13}$ cm$^{-2}$, but interestingly the higher $1 \times 10^{14}$ cm$^{-2}$ fluence implanted sample shows roughly half the increase measured in the $1 \times 10^{13}$ cm$^{-2}$ sample.

This behaviour may be related to onset of oxide compaction, however it is also consistent with the fluence dependence of E' defect centres in the oxide as discussed in Chapter 1. Since the E' centre is positively charged it is also consistent with the observation of an increased surface potential. The fluence dependence of the surface potential might also be explained however by the interface damage reaching a maximum after implantation with a fluence of $1 \times 10^{13}$ cm$^{-2}$ where it is completely disordered. The concentration of interface traps has in fact been
Figure 6.20: Change in surface potential profiles over 15 keV P implanted disks in 15 nm SiO₂/Si layers relative to surrounding un-implanted areas for implants of various fluences. A tip sample separation of 200 nm was used for each case. A FFT smoothed fit of the data is shown as a line to guide the eye.

previously shown to saturate at a fluence of 1×10¹³ cm⁻² by Bota et al. [13]. Damage to the silicon substrate however can continue to increase since a fluence of 1×10¹⁴ 15 keV phosphorus does not create enough damage to amorphise the crystalline silicon. The effect from substrate damage may then dominate and begin to reduce the surface potential. This relies on the substrate damage resulting in a reduced surface potential and this is examine later in Section 6.5.
6.4 Implanted 50 nm Oxides

In order to investigate the effect of implantation on only the oxide, implants were made into thicker 50 nm oxides. To enable results to be directly compared to results obtained from 15 nm oxides the implant energy and fluence was kept the same. It should be noted that these 50 nm samples were subjected to a forming gas passivation anneal prior to implantation however.

The results from implants of silicon and phosphorus implants are shown in Fig. 6.21, 6.22 & 6.23. Once again there is some evidence for depressions in the sample surfaces although surfaces are rather dirty. It is a little surprising that the depressions are shallower than found in implanted 15 nm oxides given that a higher level of oxide damage is predicted from TRIM simulations (Fig. 6.6).

KFM scans show that a reduced surface potential is now observed over implanted areas. For silicon implanted samples to a fluence of $1 \times 10^{14}$ cm$^{-2}$ the average reduction in surface potential was 26 mV ($\sigma = 3$ mV) (Fig. 6.21), while for $1 \times 10^{14}$ P an average reduction of 21 mV ($\sigma = 2$ mV) was observed (Fig. 6.22).

![Figure 6.21: Surface potential map of 50 nm thermal oxide on silicon implanted with 15 keV $^{29}$Si ($1 \times 10^{14}$ cm$^{-2}$).](image)

Given that TRIM simulations predict that almost all of the damage and ions stop in the oxide, this would imply that implantation damage to the oxide results in a decrease in surface potential. If indeed these changes are due to oxide charges, then to produce a reduction in the surface potential there must be a net negative charge in the oxide. This however goes against the majority of literature that indicates that oxide damage consists mostly of positive fixed oxide charge. Regardless of the cause, a reduced surface potential observed in these samples indicates that the increased surface potential observed for implanted
Figure 6.22: Surface potential map of 50 nm thermal oxide on silicon implanted with 15 keV P ($1 \times 10^{14}$ cm$^{-2}$).

Figure 6.23: Plot of the relative surface potentials of 50 nm thermal oxide on silicon implanted with either Si or P to a fluence of $1 \times 10^{14}$ ions/cm$^{-2}$. A FFT smoothed fit of the data is shown as a line to guide the eye.
15 nm oxides is unlikely to be due to an oxide related effect and is due to either the interface or the substrate.

The slight difference in the signal between phosphorus and silicon implanted samples might be once again due to photo-resist apertures not being fully developed and attenuating the number of ions into the oxide. This would have resulted in less damage and therefore a smaller reduction in surface potential. However, this is also consistent with results from the previous section which showed that phosphorus implanted samples had a higher surface potential than silicon implanted samples.

6.4.1 Effect of Annealing

Six months after initial measurements these samples were subjected to a rapid thermal anneal at 1000°C for 5 seconds. Both phosphorus and silicon implanted 50 nm oxides now show a decrease in the surface potential of ≈45 mV (Fig. 6.24 & 6.25). Although it should be noted that most scans of the silicon implanted chip revealed no change to the surface potential consistent with the mask pattern, this could be the result of it being difficult to position the probe over the implanted region of the sample. To the best of my knowledge however this is not the case. Both samples also show an increase in the topography over implanted areas of up to 1 nm. This is not a uniform increase in height over the implanted areas however and the averages may be only 0.1-0.5 nm.

![Topography and Relative Surface Potential](image)

Figure 6.24: Surface potential map of 50 nm thermal oxide on silicon implanted with 15 keV $^{29}$Si ($1 \times 10^{14}$ cm$^{-2}$) after rapid thermal annealing at 1000°C for 5 seconds.

This residual sample swelling is most likely due to a swelling of the oxide. It is not expected to be due to a swelling of the silicon substrate since TRIM
Figure 6.25: Surface potential map of 50 nm thermal oxide on silicon implanted with 15 keV P ($1 \times 10^{14}$ cm$^{-2}$) after rapid thermal annealing at 1000°C for 5 seconds.

Simulations predict that there is little damage produced in the substrate. It is possible the oxide was damaged to such a degree that it cannot be repaired with the anneal used and that perhaps a different stoichiometry or structure with a lower density results.

The fact that there is still a reduction in the surface potential over implanted areas observed after annealing also suggests that the anneal used is not sufficient to repair the implantation damage for the implants. This is consistent with the literature which suggests that oxide damage requires anneals up to 1100°C to remove all the implantation damage (c.f. Chapter 1). It is a little suspicious however that the surface potential of the implanted area has in fact reduced even further after annealing. Given that the anneal was performed some six months after initial measurements this observation may suggest that there are impurities getterted into the sample that lead to a reduced surface potential.

This also indicates that neither the presence of phosphorus or residual oxide damage can be responsible for the residual increase in surface potential observed in implanted and annealed 15 nm thick oxide samples. Although, it should be noted that since all the ions stop in the oxide in the case of 50 nm thick oxides, that there is a larger amount of damage to the oxide in comparison with implants of the same fluence in 5 nm and 15 nm oxides and the case may be different for those samples.
6.5 Implanted 5 nm Oxides

6.5.1 Species Dependence

In 5 nm thick oxide samples, it was found that often there was a small increase (up to 1 nm) in height over implanted regions (Fig. 6.26a). This is presumed to be due to damage in the silicon substrate, possibly due to formation of small amorphous regions since amorphous silicon has a lower density than its crystalline form. It should be noted that TEM measurements conducted by other researchers within the group show that the 15 keV phosphorus implants do not create a continuous amorphous region in the silicon substrate. In any case, that there is a high level of damage and optical microscope images support this by revealing that the implanted regions have a different reflectivity (Fig. 6.27). Since this is a damage related effect, similar reflectivity variations were observed for both silicon and phosphorus implanted samples. There were no topographic or optical changes found (nor expected) in boron implanted samples due to the comparatively small amount of damage associated with boron implantations.

Since the bulk of the damage is expected to be in the substrate it is highly unlikely, although possible that the oxide has swollen [12]. Oxide etching experiments discussed later will shed some light on this. Given that samples were coated with photo-resist, it is also possible that the apertures did not fully develop and that some of this was cross-stitched to the surface. The Piranha solution cleaning should have easily removed this however.

A typical surface potential map obtained with KFM for a 5 nm thick oxide implanted with 15 keV phosphorus to a fluence of $1 \times 10^{14}$ cm$^{-2}$ is shown in Fig. 6.26. Implanted areas can be seen as circular regions of $\approx 3 \mu m$ diameter where the surface potential is decreased by an average of 33 mV ($\sigma = 2$ mV). The KFM scans obtained from silicon implanted samples implanted to the same fluence are shown in Fig. 6.28; these show a reduction in the surface potential of 24 mV ($\sigma = 3$ mV). Scans of boron implanted samples are shown in Fig. 6.29; these led to a 7 mV ($\sigma = 3$ mV) reduction in the surface potential. Typical line profiles of the surface potential over implanted areas relative to un-implanted areas are shown in Fig. 6.30.

We can clearly see from Fig. 6.30 that as the mass of the ion is increased there is a commensurate decrease in the relative surface potential. The amount that the surface potential is reduced by appears to be directly related to the
Figure 6.26: KFM surface potential map of 5 nm thermal oxide on silicon implanted with 15 keV P to a fluence of $1 \times 10^{14}$ ions/cm$^2$.

Figure 6.27: False colour optical image of 15 keV Si ($1 \times 10^{14}$ cm$^{-2}$) implanted 5 nm thermal oxide on silicon.
Figure 6.28: KFM map of 5 nm thermal oxide on silicon implanted with 15 keV $^{29}$Si to a fluence of $1 \times 10^{14}$ ions/cm$^2$. Inset square to highlight region with raised topography.

Figure 6.29: KFM map of 5 nm thermal oxide on silicon implanted with 10 keV $^{10}$B to a fluence of $1 \times 10^{14}$ ions/cm$^2$. 
Figure 6.30: Plot of the relative surface potentials of 5 nm thermal oxide on silicon implanted with either B, Si, or P to a fluence of $1 \times 10^{14}$ ions/cm$^{-2}$. A FFT smoothed fit of the data is shown as a line to guide the eye.

amount of damage created given that heavier ions produce more damage.

There are no chemical effects expected in these samples since almost all of the ions are implanted into the substrate where there is little chemical interaction with silicon. These implanted ions will mostly reside in interstitial positions and in the case of phosphorus and boron, they will only act as dopants when thermally activated by annealing. According to TRIM simulations (Fig. 6.5) there is still an implanted phosphorus concentration of up to $1 \times 10^{18}$ cm$^{-3}$ predicted to be implanted into the oxide. This is a relatively high concentration of ions although the total number of ions is much less than what is implanted into the substrate. As seen in the previous section implantation into the oxide also leads to a reduction in surface potential.

Although simulations predict that the majority of damage is to the substrate silicon, the reduction in surface potential is not consistent with implantation damage compensating the background dopants in the substrate. A reduction of background n-type dopants should lead to an increased semiconductor work-function and therefore an increased surface potential following Eq. 2.32 and Fig. 2.11.

Based on the background provided in Section 2.3.3, if the observed reduction in surface potential is due to charge in the sample it must be a net negative charge. This is plausible since the dominant bulk silicon trap is the di-vacancy which as noted in Section 1.1.1 is known to be negatively charged when electrons
are trapped by it. It should also be noted that due to the high fluence of implants higher order clusters (triple vacancies or larger, interstitial clusters) may also have formed. If the reduction in surface potential is indeed due to charge this should in principle be detectable with Electrostatic Force Microscopy. Although, the traps may be too rapidly emptied if the electric fields created are too high. HF etching of as-implanted samples to leave only the substrate may shed some light on this.

Also, as with the implants into 15 nm oxides, TRIM simulations predict that a fraction of the created oxygen recoils are knocked into the silicon substrate and may form SiO$_2$ precipitates which may affect the surface potential. HF etching of as-implanted samples to leave only the substrate may also shed some light on this.

### 6.5.2 Oxide Removal

To eliminate any contribution from the oxide, oxide interface or oxide surface on the surface potential, the samples were examined after oxide etching with hydrofluoric acid. Unfortunately, it was not known at the time that the surface potential of samples reduced over time and experiments were conducted 6 months after initial measurements. Results for phosphorus implanted samples are shown in Fig. 6.31, silicon implanted samples in Fig. 6.32.

![Figure 6.31: Kelvin-probe scans of a oxide etched 5 nm oxides on silicon that was implanted with 15 keV P to a fluence of 1×10$^{14}$ cm$^{-2}$.](image)

The topography in each case shows that implanted areas have sections that are raised by up to 1.5 nm. This is most likely due to formation of amorphous zones which are less dense and hence lead to swelling in the implanted region. Note also that the phosphorus implanted sample seems to also show depressions up to 0.5 nm deep in the sample surface. It is possible that this is the result of
Figure 6.32: Kelvin-probe scans of oxide etched 5 nm oxides on silicon that was implanted with 15 keV $^{29}$Si to a fluence of $1 \times 10^{14}$ cm$^{-2}$. 
the acid etching away regions where the oxygen recoils have formed SiO$_2$ precipitates or even a continuous layer. Although, this was not observed in 15 nm thick oxide samples where it is predicted that there is a higher concentration of oxygen recoils knocked into the silicon substrate.

The surface potential in each sample still clearly shows a reduced surface potential. The surface potential is however much lower than in initial measurements where the oxide is intact; phosphorus implanted samples now show up to a 200 mV reduction in the surface potential while silicon implanted samples show up to a 150 mV reduction. The implanted areas however do not show a uniform reduction and implanted areas that exhibit a raised topography have a surface potential that is between 50-100 mV higher than implanted areas that do not.

Importantly, these results show that when the oxide is removed and only damage to the substrate remains, a reduced surface potential is observed. This implies that it is not just damage to the oxide (as observed in the previous section) that led to a reduced surface potential in as-implanted samples. This again may be the result of the sample gettering impurities over the six month period after initial scanning and a repeat experiment is required to test this.

Results suggest that either the oxide or oxide interface is responsible for increasing the surface potential. Given that results from implanted 50 nm oxides show that oxide damage leads to a lower surface potential, this suggest that the oxide interface is responsible for an increased surface potential. This is also consistent with implanted 15 nm oxides given that TRIM predicted that there is a large concentration of damage at the interface in these samples and also supports the claim that the raised areas observed in these samples are in fact where the oxide is still intact.

### 6.5.3 Effect of Photo-resist Mask

As was previously discussed for 15 nm oxides in Section 6.3.3 both phosphorus and silicon implantation was repeated through nickel grid apertures into these 5 nm samples to determine if the photo-resist apertures had affected the implantation in any way. As previously, the beam was raster scanned over a 2.56 cm$^2$ grid metallic holder that held four grids and was in direct contact with the sample surface. The scanned beam current used for silicon implants was $\approx$100 nA corresponding to an ion flux of $\approx$2.4$\times$10$^{11}$ cm$^{-2}$s$^{-1}$, while only a 70–75 nA scanned beam current was obtained for phosphorus implants, this corresponded to an ion flux of $\approx$1.8$\times$10$^{11}$ cm$^{-2}$s$^{-1}$. Since there was no photo-resist to remove samples
were only cleaned with acetone and iso-propanol.

![Image](image_url)

(a) Topography 
(b) Relative Surface Potential

Figure 6.33: Kelvin-probe scans of 5 nm thermal oxide on silicon implanted with 15 keV P (1×10^{14} cm^{-2}) implanted through a Ni-grid mask.

Results show that samples now show an increased surface potential rather than a reduced surface potential observed in photo-resist masked samples. Phosphorus implanted samples to a fluence of 1×10^{14} cm^{-2} show an increase in the range 35-60 mV, however as observed in the 15 nm oxides implanted through a nickel grid, the silicon implanted sample implanted to the same fluence shows a larger increase in surface potential of ≈75 mV.

Based on results for the 15 nm implanted oxides in Section 6.3.3, for the 5 nm oxide the the silicon implanted sample not surprisingly also shows an increase in the topography of the implanted area of 2-3 nm, slightly more than observed for the 15 nm oxides. Note that phosphorus implanted samples show no increase in the topography. As discussed earlier in the case of the 15 nm oxides the difference between the topography of silicon and phosphorus implanted samples may be due to a flux dependence, although TRIM (which doesn’t take flux dependence into account) predicts that silicon and phosphorus implants are expected to produce very similar levels of damage. This flux dependence however is not consistent with a higher flux leading to a reduced amount of damage since denser damage cascades are expected to result in more efficient defect annihilation. Carbon stitching is also suggested as a possible cause of an increased surface topography.

Although the increase in surface potential here disagrees with results from photo-resist masked samples, this may be due to the fact that these samples were not subjected to a Piranha solution clean. Three months after initial measurements were made, the samples were cleaned with Piranha solution and re-examined.

No increase in the topography of the implanted areas in either sample is
Figure 6.34: Kelvin-probe scans of 5 nm thermal oxide on silicon implanted with 15 keV $^{28}$Si ($1 \times 10^{14}$ cm$^{-2}$) implanted through a Ni-grid mask.
observed now (See Fig. 6.35a, 6.36a). Furthermore, both samples now show a 10 mV reduction in surface potential (Fig. 6.35b & 6.36b).

Since cleaning in a Piranha solution is expected to completely remove any carbon based substances present these results are consistent with the postulate that carbon stitching was responsible for the change in topography observed. Although as discussed earlier, it is possible that there is also a reduction in surface potential over the 3 month period. It is therefore unclear if these results really do support those obtained from photo-resist masked samples. Piranha etching of samples implanted through nickel grid masks would need to be conducted directly after implantation to confirm results.

![Image] Figure 6.35: Kelvin-probe scans of 5 nm thermal oxide on silicon implanted with 15 keV P (1×10^{14} cm^{-2}) implanted through a Ni-grid mask and subjected to a Piranha solution clean.

### 6.5.4 Activation Annealing

Thermal annealing is expected to repair implantation damage as well as to activate implanted dopants. After annealing samples, the back face was re-abraded in the event that an additional oxide layer was formed. Although this would be unlikely given that samples were placed face up during annealing, were only at elevated temperatures for a few minutes at most and annealing was performed in an argon ambient.

Since the annealing of silicon implanted samples is not expected to produce a change to the electronic structure of the silicon substrate, no difference in the surface potential is expected between implanted and un-implanted regions after annealing. This is confirmed by results. However, there was some inconsistency
Figure 6.36: Kelvin-probe scans of 5 nm thermal oxide on silicon implanted with 15 keV $^{29}$Si ($1 \times 10^{14}$ cm$^{-2}$) implanted through a Ni-grid mask and subjected to a Piranha solution clean.
found with the surface potentials of implanted areas, and in some sectors an increase of up to 30 mV was observed (Fig. 6.37). Any difference between implanted and un-implanted material should be due to implantation damage alone, which suggest that this is the result of there being more damage in these areas and that it is not annealed out. This variation over the sample may have been due to incomplete photolithography leaving undeveloped resist at the bottom of the aperture in these areas, which in turn attenuated the ion beam and resulted in more ions stopping at the interface and creating more interface damage. Since samples were Piranha etched prior to annealing it is not expected to be due to a dirty surface. It is also not believed to be due to more oxide damage since this was previously shown to result in a reduced surface potential. As indicated earlier any residual change may also be the result of SiO₂ precipitates in the substrate or interface damage.

As expected, boron implanted samples show an increased surface potential (Fig. 6.38a) due to the increased work function. The measured relative surface potential of up to 80 mV however is much smaller than estimates provided in section 2.3.2. This was also observed by Henning et al. [14] who identified several possible causes including stray capacitance contributions from the cantilever, surface contamination, oxide charges and interface states. As discussed in the previous section, if there is a reduction in the surface potential due to charge, it implies the presence of negative charge states. It is also possible that the anneal did not fully activate the boron dopants. Jacobs et al. [15] have also shown that higher tip sample separations and other tip sample geometries will affect the stray capacitances and reduce the resolution and contrast obtained in measurements.

![Figure 6.37: Relative surface potential map of a 5 nm oxide on silicon that was implanted with 15 keV ²⁹Si to a fluence of 1×10¹⁴ cm⁻² annealed at 1000°C for 5 seconds.](image-url)
Figure 6.38: 5 nm oxide on silicon implanted with 10 keV $^{10}$B to a fluence of $1 \times 10^{14}$ cm$^{-2}$ and annealed at 1000°C 5 sec annealed.

Figure 6.39: Relative surface potential map of a 5 nm oxide on silicon that was implanted with 15 keV P to a fluence of $1 \times 10^{14}$ cm$^{-2}$ annealed at 1000°C for 5 seconds.

Phosphorus implanted samples, like silicon implanted samples mostly showed no change to the surface potential. Also, like silicon implanted samples some scans revealed an increased surface potential, in this case up to 50 mV (Fig. 6.39). This variability is again attributed to incomplete photo-resist development leading to increased damage over implanted areas.

The failure to observe a reduced surface potential however is in contrast to our expectations after phosphorus activation to create an n$^+$ region (c.f. Section 2.3.2). It is possible that un-annealed damage contributes to increasing the surface potential leaving no change to the surface potential over most areas, and in some areas where there is more damage, an increased surface potential. This is unlikely since silicon implantation should have consistently resulted in an increased surface potential if this were the case. That is, because silicon implantation is
expected to produce the same amount of damage as phosphorus implantation without the decrease in surface potential associated with donor activation. This suggests that there is another mechanism for suppressing the expected surface potential reduction. For example, it may be that there are defects present that only interact with phosphorus, although if this were the case they should also interact with the background phosphorus dopants in the silicon implanted samples. It was also believed that the oxide perhaps affects the activated dopants in some way and oxide etching experiments were conducted to examine this.

Oxide Removal

HF etching was performed on the annealed samples to remove the oxide and any effect it may have on the surface potential. Unlike earlier oxide etching experiments however, these were conducted within a few weeks of the initial experiments.

Experiments reveal that silicon implanted samples do not show any change to the surface potential in a pattern consistent with the implant mask after the oxide is removed from an annealed sample. In the case of phosphorus implanted samples however, they now consistently show a reduced surface potential over implanted areas (Fig. 6.40 & 6.41, blue squares) as expected from an increase in Fermi energy due to activated dopants. This seems to confirm that the oxide or interface is somehow responsible for increasing the surface potential in samples or compensating activated dopants. But, it is unclear why no effect is observed in silicon implanted samples.

Note however that the topography shows a non-uniform increase in height over the implanted areas. As with previous oxide etched samples this may be due to un-etched oxide. However, if this is the case it is unclear why the surface potential is different now.

Like the magnitude of the shift in surface potential for annealed boron implanted samples, the average relative surface potential of -40 mV again has a magnitude less than what might be expected based on estimates shown in Section 2.3.2. This would seem to indicate either incomplete activation or other factors increasing the measured surface potential from an estimated change of hundreds of milli-Volts. Since the relative surface potential is now higher than expected compared to the case of boron implanted samples where it was lower,
Figure 6.40: Kelvin-probe scans of an annealed 5 nm oxide on silicon implanted with 15 keV P to a fluence of $1 \times 10^{14}$ cm$^{-2}$ after oxide etching.
Figure 6.41: Plot of the relative surface potential for 1000°C 5 sec annealed HF etched and un-etched 5 nm oxides on silicon implanted with 15 keV P to a fluence of $1 \times 10^{14}$ cm$^{-2}$. A FFT smoothed fit of the data is shown as a line to guide the eye. A FFT smoothed fit of the data is shown as a line to guide the eye.

...this points towards a reduced contrast in surface potential as a result of factors relating to the geometry and stray capacitance of the tip and cantilever as outlined by Jacobs et al. [15]. In essence the surface potential we measure isn’t the true surface potential since we are performing the measurement at a tip sample separation of 200 nm. This effect is briefly examined in Section 6.6.

HF etching experiments were also performed on boron implanted samples for completion. Results show very little if any change in the relative surface potential (Fig. 6.42) compared to the sample prior to oxide etching. This would indicate that there was little residual damage in annealed boron implanted samples compared to phosphorus implanted samples as has been shown in the literature before [16]. Note also that there is a slightly increased height over implanted spots. It is likely that the substrate has swollen, although the level of substrate damage is expected to be much less than in phosphorus or silicon implanted samples.

Although some care was taken to measure samples promptly after etching, it should be noted that there is some question about the reliability of the surface termination and quality of the native oxide that may regrow before measurement. Though if there is a uniform effect, this should not affect the relative surface potentials of implanted and un-implanted regions. The concern is if an implanted area leads to a different surface termination or formation of SiO$_2$ precipitates.
Figure 6.42: Kelvin-probe scans of a 5 nm oxide on silicon implanted with 10 keV $^{10}$B to a fluence of $1 \times 10^{14}$ cm$^{-2}$, annealed at 1000°C for 5 seconds and then oxide etched with 5% hydrofluoric acid.

6.6 Variation with tip-scanning height

Samples were also scanned at different tip sample separations. Presented in Fig. 6.43 are relative surface potentials of implanted areas of 15 nm thick oxides on silicon implanted with 15 keV phosphorus to various fluences. The results of measurements were averaged and twice the standard deviation taken as the error. Fig. 6.43 clearly shows that scanning closer to the sample leads to a higher measured relative surface potential. This is to say that there is a higher contrast near the surface since the difference between an un-implanted area and implanted area is larger. This supports results previously presented by Jacobs et al. [15].

It was originally hoped that the changes in potential with height could be fitted to analytical equations describing the expected change due to a net charge. If so, the charge concentration could then be calculated. The attempts at determining an analytical equation for the system are presented in the next section.

6.7 Effect of net Charge on KFM

During the course of this research it was postulated that any observed change in surface potential might be due to buried charge in the sample. Indeed it is known that defects in the oxide, can have a net charge. The difficulty however remains,
Figure 6.43: Change in surface potential over 15 keV P implanted disks in 15 nm SiO₂/Si layers relative to surrounding un-implanted areas plotted as a function of tip height for implants at various fluences. Lines of best fit are shown to guide the eye. A FFT smoothed fit of the data is shown as a line to guide the eye.
in separating any changes to the work-function and the effect of charge on the surface potential. Despite this, it may still be possible to at least gain an insight into the effect of sample charge on the potential at the tip.

From Equation 2.32, if the capacitance and capacitance gradient are known then it should be possible to calculate the electric field due to any charge in the sample from surface potential measurements. If we consider the difference in surface potential between two areas on a sample we have:

\[ \Delta \phi_{\text{surf}} = -\Delta V_{fb} = \phi'_s - \phi_s + \left( \frac{1}{C} \frac{dC}{dz} \right)^{-1} E_q \]  

(6.1)

Where we assume that the capacitance and its gradient is not different over the two areas. What remains however are expressions for them so that they can be calculated.

### 6.7.1 Analytical models for the Tip

As discussed in Chapter 2, the capacitance gradient of the tip is easily calculated from equations developed to describe the electrostatic force for EFM. The capacitance of the tip sample system however is not as well documented. In principle the capacitance should be able to be calculated by simply integrating the capacitance gradient. Results of these calculations are shown here.

The capacitance of the tip point can be calculated from the equation given for the simplified sphere model (Eq. 2.33). This gives the capacitance as:

\[ |C|_{z<R} = -2\pi \varepsilon_0 R \log_e(z) \]

This was determined by Belaidi et al. [17] to only be accurate at small tip-sample separations. At larger separations the full sphere model is required (Eq. 2.35). Fortunately the capacitance for the sphere plane system is well known and does not require Eq. 2.35 to be integrated:

\[ C = 4\pi \varepsilon R \sinh \left[ \text{ArcCosh}(\alpha) \right] \sum_{n=1}^{\infty} \frac{1}{\sinh \left[ n \cdot \text{ArcCosh}(\alpha) \right]} \]  

(6.2)

These equations have been plot in Fig. 6.44 using the nominal 35 nm radius of tips used in experiments. Note that although the capacitance gradient for the simplified sphere was a good approximation for the full sphere at small tip-sample
separations we can clearly see that this is not true of the capacitance and is at best a factor of 2 larger. To this end, the full sphere model needs to be used to calculate the capacitance.

![Figure 6.44: Plot of the capacitances calculated from analytical models of tip sample geometries as a function of tip sample separation.](image)

For tip sample separations much smaller than the tip length and small cone angles, it was found by Belaidi et al. that the tip cone begins to contribute to the capacitance gradient. Integrating the equation from the approximation for the tip-cone model (Eq.2.35) that was found to best describe the tip cone capacitance gradient however leads to negative values for the capacitance. This is considered to be un-physical and a constant of integration is required. The integration results in the following expression:

$$|C|_{R<z<\ell} = C_0 - \frac{2\pi\varepsilon_0}{Arc\sinh^2(Cot(\theta))} \left[ z + z \log_e \left( \frac{L}{4z} \right) \right]$$  \hspace{1cm} (6.3)

Where $C_0$ is a constant of integration. Unfortunately, it is not entirely clear what this constant should be. A lower limit for it however can be determined so that the capacitance is positive for all values of $z$:

$$C_{0,\text{min}} > \frac{3L\pi\varepsilon_0}{2 \cdot Arc\sinh^2(Cot(\theta))}$$  \hspace{1cm} (6.4)

Although not shown in the plot, the calculated values in fact reach a local
6.7.2 Analytical Models of Buried Charge

Most analytical formulae consider a single dielectric or vacuum between electrodes. In our case however there is a thin oxide between the electrodes that will affect the capacitance as well as the potentials in our system. These effects need to be considered for a correct calculation of charge in the system.

As an example, the effect of adding a thin dielectric layer into the gap of a parallel plate capacitor is presented. In this case the gap between the dielectric layer and top electrode is $d_1$ and the thickness of the dielectric $d_2$. The standard parallel plate capacitor equation is modified to read:

\[
C = \frac{\varepsilon_0 A}{d_1 + d_2}
\]

Where $\varepsilon$ is the relative permittivity of the gap and $\varepsilon_0$ the relative permittivity of the dielectric. Clearly this reduces to the conventional parallel plate capacitor equation when the thickness of the dielectric is zero.

Furthermore, since the charges that affect the scanning probe are buried rather than charges on the surface, the potential from the charge is screened to a certain extent. An alternative method for looking at this is to consider an effective screened charge, $q$. For a point charge buried in a dielectric with a relative permittivity, we have for the effective charge [18]:

\[
q = \left(\frac{\varepsilon_0 + \varepsilon}{\varepsilon_0 + 2\varepsilon}\right)Q
\]

The full model for the tip-one given by the uniformly charged line model (Eq. 2.37) is also readily integrated to calculate the capacitance but the solution does not lead to a simple form. Instead, it has been numerically evaluated at various tip sample separations and is given in Fig. 64. In fact the capacitance obtained using the approximations only diverges away from that obtained from the full equation as the tip sample separation reaches large values. By about 2 $\mu$m we find there is about a 10% error.
6.7.3 Electric Field of Charge Pancake

It is also important to note that we do not have point charges in our system and that the geometry of charge area will affect the electric fields and potentials. In our case we simply consider the electric field from a disk since the longitudinal implant straggles of 10 nm or so, as obtained from TRIM, is much smaller than the aperture diameter of 3 \( \mu m \). The electric field at a height \( z \) above the centre of a disk of charge with a radius \( R \), only has a vertical component and is given by:

\[
E_z = \frac{Q_s}{2\varepsilon_0 R^2} \left( 1 - \frac{z}{\sqrt{z^2 + R^2}} \right)
\]

Substituting this into Equation 2.32 yields:

\[
V_{dc} = \phi_{ts} - \left( \frac{1}{C} \frac{dC}{dz} \right)^{-1} \frac{Q_s}{2\varepsilon_0 R^2} \left( 1 - \frac{z}{\sqrt{z^2 + R^2}} \right)
\]

It however relatively simple to perform the full calculation if we consider our buried charge to be in the shape of a pancake, i.e. have a finite thickness. By integrating over \( z \) we obtain for the electric field:

\[
E_z = \frac{Q_s}{4\varepsilon_0 R^2} \frac{1}{t} \left( 2t + \sqrt{z^2 + R^2} - \sqrt{(z + t)^2 + R^2} \right)
\]

Where \( t \) is the thickness of the charge pancake.

When these expressions for the electric field along with calculated values for the capacitance and the capacitance gradients (calculated in Chapter 2) are feed into Eq. 6.1 however, we find that the change in surface potential is predicted to increase with tip-sample separation rather than decrease. This would imply that either the electric field or capacitance terms does not decay fast enough or that the calculated capacitance gradient decreases too fast. Unfortunately, pursuing this theoretical work further is beyond the scope of this work. Some efforts were made at numerically simulating the system however and are presented in the next section.

6.7.4 Numerical Modelling of Buried Charge

Our implants however were made into a patterned array. Given that the analytical equations do not take the full array of charge into account, to calculate the tip sample capacitances and potentials numerical simulations of the system can be made. To this end, some work was also performed to calculate the potential due to charges buried in the sample using the TCAD package to determine the
capacitances and potentials by numerically solving the Poisson equation over a fixed set of grid points. These simulations were made for a 15 nm thick oxide and an array of flat charge islands buried in the oxide with the equivalent amount of positive charge from an implant to a fluence of $1 \times 10^{14}$ cm$^{-2}$. The tip was simply taken to be a 70x70 nm$^2$ electrically earthed electrode. Typically 20,000 grid points were used to simulate the system and simulations took up to 12 hours to complete, if they reached completion at all. Often simulations would crash and the grid geometry would need to be adjusted to optimise for a finer mesh of grid points were the potentials were found to change by a large amount.

The capacitance gradients and capacitances calculated from TCAD are shown in Fig. 2.12 & 6.44. As can be seen from the figures the values calculated are quite reasonable despite the very simplistic geometries taken. Given this agreement with analytical results and the work required to setup and run simulations it is unclear if there is any benefit in performing the simulations.

6.8 Conclusion

It has been demonstrated for the first time that by implanting thin oxides on silicon through a patterned mask, and producing a surface potential map of samples with Kelvin-probe Force Microscopy, it was possible to clearly identify implanted regions and compare them to the un-implanted surroundings. In this way different samples can be compared with more confidence, since complications that may arise from using different tips to determine the absolute or true surface potential are eliminated. The explanation of the cause of this contrast however is non-trivial. There are many factors that at the commencement of this work which were not known to affect sample surface potentials but are now believed to. It was found that the relative surface potentials reduced over time, an effect that is attributed to the gettering of negative ions such as chlorine. Any future researchers working on this area must be mindful of this and measurements must be made as soon as possible after implantation, samples should be cleaned and stored in a clean-room environment to limit sample exposure to impurities. Never the less, several important conclusions can be drawn from this work.

It was found that implantation of samples led to depressions in the 15 nm oxides, however swelling was observed in 5 nm oxides. Whether the oxide swells or compacts has been shown to be dependent on the level of damage. Results indicate that the lower damage levels in 5 nm oxides leads to oxide swelling. This was also observed to change over time suggesting room temperature annealing.
CHAPTER 6. IMPLANTATION EFFECTS ON SURFACE POTENTIAL

It is unclear if there is also an effect from the substrate swelling due to damage in the silicon substrate. However, since this was not the main focus of this work it was not further explored.

In the 15 nm samples the surface potential of implanted areas was found to be higher than un-implanted areas. This was initially attributed to positively charged oxide traps such as the E' centre, or compensation of n-type dopants in the substrate. However, implanted 50 nm oxides showed a reduced surface potential which suggests the presence of negative charges in the oxide, and implanted 5 nm thick oxides also showed a reduced surface potential, suggesting that n-type dopants are not compensated. Both these samples were however cleaned with a Piranha solution rather than organic solvents. It is postulated that perhaps there is a certain level of carbon stitching as a result of implantation that increased the surface potential and is only removed with a Piranha solution. The carbon could be from residual hydrocarbons in the chamber vacuum or more likely due to the photo-resist itself. A 15 nm sample was subjected to a Piranha etch and indeed a reduced surface potential was observed, however this was conducted many months after the sample had been prepared and even samples not cleaned with Piranha solution showed a reduced surface potential after a similar time period.

Additional samples implanted through a Ni-grid did indeed reveal that even 5 nm samples when not subjected to a Piranha etch show an increased surface potential. These samples were then subjected to a Piranha etch (albeit 3 months later) which then showed a reduction in the surface potential. To clarify whether there is carbon-stitching or if potentials are reduced due to contamination, experiments need to be conducted immediately after implantation.

Alternatively, it is also possible that the interface traps are responsible for an increased surface potential. Results from TRIM simulations predicted that there is more interface damage in the implanted 15 nm oxides compared to the other samples. Since implanted 50 nm oxides, where the majority of the damage is within the oxide, and 5 nm oxides where the majority of the damage is in the substrate silicon, both show a reduction in surface potential, this may also suggest that the increase in surface potential observed in 15 nm oxides is in fact due to interface damage. However, the 15 nm oxides are not predicted to have much more damage than the 5 nm oxides at the interface and it is unclear why the 5 nm oxides do not exhibit a similar behaviour.

If indeed implantation damaged silicon has a lower surface potential, as noted earlier, this cannot be as a result of dopant compensation. Compensated n-type donors leads to a larger work-function and therefore a higher surface potential.
Instead, it is proposed that the reduced surface potential is a result of defects with a negative charge state. This is certainly plausible given that (at least at lower fluences) the di-vacancy is the most common defect present in silicon and has negative charge states. It is also possible that at these higher fluences, larger vacancy clusters also exist which also have negative charge states.

The fluence dependence of implanted 15 nm oxides showed that the surface potential increased until a fluence of $1 \times 10^{13} \text{ cm}^{-2}$ and was reduced after an implant of $1 \times 10^{14} \text{ cm}^{-2}$. This trend is consistent with the behaviour of the E' centre [19, 20], and perhaps indicates that it is responsible for the increase in surface potential. It is also suggested however that the interface damage may also saturate after implantation to a threshold fluence since there are a fixed number of atoms at the interface.

With regard to the species dependence it was found that in 15 nm and 50 nm oxides the phosphorus implanted samples showed a higher surface potential than silicon implanted samples. This is to say the relative surface potential was more positive, so in fact the magnitude of the change was larger by $\approx 100 \text{ mV}$ for 15 nm samples where the relative surface potential was positive (Fig. 6.10), and a smaller magnitude by $\approx 10 \text{ mV}$ for 50 nm where the relative surface potential was negative (Fig. 6.23). However, there was a clear reduction of the surface potential with increasing ion mass observed in implanted 5 nm samples (Fig. 6.30). Since there is a substantial amount of phosphorus that is implanted into the oxide for 15 & 50 nm samples this perhaps suggests that phosphorus chemically reacts with the oxide to increase the surface potential. Indeed it has been suggested by others that phosphorus can act as a charge trap within the oxide [21] and may bond with either oxygen [22] or silicon atoms [23].

After annealing at 1000°C for 5 seconds phosphorus and silicon implanted 15 nm samples both show an increased surface potential. While for 5 nm samples a small non-uniform increase or nothing was observed in the case of phosphorus or silicon implants, and an increased surface potential is observed for boron implanted samples.

Given that the anneal is expected to activate the implanted dopants the surface potential is expected to be higher for boron implanted samples and lower for phosphorus implanted samples, while no change is expected from silicon implanted samples. The results however indicate that there is either an incomplete activation in the case of phosphorus implanted samples or that there are residual
defects that also affect the surface potential.

HF etching of annealed phosphorus implanted samples however show that the surface potential is indeed reduced after the oxide is removed, suggesting that the phosphorus was indeed activated and that the presence of the oxide somehow suppressed the effect of activated phosphorus in decreasing the surface potential while not actually leading to an increased surface potential since this would be present in silicon implanted samples.

Furthermore, studies of annealed 50 nm samples show that the relative surface potential is further reduced upon annealing. This may be the result of the experiments being conducted 6 months after implantation however. If indeed annealed implanted oxides result in a further reduction of the surface potential, it would indicate that residual oxide damage cannot be the cause of an increased surface potential in implanted 15 nm oxides. Curiously, annealed 50 nm oxides showed swelling over implanted regions which would indicate residual oxide damage. However, it should be noted that the level of damage in the 50 nm oxides is much higher than would be present in the thinner oxides since all the ions stop within it.

It is also possible that oxygen recoils from the oxides have formed acceptor-type donors or silicon dioxide precipitates in the near interface region. Indeed it has been shown in the literature that anneals at 1000°C may not be sufficient to remove all the oxide damage. This supports the observations of annealed 15 nm oxides, however, it is unclear why there is a non-uniform signal obtained from 5 nm thick oxide samples. Given that there is less oxide damage expected in 5 nm oxides perhaps a lateral non-uniformity in the oxide damage may be more noticeable. HF etching of the samples also revealed what appear to be etch pits in the sample. This supports the idea that there are silicon dioxide precipitates or even a layer that forms in the substrate that is subsequently etched away by HF.

The magnitude of the change in the surface potential after annealing in boron implanted samples and in HF etched phosphorus samples, is smaller than expected for the concentration of ions implanted. This was also noted by Henning et al. [14] who examined the potentials over boron doped regions. This is attributed to the fact that we are not actually scanning at the surface of the sample but 200 nm away from it. The geometry of the tip and cantilever are also known to affect the measured surface potentials and the resolution and contrast with which it is measured.

To this end, the relative surface potential was also measured as a function of tip sample separation. Results show that the change in surface potential is
reduced as separation is increased. This is consistent with the work by Jacobs et al. [15] who showed that resolution or contrast is reduced with increasing separation. Some theoretical work was conducted on modelling how the surface potential changes with tip sample separation. Unfortunately the data was not able to be re-produced with the analytical models used. This was attributed to the calculated capacitance not decreasing fast enough with increasing separation. Given that most of the capacitances were calculated by integrating the capacitance gradients published in the literature this suggests that this may not be a valid method for calculating the capacitance.
References


REFERENCES


Chapter 7

Concluding Remarks

We have experimentally measured the vacancy profile from axial-channelled implanted silicon samples for the first time. It was revealed that there were large departures from profiles predicted by Crystal-TRIM simulations near the surface. There were far fewer vacancies found near the surface up to a depth of 1 $\mu m$ in both channelled and random-oriented implanted samples. This effect was attributed to surface enhanced annihilation. Deeper into the sample however the simulations seem to provide an adequate prediction of the profile of vacancies for both random-oriented and channelled implanted silicon, although it was not possible to experimentally profile up to the predicted end of range for channelled implanted samples. Furthermore, it was found that in contrast to previously published work by others, the defect species created do not change with implantation angle. Only the concentration and depth profiles of defects was found to change with angle.

Our studies into the formation and evolution of extended defects upon annealing of implanted silicon samples show that the implant fluence required for their formation depends on the annealing duration. Depending on the defect concentration present, a longer annealing time may be required before extended defects can be observed to form. The study of the effect of channelling implantation on extended defect formation upon annealing for intermediate temperatures
and durations was also examined for the first time. Results were by and large found to support the published literature, ion channelling results in less extended defects but the implant conditions required for their formation are the same. After annealing lower fluence implants for a slightly longer period of time there is some evidence to suggest that loop formation is inhibited by channelling implantation. In this work, the effect of ion channelling on the formation of short rod-like defects was also studied for the first time. Unfortunately, there was insufficient evidence to test if implant fluences rather than defect concentrations were the key parameter in determining whether extended defects will form or not. On the face of it, although the same fluence is required for formation with channelling or random-orientation implants and these have differing defect profiles and concentrations, both of these may be above the required amount of damage since they are not drastically different.

It was found that Crystal-TRIM Monte-Carlo simulations produced a good prediction for the peak concentration of displaced atoms measured from Rutherford Backscattering Spectroscopy analysis in samples implanted at a random-orientation to a medium fluence. Simulations in general do a good job for what they are intended to simulate. Effects such as surface-enhanced annihilation of defects and defect accumulation that are not taken into account must also be considered when attempting to predict defect profiles and concentrations in a real sample. It was found that simulations for channelling implants were only reasonable at lower fluences. As the fluence is increased de-channelling due to damage accumulation begins to affect the defect profiles.

Kelvin-probe Force Microscopy (KFM) has been demonstrated to be an effective technique for laterally resolving implanted oxide on silicon structures. Implantation to a medium fluence was found to produce a clear change to the surface potential of samples, although there were some difficulties in attempting to understand the cause of this. However, it is clear that implanted and annealed samples where the oxide has been removed, that the sign of the surface potential
change agree with expectations for P-doped, B-doped and Si (intrinsic) implants. Results for samples in which the oxide was present were rather variable and difficult to interpret. It was found that both oxide damage and substrate damage resulted in a reduced surface potential. However, in some samples an increased surface potential was observed. It is unclear from experiments what this increased surface potential is due to. There is some evidence to suggest that this is due to interface trapped charge. However, samples that showed an increased surface potential were not predicted to have a significantly higher amount of interface damage than other samples. It is also possible that it is due to carbon-stitching on the surface of the sample and further experiments are required to clarify this. The reduction in surface potential over a period of months also clearly indicated that there is an aging process in the implanted regions which may be related to impurity gettering.

It came as a surprise that the majority of samples exhibited a reduced surface potential as this suggests either a decrease in the work function of the sample or the presence of negative charge. Implantation was expected to compensate donors in the substrate and lead to an increased work-function or surface potential, the bulk of the literature also indicates that oxide charges are predominantly positive. In the silicon substrate, vacancy clusters such as the di-vacancy are possible candidates for negative charge. In the case of a implanted thicker oxides where the bulk of the damage is contained within the oxide, it is possible that the negative charge is in fact due to the implanted ions themselves. This is not expected for other samples as the charge should rapidly drain away through the silicon substrate during implantation. If this is the case, it is possible that the positive oxide charges are being masked in these samples and the increase in surface potential observed in other samples is in fact due to oxide charges or defects such as the E’ centre.

It is clear that KFM is able to map changes in surface potentials for implanted SiO₂/Si samples over many months and may eventually be a valuable technique
for analysing such changes. But the various factors involved still need to be understood.

Thermal annealing of samples for dopant activation and damage repair also seems to indicate that the oxide damage created by phosphorus implantation was not repaired by high temperature rapid thermal anneals. Curiously, silicon implanted samples did not show clear evidence for residual damage in annealed samples which perhaps suggests that phosphorus chemically interacts with the oxide or the oxide interface upon annealing. The measured surface potential change after annealing was also smaller than theoretically expected. This is attributed to a geometric effect due to the tip shape as well as the tip-sample separation. Both numerical and analytical models were used to examine this. Unfortunately, it was found that the analytical models did not fit the experimental results while numerical simulations were too time consuming. In particular, it was found that the tip-sample capacitances did not reduce to zero fast enough with increasing separation. This is despite the fact that these analytical models were found to work well for Electrostatic Force Microscopy and suggests that KFM is more sensitive to deviations in the capacitance and requires more accurate models. The results from the numerical simulations that were conducted did at least agree with analytical models though.

Various difficulties concerning sample contamination were encountered while conducting this work. Silicon is a very sensitive material, many elements are fast diffusers in silicon and can diffuse through the native oxide layer on the surface. Laboratory and lab-ware cleanliness is paramount for sample processing, particularly when electrical measurements are to be made. It is essential to maintain a clean working environment.

Further work that can be done includes a further investigation of whether the point defects species formed after light ion implantation change with implantation angle.
There is also scope to further investigate whether there really is a difference in the loop formation threshold for samples implanted to a lower fluence of ions and annealed for up to 20 minutes at 750°C. A channelling implanted sample implanted to a fluence of $2 \times 10^{14}$ cm$^{-2}$ should also be prepared and examined with RBSC and TEM. This is to confirm that there is no difference in the fluence required for extended defect formation between channelled and random orientation implants. It will also shed some light on whether there is a threshold total defect concentration. High-resolution cross-sectional TEM could also be performed to examine if there are any rod-like defects that form after 10 minute anneals to clarify if there is a difference in the fluence required for formation of defects.

There is clearly much scope for further work regarding the use of KFM for the study of implantation damage. In order to eliminate the possibility of sample contamination there are several experiments that should be repeated immediately after implantation. For example, to confirm that the increase in surface potential is due to an oxide or oxide interface related effect, HF etching of as-implanted 15 nm samples should be repeated. Piranha etching of these samples could also be conducted to rule out whether there is any carbon stitching on the sample. The annealing of 50 nm samples should also be repeated as this was conducted many months after implantation. Furthermore, Electrostatic Force Microscopy measurements could be attempted in order to determine the polarity and amount of charge in samples. Other complementary techniques such as Electron Paramagnetic Resonance and Photo-Luminescence measurements may be able to determine the nature of any oxide related defects that are present. Despite the many issues with KFM measurements, it does remain one of the few (quasi) electrical techniques available for examining as-implanted samples implanted to a medium to high fluence. Ordinary electrical measurements are not possible since oxides would breakdown.

Although there is much about defects in silicon that remains to be studied, it is hoped that this work has shed some light on some of the issues involved.
Author/s:
Lay, Matthew Da-Hao

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